

Research Articles

- 87 **Stretch-Flangeability of Laser Powder Bed Fusion-Processed 316L Stainless Steel**
Rae Eon Kim, Yeon Taek Choi, Sang Guk Jeong, Do Won Lee, Hyoung Seop Kim
- 95 **Ultra-Low-Temperature (4.2 K) Tensile Properties and Deformation Mechanism of Stainless Steel 304L Manufactured by Laser Powder Bed Fusion**
Seung-Min Jeon, Young-Sang Na, Young-Kyun Kim
- 104 **Flexible Hybrid Energy Harvester based on Thermoelectric Composite Film and Electrospun Piezopolymer Membranes**
Hyomin Jeon, Cheol Min Kim, Hyeon Jun Park, Bitna Bae, Hyejeong Choi, HakSu Jang, Kwi-Il Park
- 113 **Effect of Cellulose Fiber Density Variation on Energy Harvesting Performance in a Hydrovoltaic Generator**
Seung-Hwan Lee, So Hyun Baek, Hyun-Woo Lee, Yongbum Kwon, Kanghyuk Lee, Kee-Ryung Park, Yoseb Song, Bum Sung Kim, Ji Young Park, Yong-Ho Choa, Da-Woon Jeong
- 122 **Extraction of $MgSO_4$ from dolomite and synthesis of $Mg(OH)_2$ in Bittern**
HyunSeung Shim, Jiyeon Kim, Areum Choi, Nuri Oh, YooJin Kim
- 131 **Effect of Building Orientation on Tensile Properties of Hastelloy X alloy Manufactured by Laser Powder Bed Fusion**
Seong-June Youn, GooWon Noh, Seok Su Sohn, Young-Sang Na, Young-Kyun Kim
- 138 **Effect of the Initial Porosity of Needle Coke-Pitch Carbonized Blocks on Impregnation-Related Physical Properties**
U-Sang Youn, Sang-Hye Lee, Jae-Seung Roh

Critical Review

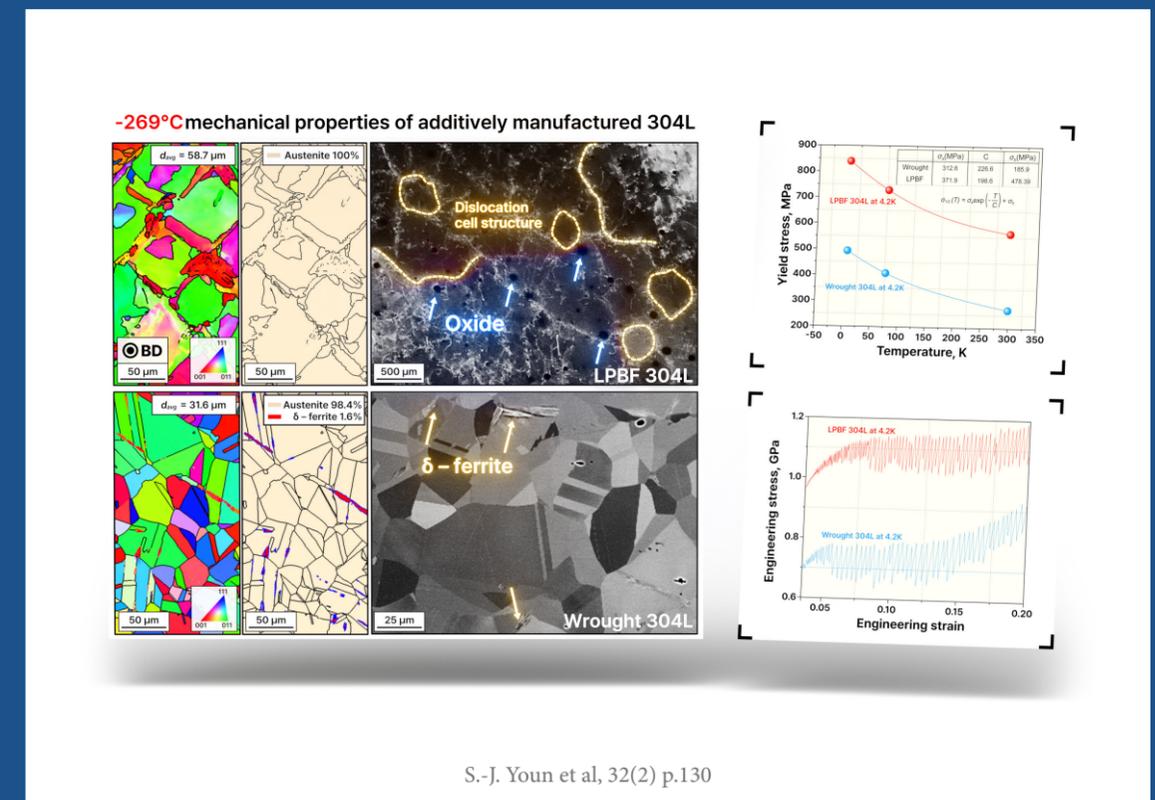
- 145 **A Review of Recent Developments in CoCrFeMnNi High-Entropy Alloys Processed by Powder Metallurgy**
Cheeneppalli Nagarjuna, Sheetal Kumar Dewangan, Hansung Lee, Eunhyo Song, K. Raja Rao, Byungmin Ahn
- 165 **CODE OF ETHICS**
- 171 **INSTRUCTIONS FOR AUTHORS**



Journal of Powder Materials

한국분말재료학회지

<https://powdermat.org>



Aims and Scope

The Journal of Powder Materials (JPM) is dedicated to sharing cutting-edge research and advanced technologies in the fields of powder metallurgy and powder-related materials science and engineering. By serving as a vital platform for both researchers and industry professionals worldwide, JPM aims to bridge the gap between fundamental research and practical applications. The journal offers valuable insights for material scientists, technologists, engineers, designers, and manufacturers.

JPM covers the entire spectrum of powder materials and processing technologies, including but not limited to: powder production (including precursor materials), milling, granulation, cold and hot compaction, sintering, cold and hot isostatic pressing, pulsed and other assisted consolidation, additive manufacturing, injection molding, and powder-based coating technologies. The journal also encompasses research on characterization, testing, quality assurance, and diverse industrial applications. Furthermore, *JPM* actively promotes research incorporating data-driven methodologies, including computational materials science, machine learning, and artificial intelligence (AI), which are increasingly shaping the future of powder materials research and process optimization.

ISO abbreviation of journal title

✓ Topic

Powder Materials	Powder Technology
- Fe-based powders	- Powder synthesis
- Non-ferrous powders	- Powder characterization/analysis
- Ceramic powders	- Powder compaction
- Particulate Composite	- Powder pretreatment
- Tool/Cemented Carbides	- Sintering
- Porous powders	- Densification process
- Electric/Electronic powders	- PIM
- Bio materials	- Post-treatment
- Magnetic powders	- Novel powder technology
- Energy conversion/storage powders	- Nanostructured powders
- Multi-functional powders	- Simulation of powder/process
- Organic/inorganic powders	- Powder test
	- Powder business/industry

The official title of the journal is 'Journal of Powder Materials' and the abbreviated title is 'J. Powder Mater.'

Year of launching (history)

Journal of Powder Materials was launched in 1993.

The frequency of publication

Journal of Powder Materials is published bi-monthly in February, April, June, August, October, and December. Supplementary issues are also published at times.

Availability of the full-text in the web, URL address

The published articles from the initial to the present issue are available free of charge at <http://ejournal.kpmi.or.kr>.

Index in database

The articles published in Journal of Powder Materials are indexed and/or abstracted in Google Scholar, KISTI, and KCI.

Fund support

“본 사업은 기획재정부의 복권기금 및 과학기술정보통신부의 과학기술진흥기금으로 추진하여 사회적 가치 실현과 국가 과학기술 발전에 기여합니다.”

“This work is supported by the ‘Lottery Fund’ of the ‘Ministry of Strategy and Finance’ and the ‘Science and Technology Promotion Fund’ of the ‘Ministry of Science and ICT’, contributing to the realization of social value and the development of national science and technology.”



Subscription info

The annual subscription fee for this journal is Korean Won ₩50,000 (US\$ 50.00 or equivalent). Back issues are available on request. The number of circulated print copies is 600. Full published papers from the initial to the present issue are available free of charge at <http://ejournal.kpmi.or.kr>. Correspondence concerning business matters should be addressed to Ms. Youn-Ho Kim, Manager, The Korean Powder Metallurgy & Materials Institute, Unit 706, (635-4, Yeoksam-Dong) 22, 7Gil, Teheran-Ro, Gangnam-Gu, Seoul 06130, Korea (Tel: +82-2-539-4603, Fax: +82-0303-0947-4603, e-mail: kpmi@kpmi.or.kr).

Submission

Manuscripts should be submitted via the online Manuscript Central website (<https://submit.powdermat.org>). Other correspondence can be sent by e-mail (ktkim@kims.re.kr or kpmi@kpmi.or.kr) to the Editor-in-Chief, Dr. Kyung Tae Kim, Korea Institute of Materials Science, Changwon, Gyeongnam 51508, Korea. All manuscripts are peer-reviewed.

Contact info (Editorial office)

The Korean Powder Metallurgy & Materials Institute Unit 706, 22, 7Gil, Teheran-Ro, Gangnam-Gu, Seoul 06130, Korea
Tel: +82-2-539-4603, Fax: +82-0303-0947-4603, E-mail: kpmi@kpmi.or.kr

Printed by M2PI

#805, 26 Sangwon 1-gil, Seongdong-gu, Seoul 04779, Korea
Tel: +82-2-6966-4930, Fax: +82-2-6966-4945, E-mail: support@m2-pi.com, Homepage: <http://m2-pi.com>

Copyright statement

© 2025 The Korean Powder Metallurgy & Materials Institute All rights reserved.

No parts of this publication may be reproduced, stored in retrieval system, or transmitted in any form, or by any means, electronic, mechanical, recording, or otherwise, without the prior permission of the publishers.

Editor-in-chief

Kyung Tae Kim *Korea Institute of Materials Science (KIMS), Republic of Korea*

Associate editors

Jeung Han Kim *Hanbat National University, Republic of Korea*
Seok-Jae Lee *Jeonbuk National University, Republic of Korea*
Hyunseok Oh *University of Wisconsin Madison, USA*
Seungkyun Yim *New Industry Creation Hatchery Center, Tohoku University, Japan*
Hyunjoo Choi *Kookmin University, Republic of Korea*
Moataz M. Attallah *University of Birmingham, School of Metallurgy and Materials, UK*
Thomas Weissgaerber *Fraunhofer IFAM, Germany*
Kwi-Il Park *Kyungpook National University, Republic of Korea*
MinHo Yang *Dankook University, Republic of Korea*
Swee Leong Sing *National University of Singapore (NUS), Singapore*
Pawel Zieba *IMMS, Poland*
Jung Shin Kang *Seoul National University, Republic of Korea*
Young-Kyun Kim *Korea Institute of Materials Science, Republic of Korea*
Jungjoon Kim *Institute for Advanced Engineering, Republic of Korea*
Jeong Min Park *Korea Institute of Materials Science, Republic of Korea*
Tae Joo Park *Hanyang University, Republic of Korea*
Jongmin Byun *Seoul National University of Science and Technology, Republic of Korea*
Jae Wung Bae *Pukyong National University, Republic of Korea*
Se-Eun Shin *Sunchon National University, Republic of Korea*
Seok Su Sohn *Korea University, Republic of Korea*
Changui Ahn *Korea Institute of Ceramic Engineering and Technology, Republic of Korea*
Bin Lee *Kyung Hee University, Republic of Korea*
Dongju Lee *Chungbuk National University, Republic of Korea*
Seung Min Yang *Korea Institute of Industrial Technology, Republic of Korea*
Seungki Jo *Korea Institute of Materials Science, Republic of Korea*
Byung Joon Choi *Seoul National University of Science and Technology, Republic of Korea*
Ma Qian *RMIT University, Australia*
Dayang Wang *Jilin University, China*

Statistics editor

Seok-Jae Lee *Jeonbuk National University, Republic of Korea*

Editorial board

Kyoung-Seok Moon *Gyeongsang National University, Republic of Korea*
Nokeun Park *Yeungnam University, Republic of Korea*
Kyoung-Tae Park *Korea Institute of Industrial Tehcnology, Republic of Korea*
Hyokyung Sung *Kookmin University, Republic of Korea*
Min Ha Lee *Korea Institute of Industrial Tehcnology, Republic of Korea*
Joon Phil Choi *Korea Institute of Machinery and Materials, Republic of Korea*
Hongjun Chae *Institute for Advanced Engineering, Republic of Korea*
John Gerard Fisher *Chonnam National University, Republic of Korea*
Hamed Asgharzadeh *University of Tabriz, Turkey*
Tamás Csanádi *Institute of Materials Research, Slovak Academy of Sciences, Slovakia*
Jan Kazior *Cracow University of Technology, Poland*
Tadeusz Pieczonka *AGH University, Poland*

Research Articles

- 87 **Stretch-Flangeability of Laser Powder Bed Fusion-Processed 316L Stainless Steel**
Rae Eon Kim, Yeon Taek Choi, Sang Guk Jeong, Do Won Lee, Hyoung Seop Kim
- 95 **Ultra-Low-Temperature (4.2 K) Tensile Properties and Deformation Mechanism of Stainless Steel 304L Manufactured by Laser Powder Bed Fusion**
Seung-Min Jeon, Young-Sang Na, Young-Kyun Kim
- 104 **Flexible Hybrid Energy Harvester based on Thermoelectric Composite Film and Electrospun Piezopolymer Membranes**
Hyomin Jeon, Cheol Min Kim, Hyeon Jun Park, Bitna Bae, Hyejeong Choi, HakSu Jang, Kwi-Il Park
- 113 **Effect of Cellulose Fiber Density Variation on Energy Harvesting Performance in a Hydrovoltaic Generator**
Seung-Hwan Lee, So Hyun Baek, Hyun-Woo Lee, Yongbum Kwon, Kanghyuk Lee, Kee-Ryung Park, Yoseb Song, Bum Sung Kim, Ji Young Park, Yong-Ho Choa, Da-Woon Jeong
- 122 **Extraction of $MgSO_4$ from dolomite and synthesis of $Mg(OH)_2$ in Bittern**
HyunSeung Shim, Jiyeon Kim, Areum Choi, Nuri Oh, YooJin Kim
- 131 **Effect of Building Orientation on Tensile Properties of Hastelloy X alloy Manufactured by Laser Powder Bed Fusion**
Seong-June Youn, GooWon Noh, Seok Su Sohn, Young-Sang Na, Young-Kyun Kim
- 138 **Effect of the Initial Porosity of Needle Coke-Pitch Carbonized Blocks on Impregnation-Related Physical Properties**
U-Sang Youn, Sang-Hye Lee, Jae-Seung Roh

Critical Review

- 145 **A Review of Recent Developments in CoCrFeMnNi High-Entropy Alloys Processed by Powder Metallurgy**
Cheenepalli Nagarjuna, Sheetal Kumar Dewangan, Hansung Lee, Eunhyo Song, K. Raja Rao, Byungmin Ahn
- 165 **CODE OF ETHICS**
- 171 **INSTRUCTIONS FOR AUTHORS**

Research Articles

- 87 Stretch-Flangeability of Laser Powder Bed Fusion-Processed 316L Stainless Steel
Rae Eon Kim, Yeon Taek Choi, Sang Guk Jeong, Do Won Lee, Hyoung Seop Kim
- 95 Ultra-Low-Temperature (4.2 K) Tensile Properties and Deformation Mechanism of Stainless Steel 304L Manufactured by Laser Powder Bed Fusion
Seung-Min Jeon, Young-Sang Na, Young-Kyun Kim
- 104 열전 복합 필름과 전기방사된 압전폴리머 멤브레인을 기반으로 하는 플렉서블 하이브리드 에너지 하베스터
전호민, 김철민, 박현준, 배빛나, 최혜정, 장학수, 박귀일
- 113 수분 기반 발전기내 셀룰로오스 섬유 간 밀도 변화가 에너지 하베스팅 성능에 미치는 영향
이승환, 백소현, 이현우, 권용범, 이강혁, 박기룡, 송요셉, 김범성, 박지영, 좌용호, 정다운
- 122 백운석에서 $MgSO_4$ 의 추출과 간수에서 $Mg(OH)_2$ 합성 연구
심현승, 김지연, 최아름, 오누리, 김유진
- 131 Laser Powder Bed Fusion 공정으로 제조된 Hastelloy X 합금의 인장 특성에 미치는 적층 방향의 영향
윤성준, 노구원, 손석수, 나영상, 김영균
- 138 침상코크스-핏치 탄화블록의 초기 기공률이 함침 후 물성 향상에 미치는 영향
윤우상, 이상혜, 노재승

Critical Review

- 145 A Review of Recent Developments in CoCrFeMnNi High-Entropy Alloys Processed by Powder Metallurgy
Cheenepalli Nagarjuna, Sheetal Kumar Dewangan, Hansung Lee, Eunhyo Song, K. Raja Rao, Byungmin Ahn
- 165 CODE OF ETHICS
- 171 INSTRUCTIONS FOR AUTHORS

Stretch-Flangeability of Laser Powder Bed Fusion-Processed 316L Stainless Steel

Rae Eon Kim¹, Yeon Taek Choi², Sang Guk Jeong³, Do Won Lee², Hyoung Seop Kim^{1,2,3,*}

¹Graduate Institute of Ferrous & Eco Materials Technology, Pohang University of Science and Technology (POSTECH), Pohang 37673, Republic of Korea

²Department of Materials Science and Engineering, Pohang University of Science and Technology (POSTECH), Pohang 37673, Republic of Korea

³Tohoku University Advanced Institute for Materials Research (WPI-AIMR), Sendai Miyagi 980-8577, Japan

Received: January 15, 2025

Revised: March 10, 2025

Accepted: April 9, 2025

***Corresponding author:**

Hyoung Seop Kim

TEL: +82-10-4366-6596

E-mail: hskim@postech.ac.kr

Metal additive manufacturing (AM) facilitates the production of complex geometries with enhanced functionality. Among various AM techniques, laser powder bed fusion (LPBF) is distinguished by its precision and exceptional mechanical properties achieved via laser fusion deposition. Recent advancements in AM have focused on combining LPBF with post-processing methods such as cold rolling, high-pressure torsion, and forming processes. Therefore, understanding the forming behavior of LPBF-processed materials is essential for industrial adoption. This study investigates the stretch-flangeability of LPBF-fabricated 316L stainless steel, emphasizing its anisotropic microstructure and mechanical properties. Hole expansion tests were employed to assess stretch-flangeability in comparison to wrought 316L stainless steel. The results demonstrate that LPBF-processed samples exhibit significant anisotropic behavior, demonstrating the influence of microstructural evolution on formability. These findings contribute valuable insights into optimizing LPBF materials for industrial forming applications.

Keywords: Hole expansion ratio; Laser powder bed fusion; 316L stainless steel; Sheet metal forming; Stretch flangeability

1. Introduction

Metal additive manufacturing (AM) is an advanced technology that facilitates the production of intricate structures with multifunctional capabilities [1]. Among various AM techniques, laser-based processes like laser powder bed fusion (LPBF), which utilize laser fusion deposition, stand out for their high dimensional precision and superior mechanical properties [2-4]. In LPBF, a high-energy laser beam scans a powder bed selectively, inducing localized melting and solidification layer by layer. This process provides unparalleled design flexibility, enabling geometric optimization tailored to specific service conditions. Additionally, the rapid heating and cooling cycles inherent to LPBF, along with its localized thermal effects,

result in the formation of non-equilibrium microstructures. These microstructures are characterized by dislocation cell structures and heterogeneous grain morphologies [5]. Such unique features significantly enhance the strength and performance of LPBF-processed materials. Lemarquis et al. suggested that applying cold rolling on the AMed samples enhances mechanical properties [6, 7]. Similarly, Al-Zubaydi et al also proposed that severe plastic deformation via high-pressure torsion results in exceptional mechanical performance [8-10]. Therefore, the postprocessing of high deformation on the AMed sample holds a high potential for achieving excellent mechanical properties, which was not obtainable in conventional materials. These hybrid approaches necessitate additional forming processes to produce parts with customized shapes. Furthermore, the low productivity issues of the AM process can be complemented by combining the AM process with sheet metal forming [11, 12]. The hybrid fabrication approaches that inte-

<https://doi.org/10.4150/jpm.2025.00017>

© 2025 The Korean Powder Metallurgy & Materials Institute

grate sheet metal forming with AM have recently been proposed [11, 12]. Therefore, as the use of AM materials spreads, it is increasingly important to study the forming processes applicable to these materials to fully harness their potential. While these methods sacrifice some of the design freedom inherent to AM, they successfully enhance the mechanical properties of the final components. Moreover, hybrid fabrication approaches that integrate sheet metal forming with AM have recently been proposed [11, 12]. This approach offers two key advantages: the high productivity of sheet metal forming and the design flexibility of additive manufacturing, paving the way for broader industrial applications. However, further research on the formability of AM-processed materials is necessary to fully unlock their potential in industrial settings.

Formability is a critical parameter for the industrial application of structural materials, enabling the efficient production of components with complex geometries through high-productivity stamping processes [13]. Among the various formability factors, stretch-flangeability is particularly important, as it is closely linked to edge cracking during forming operations. Edge cracking occurs when substrates with sheared edges undergo forming, resulting in crack initiation and propagation due to pre-existing damage at the edges [14]. This mode of failure is especially challenging because it cannot be predicted using traditional forming limit diagrams [14]. Paul et al. [15] reported the relationship between the hole expansion ratio and the tensile properties including yield strength, ultimate strength, normal anisotropy, total elongation, and post elongation. Generally, high coefficient normal anisotropy and excellent post-uniform elongation are reported to have a superior hole expansion ratio. Meanwhile, Yoon et al. [16] suggest a clear correlation between hole expansion ratio and fracture toughness rather than tensile properties. Their studies directly examined the relationship between fracture toughness and HER, confirming a linear correlation. They attributed this to the fact that materials with higher fracture toughness demand greater energy for crack initiation and propagation, making through-thickness crack formation more challenging.

To address this issue, stretch-flangeability is commonly evaluated using hole expansion tests (HET). The resulting hole expansion ratio (HER) serves as a quantitative metric to measure the resistance of a material to edge cracking. This study aims to investigate the interplay between the unique microstructure of LPBF-processed materials and their stretch-flangeability, offering valuable insights for their broader industrial adoption.

2. Experimental

2.1. Fabrication

An M2 series 5 LPBF machine was utilized to fabricate 316L stainless steel samples from the stainless steel powders. The spherical powders, produced via gas atomization, had an average particle size of $\sim 31.8 \mu\text{m}$ and were suitable for LPBF processing (Fig. 1). The LPBF processing parameters are as follows: a laser power of 370 W, a hatch spacing of $0.09 \mu\text{m}$, a laser scan speed of 1350 mm/s, a layer thickness of $50 \mu\text{m}$, and a 67° rotation between layers. These LPBF-processing samples are referred to as the LPBF sample. For comparison, a wrought 316L stainless steel plate was annealed at 1050°C for 30 min, referred to as the wrought sample. Fig. 1c. illustrates the directions for the present samples.

2.2. Microstructural analysis

For microstructural analysis, specimens were polished with SiC papers up to 1200 grit and then $0.04 \mu\text{m}$ colloidal silica suspension. Electron backscatter diffraction (EBSD) and backscattered scanning electron (BSE) analysis were performed using a field emission scanning electron microscope (FE-SEM). The EBSD data were interpreted using TSL-OIM 7 software.

2.3. Mechanical tests

Uniaxial tensile tests were at a quasi-static strain rate of 1×10^{-3} along the rolling direction using an Instron 1361 universal testing machine. The tensile samples were prepared with a flat dog-bone shape with dimensions of 5 mm gauge length and 2.5 mm width. The strain was measured with an ARAMIS digital image correlation system.

Hole expansion tests (HET) were conducted using a scaled-down testing system mounted on a universal testing machine [13, 14]. Figure 2 illustrates the HET system and the specimen dimensions. The circular specimens, 10 mm in diameter and 0.5 mm thick, were punched with a 2 mm center hole. Before hole punching, to prevent the effect of surface roughness, the specimen surfaces were polished with SiC papers up to 1200 grit. The HETs were carried out with a conical punch at a punch speed of 1 mm/min. The final diameter was measured until the crack fully propagated through the thickness on the hole edge. The hole expansion ratio (HER) was calculated using the equation [17]:

$$\text{HER} = \frac{d_f - d_0}{d_0}, \quad (1)$$

where d_0 and d_f represent the initial and final hole diameters,

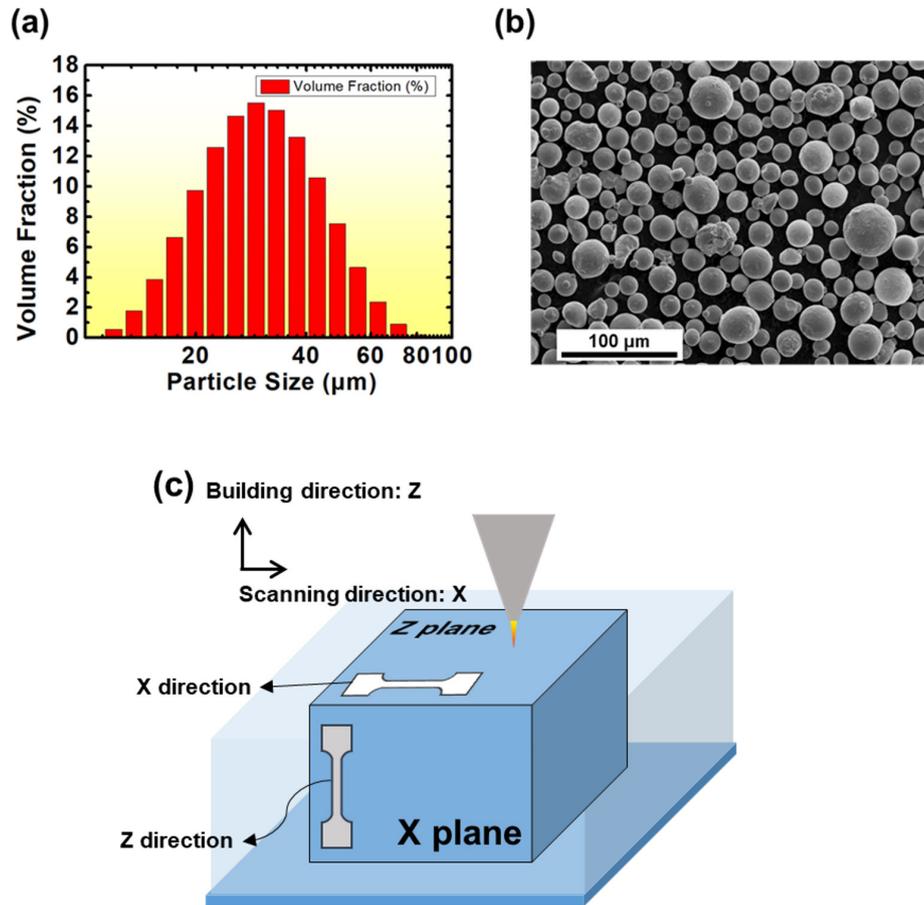


Fig. 1. (a) Particle size distribution of the STS powders and (b) Scanning electron microscopy micrograph. (c) A schematic showing the fabrication of the present sample and its directions.

respectively. The hole expansion tests were conducted on five samples of each alloy.

3. Results and Discussion

3.1. Microstructure

EBSD-inverse pole figure (IPF) of the LPBF and wrought samples are shown in Fig. 3. The X and Z directions represent scanning and building directions, respectively. The wrought sample shows fully recrystallized, exhibiting equiaxed FCC grains, with an average grain size of $115.4 \pm 6.8 \mu\text{m}$ and a low GND density of $\sim 4.5 \times 10^{12} \text{ m}^{-2}$. The grain boundaries act as the sites of crack initiation and propagation during plastic deformation, potentially deteriorating the stretch-flangeability. Interestingly, the LPBF-processed two samples show the unique microstructural evolution with high anisotropic microstructure, due to the non-uniform heat source of laser fabrication. The microstructure of the X-plane exhibited a semi-elliptical grain

morphology perpendicular to the build direction. This is attributed to the heat flow of the molten powder during the LPBF process, radiating outward from the center of the laser scan. In the X-plane of the LPBF sample, the average grain size was $\sim 58.0 \pm 33.0 \mu\text{m}$ with a GND density of $\sim 1.1 \times 10^{13} \text{ m}^{-2}$. Meanwhile, the Z plane shows the bimodal grain morphology with an average grain size of $\sim 45.4 \pm 26.5 \mu\text{m}$ and GND density of $\sim 1.2 \times 10^{13} \text{ m}^{-2}$. The grain size distribution of the LPBF sample on the Z plane shows the two peaks indicating that the bimodal grain morphology (Supplementary Fig. S1). The higher GND density of the LPBF sample than the wrought sample arises from the high thermal stress during laser deposition.

The BSE image shows the presence of cellular structure in the LPBF sample, as shown in Fig. 4. It is attributed to the cellular solidification due to ultrafast cooling rate, deformation-induced dislocations from thermal stress, and geometrically necessary dislocations (GND) by the thermal heterogeneity. During solidification of AM, solute elements are rejected and segregate

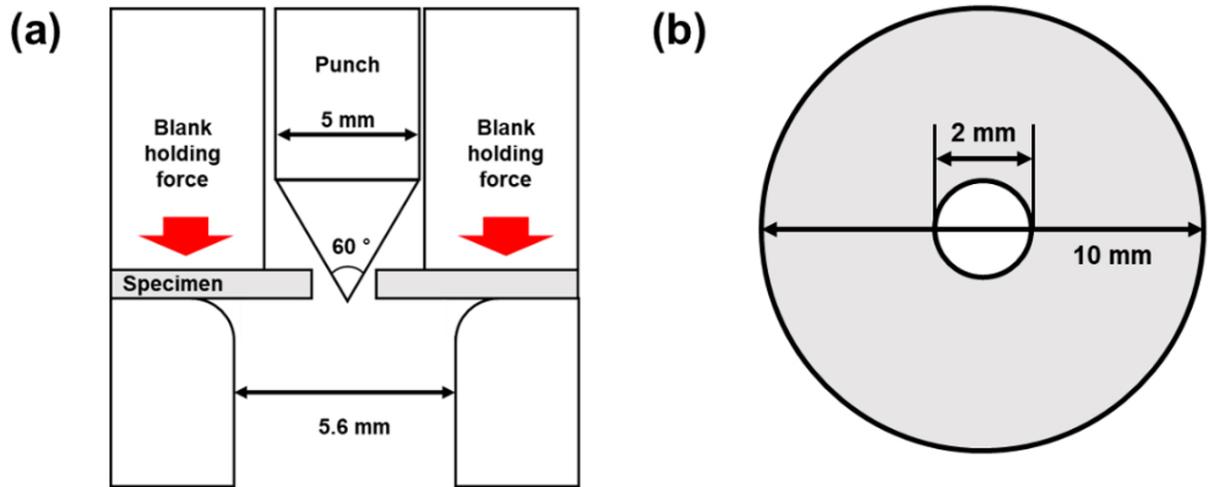


Fig. 2. Schematics of (a) hole expansion test (HET) tools and (b) the specimen dimension.

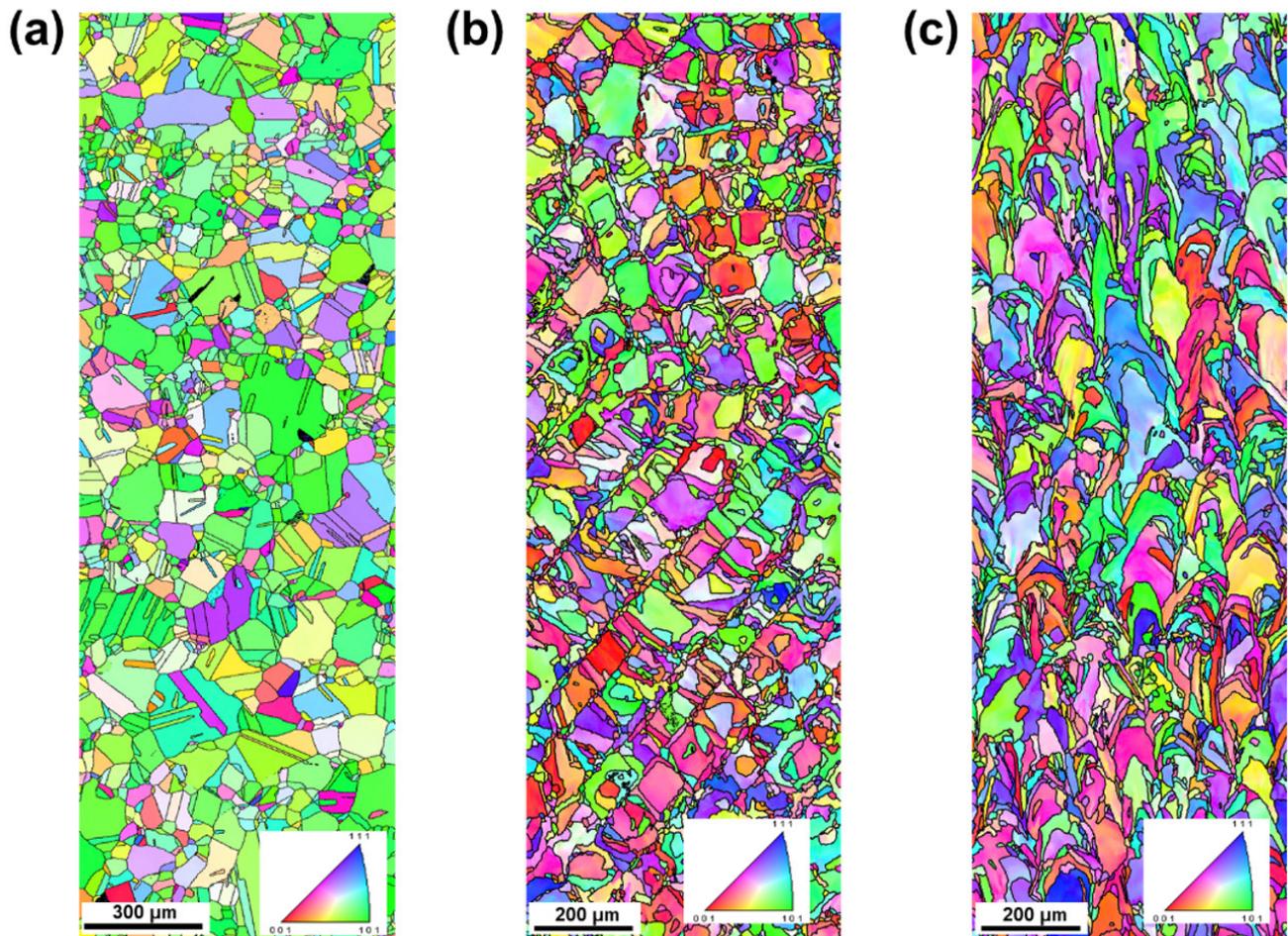


Fig. 3. Electron backscatter diffraction inverse pole figure maps of the (a) wrought sample and the LPBF sample on (b) the Z plane and (c) the X plane. LPBF, laser powder bed fusion.

into the inter-cellular dendritic regions, leading to a microstructure where cell boundaries contain a higher concentration of solute elements compared to the cell interiors [18]. Additionally, localized melting and solidification lead to dynamic tension/compression cycles [18]. The thermal stresses during laser deposition induce dislocation formation. The elevated temperature of the deposited material reduces yield strength, promoting easier plastic deformation [18].

3.2. Mechanical properties

Fig. 5a displays the engineering stress-strain curves of the present samples. The wrought sample shows a lower yield strength of ~254 MPa with high ductility (~0.96 of total elonga-

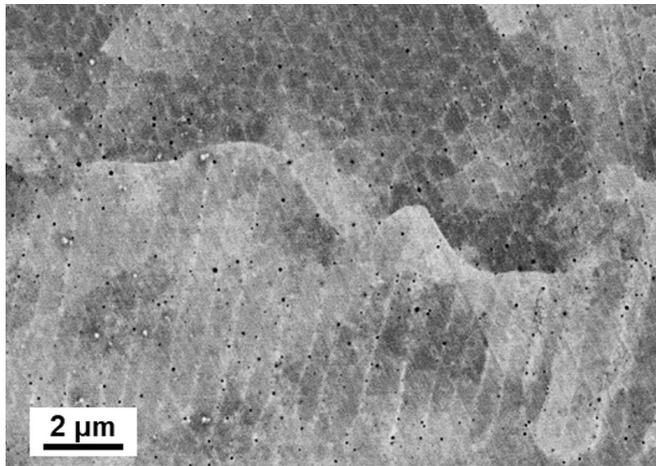


Fig. 4. Backscattered scanning electron image of the LPBF sample. LPBF, laser powder bed fusion.

tion) owing to full recrystallization. Notably, both tensile samples of LPBF exhibited superior tensile strength compared to the wrought sample. This is attributed to the hierarchical microstructure, which combines heterogeneous grain morphology and a sub-structured cellular structure, enhancing the material's strength [5]. The LPBF sample exhibits anisotropic mechanical properties [9]. Specifically, the sample along the X direction demonstrates higher strength compared to the Z direction, which is attributed to its finer grain size and high GND density.

Strain hardening rate (SHR) curves of each sample are plotted in Fig. 5b. The two drop regions in SHR are associated with easy glide and dynamic recovery. The wrought sample shows superior strain hardenability with stable deformation. This is because of the recrystallized grains with coarse grain size and low GND density.

The results of hole expansion tests are shown in Fig. 6. As shown in Fig. 7, the crack is fully propagated through the thickness of the specimens. The wrought sample exhibited the highest HER of ~19.4. The high elongation and coarse grains generally lead to excellent stretch-flangeability. Interestingly, significant HER differences were observed depending on the direction in the LPBF sample. It indicates that the microstructural anisotropy significantly influences stretch flangeability. The bimodal structure on the Z plane of the LPBF sample produces the strain partitioning between the fine and coarse grains, generating stress concentration and damage evolution [19-21]. Therefore, the strain partitioning from bimodal grains may result in an inferior resistance to crack initiation and propagation during the forming. To understand the anisotropic behavior of

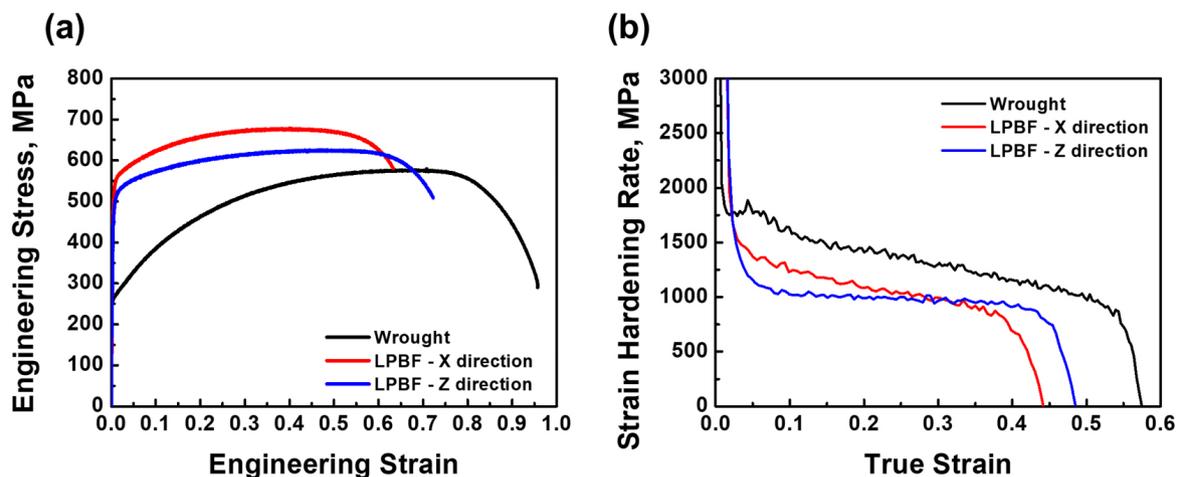


Fig. 5. (a) Engineering stress-strain curves and (b) strain hardening rate curves of the wrought and LPBF samples. LPBF, laser powder bed fusion.

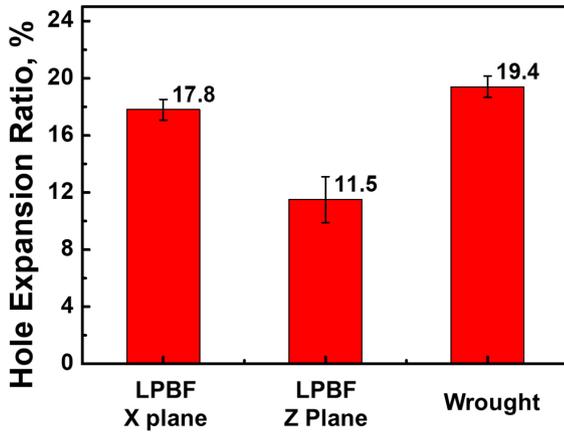


Fig. 6. Hole expansion ratio of the LPBF and wrought samples. LPBF, laser powder bed fusion.

forming, the fracture mechanism in two cases needs to be further investigated. Consequently, it is recommended to perform forming operations on the X plane of the LPBF-processed building parts.

The deformation path in the hole expansion test closely resembles that of a uniaxial tensile test. Specifically, when considering the major strain (ϵ_1) versus minor strain (ϵ_2) during deformation, the strain path for conical punching follows a uniaxial tensile mode ($\epsilon_1 = -2\epsilon_2$) [15]. The hole expansion ratio can be linked to the mechanical properties obtained from tensile testing. The crack-resistant properties during the forming test can be correlated with tensile properties in the direction on the plane of HET specimens, when considering the direction of major strain (Figs. 2 and 3) [15]. For instance, X-plane HET

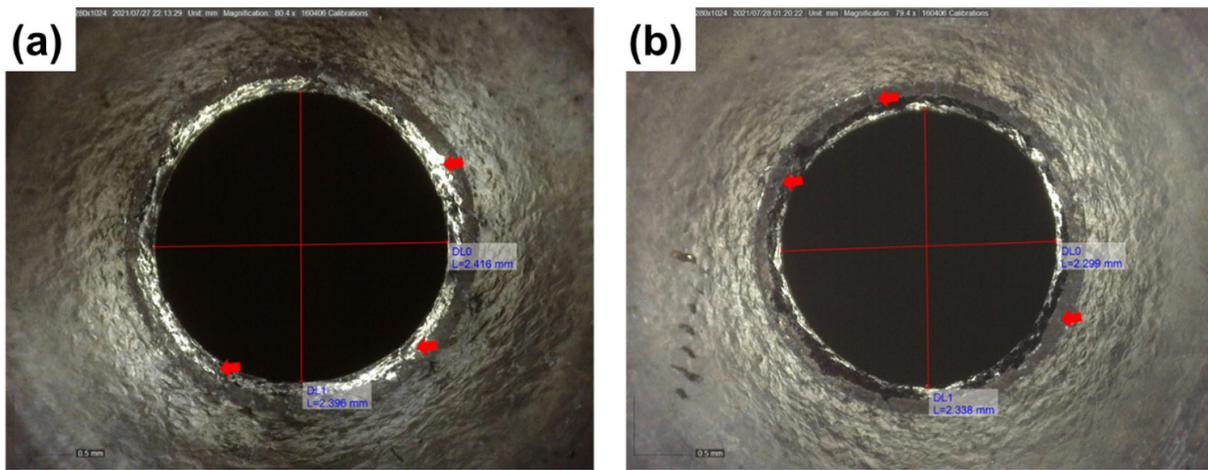


Fig. 7. Specimen after hole expansion testing of the LPBF samples in the (a) X and (b) Z directions. LPBF, laser powder bed fusion.

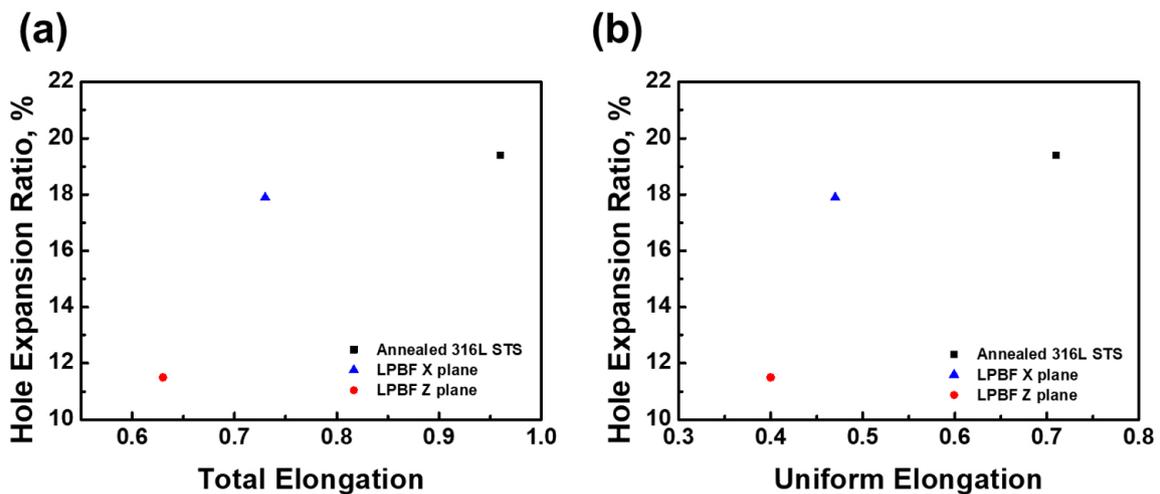


Fig. 8. Plots showing (a) the relationship between total elongation and the hole expansion ratio, and (b) the relationship between total elongation and the hole expansion ratio.

samples experience major strain on the X plane, which is related to the Z direction in tensile samples (Fig. 1c).

Figure 8 displays the relationship between ductility and hole expansion ratio. The high ductility of the sample generally leads to a high hole expansion ratio. LPBF Z plane shows the inferior hole expansion ratio related to its ductility, which is attributed to its bimodal grain morphology. During the deformation of heterostructured materials, the stress concentration occurs at the interface, leading to damage evolution [20, 21]. Therefore, the interface between coarse and fine grains in the Z plane is vulnerable to cracking, which deteriorates the crack initiation and propagation resistances.

4. Conclusion

Recent studies have demonstrated the potential of hybrid strategies combining additive manufacturing (AM) with processes such as cold rolling, high-pressure torsion, and forming processes to enhance material properties. Therefore, for AM materials to gain broader industrial acceptance, further investigation into their formability is essential. This study examines the metal-forming behavior of laser powder bed fusion (LPBF)-processed 316L stainless steel to address this gap. Hole expansion tests (HET) were performed on both wrought and LPBF samples in two orientations: the scan direction and the building direction. The results reveal pronounced anisotropy in the stretch-flangeability of LPBF materials, which can be attributed to their unique anisotropic microstructure. These findings provide valuable insights into the relationship between the microstructural characteristics of LPBF materials and their forming performance, emphasizing the importance of directional properties in industrial forming operations. By understanding and addressing the anisotropic behavior of LPBF materials, their potential for broader industrial applications can be further unlocked.

Funding

This work was supported by the National Research Foundation of Korea (NRF) grant funded by the Ministry of Science and ICT of Korea (2021R1A2C3006662).

Conflict of Interest

The authors have no conflicts of interest to declare.

Data Availability Statement

The datasets used during the current study available from the corresponding author on reasonable request.

Author Information and Contribution

Rae Eon Kim: Ph.D candidate; project administration, conceptualization, writing—original draft. Yeon Teak Choi: Ph.D; investigation. Sang Guk Jeong: Professor; investigation. Do Won Lee: Ph.D candidate; investigation. Hyoung Seop Kim: Professor; writing-review & editing, funding acquisition, supervision.

Acknowledgments

None.

References

- [1] J.-Y. Lee, J. An and C. K. Chua: *Appl. Mater. Today*, **7** (2017) 120–133.
- [2] R. E. Kim, S. G. Jeong, H. Ha, Y.-U. Heo, A. Amanov, G. H. Gu, D. J. Lee, J. Moon and H. S. Kim: *Mater. Sci. Eng. A*, **909** (2024) 146820.
- [3] J. Y. Park, B. J. Kim and J. G. Kim: *Met. Mater. Int.*, **29** (2023) 3521.
- [4] A. Jalali, A. Nikniazi, H. Gholamzadeh, S. Yin, M. Malekan, S. Y. Ahn, H. S. Kim, L. Balogh, L. Ravkov, S. Y. Persaud and V. Fallah: *Met. Mater. Int.*, **30** (2024) 3370.
- [5] Y. M. Wang, T. Voisin, J. T. McKeown, J. Ye, N. P. Calta, Z. Li, Z. Zeng, Y. Zhang, W. Chen and T. T. Roehling: *Nat. Mater.*, **17** (2018) 63.
- [6] L. Lemarquais, P. Giroux, H. Maskrot, B. Barkia, O. Hercher and P. Castany: *J. Mater. Res. Technol.*, **15** (2021) 4725.
- [7] L. Jinlong, Z. Zhiping and H. Jin: *Mater. Lett.*, **357** (2024) 135813.
- [8] A. S. Al-Zubaydi, N. Gao, J. Džugan, N. Gao, P. Podany, Y. Chen and P. A. Reed: *Mater. Sci. Technol.*, (2024) 22.
- [9] P. Snopiński: *J. Alloys Compd.*, **941** (2023) 168984.
- [10] S. Mohd Yusuf, Y. Chen, S. Yang and N. Gao: *Adv. Eng. Mater.*, **22** (2020) 2000052.
- [11] T. Ge, Y. Li, D. Gao, C. Yang and F. Li: *J. Manuf. Process.*, **124** (2024) 345.
- [12] J. Ferchow, M. Bühler, M. Schlüssel, L. Zumofen, C. Klahn, U. Hofmann, A. Kirchheim and M. Meboldt: *Int. J. Adv. Manuf. Technol.*, **119** (2022) 7947.

- [13] Y. T. Choi, P. Asghari-Rad, J. W. Bae and H. S. Kim: *Mater. Sci. Eng. A*, **852** (2022) 143683.
- [14] Y. T. Choi, J. W. Bae, J. M. Park, H. H. Lee, H. Kwon, S. Son, D.-H. Ahn and H. S. Kim: *Mater. Sci. Eng. A*, **814** (2021) 141241.
- [15] S. K. Paul: *Materialia*, **9** (2020) 100566.
- [16] J. I. Yoon, J. Jung, S.-H. Joo, T. J. Song, K.-G. Chin, M. H. Seo, S.-J. Kim, S. Lee and H. S. Kim: *Mater. Lett.*, **180** (201) 322.
- [17] IO Standardization, *Metallic Materials-Sheet and Strip-Method of Hole Expanding Test*, (2009).
- [18] G. M. Karthik, E. S. Kim, P. Sathiyamoorthi, A. Zargaran, S. G. Jeong, R. Xiong, S. H. Kang, J.-W. Cho and H. S. Kim: *Addit. Manuf.*, **47** (2021) 102314.
- [19] J. Zhou, Y. Wang, G. Zhi and L. He: *Met. Mater. Int.*, **30** (2024) 240.
- [20] H.K. Park, K. Ameyama, J. Yoo, H. Hwang and H. S. Kim: *Mater. Res. Lett.*, **6** (2018) 261.
- [21] R. E. Kim, G. H. Gu, H. Kwon, S. Y. Ahn, J. Kwon, J. A. Lee, Y. T. Choi, M. H. Seo and H. S. Kim: *J. Mater. Res. Technol.*, **21** (2022) 3514.

Ultra-Low-Temperature (4.2 K) Tensile Properties and Deformation Mechanism of Stainless Steel 304L Manufactured by Laser Powder Bed Fusion

Seung-Min Jeon^{1,2}, Young-Sang Na², Young-Kyun Kim^{2,*}

¹Department of Smart Manufacturing Engineering, Changwon National University, Changwon 51140, Republic of Korea

²Korea Institute of Materials Science, Changwon 51508, Republic of Korea

This study investigated the ultra-low-temperature (4.2 K) tensile properties and deformation mechanisms of stainless steel 304L manufactured via laser powder bed fusion (LPBF). The tensile properties of LPBF 304L were compared to those of conventional 304L to assess its suitability for cryogenic applications. The results revealed that LPBF 304L exhibited a significantly higher yield strength but lower ultimate tensile strength and elongation than conventional 304L at 4.2 K. The temperature dependence of the yield strength also favored LPBF 304L. Microstructural analysis demonstrated that LPBF 304L features a high density of dislocation cells and nano-inclusions, contributing to its greater strength. Furthermore, strain-induced martensitic transformation was observed as a key deformation mechanism at cryogenic temperatures, where austenite transformed into both hexagonal-closed packed (HCP) and body-centered cubic (BCC) martensite. Notably, BCC martensite nucleation occurred within a single HCP band. These findings provide critical insights into the mechanical behavior of LPBF 304L at cryogenic temperatures and its potential for applications in extreme environments.

Keywords: Laser powder bed fusion (LPBF); Stainless steel 304L; Extremely low temperature; Tensile properties; Microstructure

Received: February 20, 2025

Revised: April 7, 2025

Accepted: April 7, 2025

***Corresponding author:**

Young-Kyun Kim

E-mail: ykkim@kims.re.kr

1. Introduction

The hydrogen economy has emerged as a key alternative for reducing carbon emissions and mitigating greenhouse gases [1, 2]. With the increasing use of hydrogen in various sectors—including renewable energy, fuel cells, and the aerospace industry—the demand for materials that can perform reliably in hydrogen environments is expected to grow steadily [3-6]. In particular, liquid hydrogen (LH₂) has attracted significant attention due to its high gravity energy density (33.3 kWh/kg) and excellent storage efficiency compared to gaseous hydrogen. However, because LH₂ boils at -253 °C, it is imperative to evaluate the safety of materials intended for use in such ultralow temperature environments.

Metal additive manufacturing (MAM) technologies have

revolutionized production by enabling the fabrication of geometrically complex components that are unattainable through traditional manufacturing methods [7, 8]. Among various materials used at cryogenic temperatures, 304L stainless steel (STS) is highly favored owing to its outstanding stability and mechanical properties under low-temperature conditions [9-12]. In particular, laser powder bed fusion (LPBF) utilizes a high-power laser to locally melt selected areas of metal powder. The rapid cooling and solidification in LPBF enable hetero-structuring and hierarchical microstructure. Moreover, the uniform thin-layer deposition—on the order of tens to hundreds of micrometers—allows for excellent mechanical properties to be achieved, provided that optimal process parameters are employed.

Despite these advantages, metallic materials fabricated via AM frequently exhibit notable microstructural defects such as porosity, dislocation network-induced substructure, texture, and oxide formation during AM [13-15]. While controlled mi-

<https://doi.org/10.4150/jpm.2025.00066>

© 2025 The Korean Powder Metallurgy & Materials Institute

microstructural defects can sometimes impart strengthening effects and enhance mechanical performance, excessive defects are detrimental to mechanical behavior of materials. This is particularly critical in ultralow temperature environments, where the primary carriers of dislocation glide may be restricted, and reduced phase stability can lead to phase transformations from face-centered cubic (FCC) to body-centered cubic (BCC) structure. Consequently, microstructural defects can have a more pronounced adverse effect on mechanical properties at cryogenic temperatures. Thus, it is essential to evaluate the performance of AM materials under these conditions before considering their application in cryogenic environments. In the present study, we address these challenges by investigating the tensile properties of LPBF-manufactured STS 304L at 4.2 K. We discuss the correlations between the microstructure and tensile properties and compare the performance with that of conventional commercial STS 304L to provide a comprehensive understanding of the potential of AM materials for cryogenic applications.

2. Experimental procedure

2.1. Materials

Table 1 shows the chemical compositions of LPBF 304L and conventional 304L, which were chosen for their similar compositions to facilitate a direct comparison of their microstructures and tensile properties. The chemical compositions of both LPBF and conventional stainless steels are based on the manufacturer's mill sheet specifications. The LPBF 304L was produced using gas-atomized AISI 304L powder with an average particle size of 37 μm . The metal 3D printer ProX DMP 300 from 3D Systems was employed for the LPBF process. This printer utilizes a continuous laser with a spot size of 100 μm and a 175 W laser beam that traverses the powder bed at a speed of 1000 mm/s. The laser scanning strategy involves a 90° rotation between successive layers, resulting in a rectangular specimen with dimensions of 90 mm \times 23 mm \times 5 mm.

2.2. Ultralow temperature (4.2 K) tensile testing

Ultralow temperature tensile tests were performed using a

liquid helium tensile testing machine at the Korea Institute of Materials Science (KIMS) [16]. The system continuously supplies liquid helium to cool the specimen, and once the attached cryogenic temperature sensor stabilizes at 4.2 K, the tensile test is started. Dog-bone specimens with gauge dimensions of 12.0 \times 3.0 \times 1.2 mm³ were fabricated in accordance with ASTM E8. The tensile tests were conducted at an initial strain rate of 1 \times 10⁻³ s⁻¹.

2.3. Microstructural observation

The microstructures were examined using a field-emission scanning electron microscope (FE-SEM; MIRA3, TESCAN) and an electron backscatter diffraction (EBSD) detector (Nordlys Nano, Oxford Instruments). EBSD images were collected under optimized conditions at an accelerating voltage of 20 kV and a working distance of 12 mm. In addition, the electron channeling contrast (ECC) technique was utilized to investigate dislocation structures, with ECC images acquired at 30 kV and a 7 mm working distance. For sample preparation, an automatic polisher (Dualprep 3-AP4, Allied) was used. All specimens were ground using silicon carbide papers (#400–#2000) and diamond suspensions with an average particle size of 1 μm , followed by a final polishing step with colloidal silica (average particle size of 0.04 μm).

3. Results and Discussion

3.1. Initial microstructure

Fig. 1 shows the initial microstructural characteristics of LPBF 304L (a-c) and conventional STS 304L (d-f), as revealed by inverse pole figure (IPF) maps, phase maps, and ECC images. The IPF map of LPBF 304L obtained from a plane perpendicular to the build direction reveals a grid-like grain structure with an average grain size of 31.6 μm (Fig. 1a). This grid pattern is characteristic of LPBF processes where the build direction rotates by 90° between successive layers [17, 18]. Notably, no δ -ferrite is detected in LPBF 304L, which is entirely austenitic (Fig. 1b). In contrast, the conventional 304L consists of equiaxed grains with a few annealing twins, exhibiting an average grain size of 58.7 μm (Fig. 1d). It predominantly comprises

Table 1. Chemical composition of conventional STS 304L and LPBF 304L powder. (wt. %)

Wt %	Fe	Si	Mn	P	S	Cr	Ni	Mo	Co	N	C	O
Conventional STS 304L	Bal.	0.45	1.67	0.031	0.002	18.21	8.06	0.14	0.21	0.14	0.028	-
LPBF 304L powder	Bal.	0.75	1.39	0.02	0.01	18.95	9.71	-	-	0.11	0.02	0.10

LPBF, laser powder bed fusion.

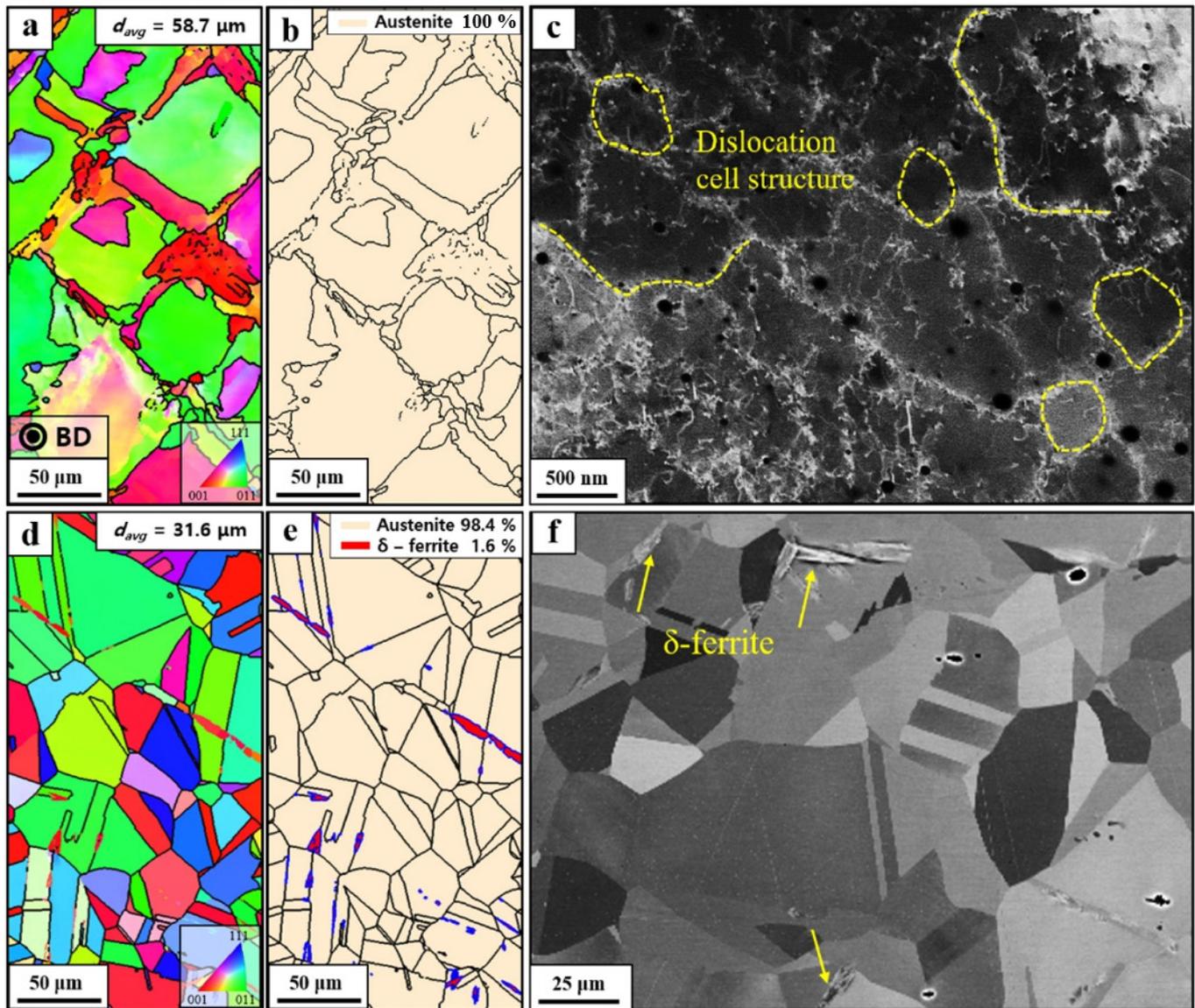


Fig. 1. (a, d) Electron backscatter diffraction inverse pole figure (IPF), (b, e) phase maps, (c, f) electron channeling contrast (ECC) image of (a-c) LPBF STS 304L and (d-f) conventional STS 304L indicating the initial microstructure. LPBF, laser powder bed fusion.

austenite, with a minor fraction (1.6%) of δ -ferrite observed (Fig. 1e).

Further insights into the microstructures were obtained through ECC analysis. As shown in Fig. 1c (LPBF 304L) and Fig. 1f (conventional 304L), the LPBF 304L exhibits a high density of dislocations arranged in a cellular structure. This dislocation cell structure likely results from the rapid solidification and repetitive thermal cycling inherent to the LPBF process, which generates and accumulates dislocations that subsequently arrange themselves to minimize the internal energy [19]. Additionally, small, dark oxide particles, which presumably formed during the LPBF process, are observed. Conversely, the

ECC image of conventional 304L (Fig. 2e) shows a near absence of dislocations, with the equiaxed grains and δ -ferrite clearly visible in the IPF and phase maps.

Due to the nature of the LPBF process, the formation of oxides and porosity can occur during fabrication. During printing, the oxygen level in the chamber was maintained at approximately 0.2%. The as-received powder contained 106 ± 5 ppm of oxygen, which increased to 440 ± 12 ppm in the printed material. This 334 ppm increase suggests the formation of oxide particles within the SS304L matrix during processing. Oxygen content was measured using a LECO TC-436 nitrogen-oxygen analyzer. Porosity in conventional STS 304L is typically

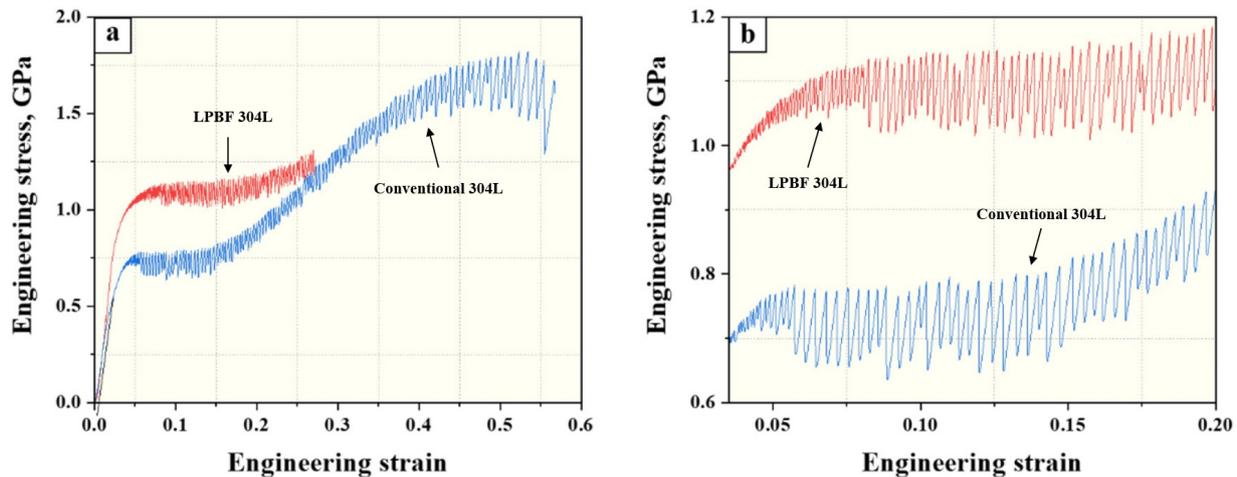


Fig. 2. (a) Engineering stress-strain curve at 4.2 K and (b) cropped image in (a) showing a different discontinuous plastic flow behavior of conventional 304L (blue line) and LPBF 304L (red line). LPBF, laser powder bed fusion.

negligible, owing to its homogeneous and densely compacted manufacturing process. In contrast, LPBF 304L exhibited a porosity of approximately 0.01%, as determined by micro-CT analysis using a Phoenix Vtomex M system from Waygate Technologies.

3.2. Ultralow temperature (4.2 K) tensile properties

Fig. 2a presents the tensile properties of LPBF 304L and conventional 304L in a liquid helium environment (4.2 K). At 4.2 K, conventional 304L exhibits a yield strength (YS) of 549.8 MPa, an ultimate tensile strength (UTS) of 1.81 GPa, and an elongation of 56.5%. In contrast, the LPBF-manufactured STS 304L shows a higher YS of 777.8 MPa, but a lower UTS of 1.31 GPa and an elongation of 27.5% compared to conventional 304L. Although the UTS and elongation of LPBF 304L are inferior, its yield strength exceeds that of conventional 304L by over 40%. This implies that LPBF 304L exhibits superior structural stability at cryogenic temperatures (i.e., liquid helium and/or liquid hydrogen) compared to conventional 304L, thereby facilitating the design of lighter metallic components.

Both materials display pronounced discontinuous plastic flow (DPF) phenomenon, characterized by load-drop in stress-strain curves. Such serrations with an unstable oscillation are typically attributed to dynamic strain aging (DSA) during deformation at intermediate temperatures [20]. However, at 4.2 K the thermal energy is insufficient to activate DSA, implying that alternative mechanisms must be responsible for the serrated behavior. Two prevailing models have been proposed:

1. Mechanical instability model: Seeger et al. [21] reported that dislocation interactions among different slip systems lead to the formation of Lomer-Cottrell (L-C) locks. At cryogenic temperatures, limited thermal activation causes dislocations to accumulate until the stress concentration reaches the theoretical shear strength, at which point a sudden collapse of the L-C locks results in a stress drop. Therefore, the sequential formation and collapse of these locks are considered to the origin of serration at extremely low temperatures.
2. Thermomechanical instability model: First proposed by Basinski [22], this model suggests that plastic deformation results in dislocation multiplication, which converts mechanical work into heat. Due to the very low specific heat at cryogenic temperatures, localized plastic deformation can lead to temperature spikes of several tens of Kelvin. This adiabatic heating lowers the flow stress locally, causing a sudden stress drop.

Although it is not definitively established which mechanism predominates, both models invoke the localized buildup and subsequent collapse of dislocations to explain the stress drops. Notably, as the strain increases, the serrations become more pronounced (Fig. 2b), and the magnitude of the stress drops grows. This is likely due to the enhanced accumulation of dislocations and L-C locks as the deformation proceeded. Although LPBF 304L exhibits roughly 40% higher yield strength, its stress drop is slightly lower, measuring at 120 MPa compared to 144 MPa for conventional 304L. This indicates that

LPBF 304L experiences fewer temperature spikes or a slower rate of dislocation generation and accumulation, and that differences in physical properties (e.g., the strength of local L-C locks or specific heat variations due to compositional differences) govern the extent of the stress drop.

3.3. Temperature dependence of yield strength for LPBF and conventional 304L

Fig. 3 illustrates the yield strengths of both conventional 304L and LPBF 304L as a function of temperature. In addition to the 4.2 K tests, tensile experiments were conducted at room temperature (298 K) and in liquid nitrogen (77 K) to assess temperature dependence. The yield strength data over these three temperatures were fitted with an exponential function from 4.2 K to 298 K, described by [23]:

$$\sigma_{Ys}(T) = \sigma_a \exp\left(-\frac{T}{C}\right) + \sigma_b \quad (1)$$

Where σ_a , σ_b , and C are fitting constants. Here, σ_a represents the thermal (temperature-dependent) component of yield strength, while σ_b accounts for the temperature independent (athermal) part.

Table 2 presents the fitting constants for both conventional 304L and LPBF 304L. The results reveal that LPBF 304L has higher values for both the thermal-dependent fitting constant (σ_a) and athermal (σ_b) components compared to conventional 304L. In current alloys, the yield strength generally stems from the intrinsic lattice resistance to dislocation motion, referred to

as the friction stress ($\Delta\sigma_f$), combined with additional strengthening increments from multiple sources: the initial dislocation density ($\Delta\sigma_{dis}$), solid solution effects ($\Delta\sigma_{ss}$), precipitates ($\Delta\sigma_{ppt}$), and grain boundary ($\Delta\sigma_{gb}$, via the Hall-Petch relationship). Hence, the yield strength can be expressed in a general form as:

$$\sigma_y = \sigma_{fr} + \Delta\sigma_{dis} + \Delta\sigma_{ss} + \Delta\sigma_{ppt} + \Delta\sigma_{gb} \quad (2)$$

Considering these strengthening components of yield strength, the higher athermal constant (σ_b) for LPBF 304L is due to the influence of σ_{fr} , $\Delta\sigma_{dis}$, $\Delta\sigma_{ppt}$, $\Delta\sigma_{gb}$. The influence of $\Delta\sigma_{ss}$ is negligible due to the little difference in composition between the two alloys. In LPBF 304L, we can see that the initial dislocation density is higher than conventional 304L, with a large number of dislocation cells (Fig. 1c and 1f). Additionally, nano inclusions, appearing as black dots, are widely distributed in large numbers. This distribution enhances the strengthening contributions of $\Delta\sigma_{dis}$ and $\Delta\sigma_{ppt}$. Furthermore, the friction stress σ_{fr} increases due to the combined effects of the high initial dislocation density and the presence of nano inclusions, which enhance the intrinsic lattice resistance to dislocation motion. Consequently, even though the average grain size of LPBF 304L (58.7 μm) is larger than that of conventional 304L (31.6 μm)—thus granting conventional 304L a higher strengthening contribution from the Hall-Petch relationship—once the other strengthening factors are taken into account, the overall yield strength of LPBF 304L remains higher, as evidenced by the athermal constant (σ_b).

Thermal-dependent constant (σ_a) is also found to be higher in LPBF 304L, indicating a significant increment in yield strength as the temperature decreases. In this context, friction stress (σ_{fr}) plays a major role. Generally, friction stress is proportional to the magnitude of the Peierls-Nabarro barrier, which refers to the shear stress required to move dislocations through the crystal lattice along a specific direction. While the Peierls-Nabarro barrier is negligible in pure FCC metals, making them relatively insensitive to temperature changes, the material in this study exhibits increasing yield strength at cryogenic temperatures, suggesting a larger Peierls-Nabarro barrier.

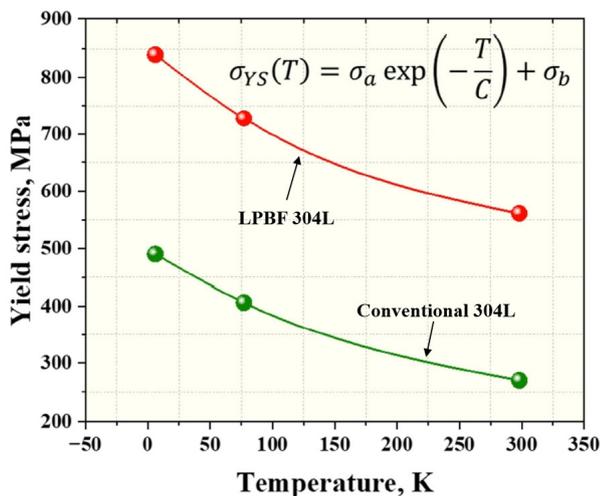


Fig. 3. Exponential function-fitted temperature dependence of the yield strength of conventional and LPBF 304L. LPBF, laser powder bed fusion.

Table 2. Fitting constants of the temperature dependence of yield strength for conventional and LPBF 304L

	σ_a (MPa)	C	σ_b (MPa)
Conventional 304L	312.6	226.6	185.9
LPBF 304L	371.9	198.6	478.4

LPBF, laser powder bed fusion.

This can be attributed to the large number of dislocation cells and nano inclusions in LPBF 304L, which hinder dislocation movement and thus require greater activation energy, thereby increasing the Peierls-Nabarro barrier. At ultra-low temperatures, the available thermal energy to activate these dislocations is even more limited, so the Peierls-Nabarro barrier is expected to be larger still. Consequently, the yield strength increases further as the temperature decreases, and its temperature dependence also becomes more pronounced.

As a result, LPBF 304L has a higher initial dislocation density

and contains more nano-inclusions, which leads to a higher thermal constant (σ_b) and thus a higher yield strength at room temperature. This also increases the Peierls-Nabarro barrier, thereby raising the temperature-dependent constant (σ_a) of the yield strength in LPBF 304L compared to conventional 304L.

3.4. Deformation behavior

Fig. 4 shows the deformed microstructure of LPBF 304L after tensile testing at 4.2 K. IPF map for the deformed specimen at 4.2 K reveals that the original grid-like grain structure evolved

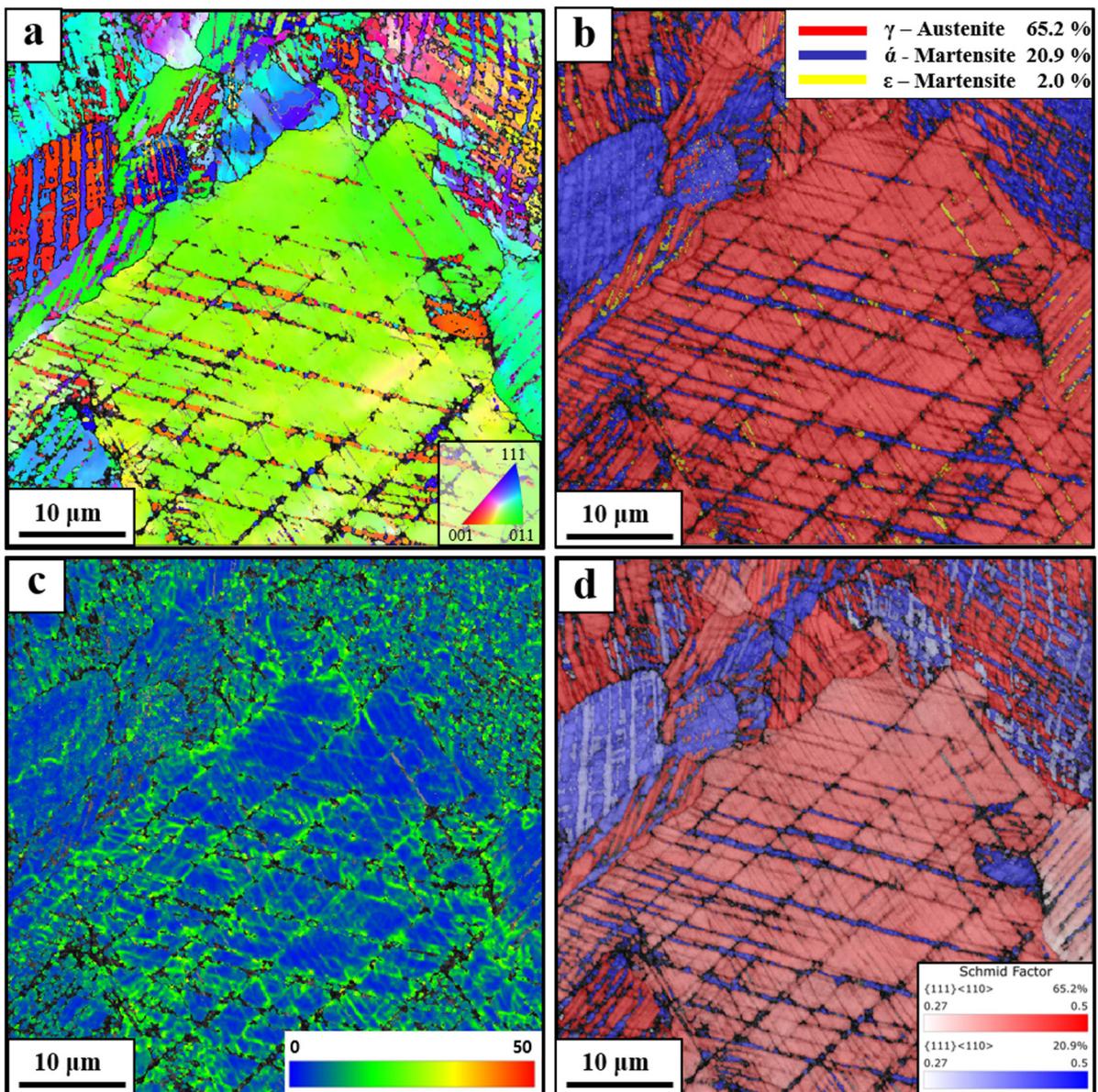


Fig. 4. 4.2 K Deformed microstructure of LPBF 304L. (a) Inverse pole figure (IPF) map, (b) phase map, (c) geometrically necessary dislocation (GND) map, (d) Schmid factor mapping (red: FCC phase, blue: BCC phase). LPBF, laser powder bed fusion; FCC, face-centered cubic; BCC, body-centered cubic.

into numerous deformation bands as strain was accommodated (Fig. 4a). In the phase map (Fig. 4b), these deformation bands are predominantly identified as the BCC phase, with a minor presence of the Hexagonal-closed packed (HCP) phase. It is worth noting that the volume fractions measured were 65.2% FCC, 20.9% BCC, and 2.0% HCP, respectively. These BCC bands are primarily generated by deformation and are indicative of strain-induced martensitic transformation (SIMT) [24, 25]. In stainless steels with low stacking fault energy (SFE), SIMT is known to alleviate strain concentration and promote more homogeneous deformation [26, 27]. Given that SIMT typically occurs in stainless steels with SFE in the range of 15–20 mJ/m² [27–29], it is evident that the primary deformation mechanism at 4.2 K in this material is the transformation to HCP or BCC martensite, facilitated by its low SFE. Fig. 4c presents a map of geometrically necessary dislocations (GNDs), revealing a substantial density of dislocations with an average GND density of $9.32 \times 10^{14}/\text{m}^2$. The GND density is notably higher near the BCC martensite regions, suggesting that the BCC martensite effectively impedes dislocation motion. Moreover, BCC martensite formed where the dislocations concentrated. Furthermore, the Schmid factor map (Fig. 4d) presents how well the external load (primarily in the tensile direction) is geometrically aligned with each grain's active slip system (or dislocation activity). A higher Schmid factor indicates that the slip system more readily contributes to deformation. SIMT at 4.2 K shows that it activates the slip system in the BCC region, which in turn relaxes the stress concentration in LPBF 304L, allowing for more uniform deformation.

To further elucidate the deformation mechanisms, ECCI analysis was performed on the deformed specimen at 4.2 K. Fig. 5 shows ECC images of a tensile fracture surface obtained at 4.2 K. Here, we present ECC images from a region exhibiting partial SIMT (a) and one predominantly undergoing SIMT (b). For the partial SIMT region (Fig. 5a), numerous dislocations and stacking faults are visible in FCC domain where SIMT has not yet occurred. In contrast, the region to the right of the dashed line is characterized by abundant HCP bands and localized BCC martensite formation. This observation is consistent with the EBSD results in Fig. 4 and clearly illustrates the evolution of dislocation behavior before and after SIMT. On the other hand, the ECC image reveals that LPBF 304L has a low SFE yet still retains some FCC domains. This outcome is likely due to the presence of numerous micro-defects, such as pores, in the additively manufactured material, which impede further progression of the SIMT and lead to premature fracture, leaving a portion of the FCC domains untransformed.

Fig. 5b provides a detailed view of the nucleation of BCC martensite, further corroborating the role of dislocation accumulation and SIMT in the deformation process. ECCI observations across multiple regions reveal that BCC martensite nucleates and grows via SIMT within a single HCP band. Although the exact nucleation sites of the fully developed martensitic regions cannot be identified, this transformation behavior differs from that typically observed in conventional STS under cryogenic conditions. It is generally reported that SIMT of STS results in BCC nucleation at the intersection of HCP bands [30, 31]. Ho et al. [30] and Kruml et al. [31] reported that at low

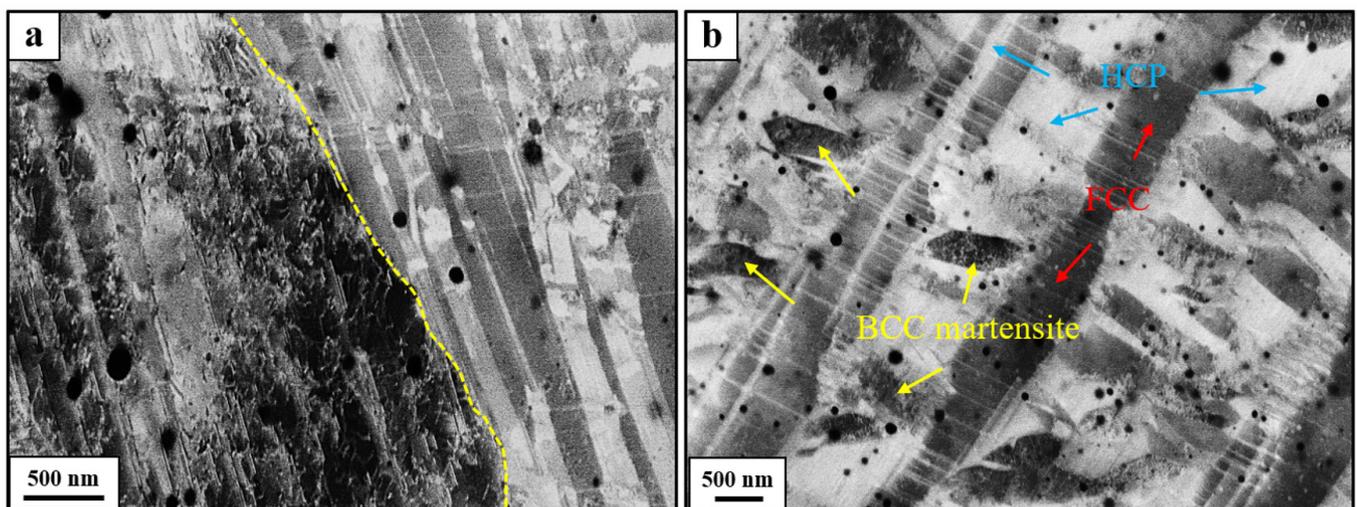


Fig. 5. Electron channeling contrast (ECC) image of a tensile sample deformed at 4.2 K showing (a) dislocation behavior and (b) strain-induced transformation.

temperatures, due to the low SFE, a perfect dislocation splits into two Shockley partial dislocations. The migration of these partial dislocations leads to the formation of HCP bands by introducing stacking fault. They also noted that the BCC martensite, which forms between two HCP bands, does not transform directly from austenite (FCC) to martensite (BCC). Instead, austenite first transforms into the energetically stable HCP phase, which then transitions into BCC martensite at the HCP band intersection. However, in the case of LPBF 304L, BCC nucleation occurred within a single HCP band, which differs from previous reports [30, 31]. This is likely due to the low activation energy for BCC martensite formation, which results from differences in the degree of activation of the slip system and austenite stability [32-34].

4. Conclusion

In this work, the ultra-low temperature (4.2 K) tensile properties and deformation mechanisms of stainless steel 304L manufactured via laser powder bed fusion (LPBF) were investigated. The summarized conclusions are as follows:

1. The LPBF-manufactured 304L exhibited a significantly higher yield strength at 4.2 K compared to conventional 304L. This enhancement is attributed to the high initial dislocation density and the presence of nano inclusions, which increase lattice resistance to dislocation motion.
2. The LPBF 304L exhibited a greater temperature dependence in yield strength compared to conventional 304L. The Peierls-Nabarro barrier, influenced by initial dislocation interactions and nano inclusions, contributed to this effect, highlighting the material's unique response to cryogenic conditions. In addition, a discontinuous plastic flow (DPF) was observed at 4.2 K, which was attributed to differences in the intrinsic physical properties.
3. Both HCP and BCC martensite phases were observed in the deformed microstructure, confirming that SIMT plays a critical role in the plastic deformation of LPBF 304L at 4.2 K. This transformation helps accommodate strain and contributes to mechanical stability under extreme conditions.
4. Unlike previous reports where BCC martensite nucleates at the intersection of HCP bands, this study observed BCC formation within single HCP bands in LPBF 304L. This distinct transformation pathway requires further investigation to fully understand its implications on mechanical behavior.

5. The superior yield strength and deformation characteristics of LPBF 304L indicate its potential for applications in cryogenic environments, such as hydrogen storage and aerospace structures. However, its reduced ductility and susceptibility to microstructural defects must be carefully considered in design and processing.

Funding

This study was supported financially by Fundamental Research Program of the Korea Institute of Materials Science (No. PNKA320); and the Nano Material Technology Development Program (No. RS-2024-00445038) through the National Research Foundation of Korea).

Conflict of Interest

The authors declare no competing financial interests or personal relationships.

Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

Author Information and Contribution

S.-M. Jeon: Investigation, Methodology, Writing – original draft. Y.-S. Na: Writing – review & editing, Supervision. Y.-K. Kim: Investigation, Methodology, Writing – original draft, Writing – review & editing, Supervision, Conceptualization.

Acknowledgments

None.

References

- [1] S. Griffiths, B. K. Sovacool, J. Kim, M. Bazilian and J. M. Uratani: *Energy Res. Soc. Sci.*, **80** (2021) 102208.
- [2] T. Zhang, J. Uratani, Y. Huang, L. Xu, S. Griffiths and Y. Ding: *Renewable Sustainable Energy Rev.*, **176** (2023) 113204.
- [3] D. Kang, S. Yun and B. Kim: *Energies*, **15** (2022) 4357.
- [4] M. Aziz: *Energies*, **14** (2021) 5917.
- [5] J. Fesmire, A. Swanger, J. Jacobson and W. Notardonato:

- IOP Conf. Ser.: Mater. Sci. Eng., **1240** (2022) 012088.
- [6] L. Yin, H. Yang and Y. Ju: *Int. J. Hydrog. Energy*, **57** (2024) 1302.
- [7] D. Herzog, V. Seyda, E. Wycisk and C. Emmelmann: *Acta Mater.*, **117** (2016) 371.
- [8] B. H. Jared, M. A. Aguilo, L. L. Beghini, B. L. Boyce, B. W. Clark, A. Cook, B. J. Kaehr and J. Robbins: *Scr. Mater.*, **135** (2017) 141.
- [9] T. DebRoy, H. L. Wei, J. S. Zuback, T. Mukherjee, J. W. Elmer, J. O. Milewski, A. M. Beese, A. Wilson-Heid, A. De and W. Zhang: *Prog. Mater. Sci.*, **92** (2018) 112.
- [10] C. Zheng and W. Yu: *Mater. Sci. Eng. A*, **710** (2018) 359.
- [11] M. S. Kim, T. Lee, J. W. Part and Y. Kim: *Metals*, **13** (2023) 1774.
- [12] T. Sakurai, O. Umezawa and Y. Ono: *IOP Conf. Ser.: Mater. Sci. Eng.*, **1302** (2024) 012002.
- [13] S. Chowdhury, N. Yadaiah, C. Prakash, S. Ramakrishna, S. Dixit, L. R. Gupta and D. Buddhi: *J. Mater. Res. Technol.*, **20** (2022) 2109.
- [14] S. R. Narasimharaju, W. Zeng, T. L. See, P. Scott, X. Jiang and S. Lou: *J. Manuf. Processes*, **75** (2022) 375.
- [15] W. H. Kan, L. N. S. Chiu, C. V. S. Lim, Y. Zhu, Y. Tian, D. Jiang and A. Huang: *J. Mater. Sci.*, **57** (2022) 9818.
- [16] Y.-K. Kim, K.-R. Lim and Y.-S. Na: *Korean J. Met. Mater.*, **61** (2023) 389.
- [17] N. Nadammal, T. Mishurova, T. Frisch, I. Serrano-Munoz, A. Kromm, C. Haberland, P. D. Portella and G. Bruno: *Addit. Manuf.*, **38** (2021) 101792.
- [18] B. Dovgyy, A. Piglione, P. A. Hooper and M. S. Pham: *Mater. Des.*, **194** (2020) 108845.
- [19] X. He, X. K. Shang, J. He and B. B. He: *Mater. Charact.*, **217** (2024) 114335.
- [20] S.-Y. Lee, C. Takushima, J.-I. Hamada and N. Nakada: *Acta Mater.*, **205** (2021) 116560.
- [21] A. Seeger, J. Diehl, S. Mader and H. Rebstock: *Phil. Mag.*, **2** (1957) 323.
- [22] Z. S. Basinski: *Proc. R. Soc. London, Ser. A*, **240** (1957) 229.
- [23] Z. Wu, H. Bei, G. M. Pharr and E. P. George: *Acta Mater.*, **81** (2014) 428.
- [24] Y. F. Shena, X. X. Li, X. Sunb, Y. D. Wanga and L. Zuo: *Mater. Sci. Eng. A*, **552** (2012) 514.
- [25] D. Molnar, X. Sun, S. Lu, W. Li, G. Engberg and L. Vitos: *Mater. Sci. Eng. A*, **759** (2019) 490.
- [26] N. J. Simon and R. P. Reed: *J. Nucl. Mater.*, **141-143** (1986) 44.
- [27] S. Martin, S. Wolf, U. Martin, L. Krüger and D. Rafaja: *Metall. Mater. Trans. A*, **47** (2016) 49.
- [28] L. Remy and A. Pineau: *Mater. Sci. Eng.*, **28** (1977) 99.
- [29] K. Sato, M. Ichinose, Y. Hirotsu and Y. Inoue: *ISIJ Int.*, **29** (1989) 868.
- [30] K. H. Lo, C. H. Shek and J. K. L. Lai: *Mater. Sci. Eng.: R: Rep.*, **65** (2009) 39.
- [31] T. Kruml, J. Polak and S. Degallaix: *Mater. Sci. Eng. A*, **293** (2000) 275.
- [32] X.-S. Yang, S. Sun and T.-Y. Zhang: *Acta Mater.*, **95** (2015) 264.
- [33] Y. Tian, O. I. Gorbatov, A. Borgenstam, A. V. Ruban and P. Hedstrom: *Metall. Mater. Trans. A*, **48** (2017) 1.
- [34] B. Wang, C. Hong, G. Winther, T. L. Christiansen and M. A. J. Somers: *Mater.*, **12** (2020) 100751.

열전 복합 필름과 전기방사된 압전폴리머 멤브레인을 기반으로 하는 플렉서블 하이브리드 에너지 하베스터

전효민^{1,2,*}, 김철민^{1,2,*}, 박현준^{1,2}, 배빛나^{1,2}, 최혜정^{1,2}, 장학수^{1,2}, 박귀일^{1,2,3,†}¹경북대학교 금속재료공학과²경북대학교 미래 모빌리티용 시스템반도체 혁신인재 교육연구단³경북대학교 자동차부품소재연구소

Flexible Hybrid Energy Harvester based on Thermoelectric Composite Film and Electrospun Piezopolymer Membranes

Hyomin Jeon^{1,2,*}, Cheol Min Kim^{1,2,*}, Hyeon Jun Park^{1,2}, Bitna Bae^{1,2}, Hyejeong Choi^{1,2}, HakSu Jang^{1,2}, Kwi-Il Park^{1,2,3,†}¹Department of Materials Science and Metallurgical Engineering, Kyungpook National University, 80 Daehak-ro, Buk-gu, Daegu, 41566, Republic of Korea²Innovative Semiconductor Education and Research Center for Future Mobility, Kyungpook National University, 80 Daehak-ro, Buk-gu, Daegu, 41566, Republic of Korea³Research Institute of Automotive Parts and Materials, Kyungpook National University, 80 Daehak-ro, Buk-gu, Daegu, 41566, Republic of Korea

A hybrid energy harvester that consisted of thermoelectric (TE) composite film and electrospun piezoelectric (PE) polymeric membranes was constructed. TE composites were fabricated by dispersing inorganic TE powders inside polyvinylidene fluoride elastomer using a drop-casting technique. The polyvinylidene fluoride-trifluoroethylene, which was chosen due to its excellent chemical resistance, mechanical stability, and biocompatibility, was electrospun onto an aluminum foil to fabricate the ultra-flexible PE membranes. To create a hybrid energy harvester that can simultaneously convert heat and mechanical energy resources into electricity, the TE composite films attached to the PE membrane were encapsulated with protective polydimethylsiloxane. The fabricated energy harvester converted the outputs with a maximum voltage of 4 V (PE performance) and current signals of 0.2 μ A (TE performance) under periodical heat input and mechanical bending in hybrid modes. This study demonstrates the potential of the hybrid energy harvester for powering flexible and wearable electronics, offering a sustainable and reliable power source.

Keywords: piezoelectric; thermoelectric; flexible; energy harvester; P(VDF-TrFE)

Received: November 29, 2024**Revised:** December 24, 2024**Accepted:** December 30, 2024***Corresponding author:**

Kwi-Il Park

E-mail: kipark@knu.ac.kr

*Hyomin Jeon and Cheol Min Kim equally contributed to this work.

1. Introduction

무선 센서 및 웨어러블 전자 장치에 대한 수요가 증가함에 따라, 소형 배터리 기반 전력 공급의 한계와 짧은 수명으로 인한 충전 및

교체의 필요성이 주요 단점으로 부각되고 있다[1, 2]. 이러한 문제를 해결하기 위해 바람, 파도, 동물의 움직임, 물의 흐름 등 주변 에너지를 전기 에너지로 변환하는 기술이 도입되고 있으며, 주변에서 버려지는 다양한 에너지를 효과적으로 수확 및 변환하는 방법으로 지속 가능한 전력 공급의 효율적인 전략이 될 수 있다[3, 4].

열전 기반의 에너지 하베스팅 기술은 기기와 주변 환경 사이에서 발생하는 온도 차를 열적 자원으로 간단하게 전력을 생산할 수 있다. 제백효과(Seebeck effect)[5]를 갖는 열전 재료를 기반으로 제

<https://doi.org/10.4150/jpm.2024.00458>

© 2025 The Korean Powder Metallurgy & Materials Institute

작된 소자는 형태에 관계없이 고온 및 저온 표면에서 모두 전력 수확이 가능하다. 다양한 열전 재료 Bi-Te-, Pb-Te-, Sn-Se 기반의 합금 중에서 Bi-Te 기반의 재료는 실온에서 뛰어난 열전 효율을 보이는 장점으로 주목을 받고 있다[6, 7]. 열전 고분자로는 PEDOT: PSS, PANI 등 이 존재한다[8]. 이 열전 재료들을 이용해 제백효과를 기반으로 소재 사이에 온도차가 형성될 때 고온부와 저온부 사이의 캐리어가 이동하여 전기 에너지가 발생한다[9, 10].

압전 기반의 에너지 하베스팅 기술은 외부의 기계적 에너지로부터 전력을 생산할 수 있다. 압전 효과를 갖는 압전 재료를 기반으로 제작된 소자는 다양한 형태의 응력(진동, 충격, 굽힘, 압력 등)으로부터 전력 수확이 가능하다[11, 12]. 압전 성능을 가지는 다양한 물질 중 압전 세라믹은 Pb(Zr, Ti)O₃(PZT), BaTiO₃, (K, Na)NbO₃ 등의 종류가 존재한다[13, 14]. 또한 압전 고분자 재료로는 Polyvinylidene fluoride (PVDF)계 고분자, Cellulose, Polylactic acid, Polyurea 등이 존재한다. 이 압전 재료들에 응력이 가해지면 쌍극자 모멘트를 형성하고 있는 결합 구조들 사이에서 유전 분극 현상이 발생된다[15, 16].

기존에 널리 사용되는 벌크형 열전 및 압전 소재 기반의 에너지 하베스터는 소재의 낮은 안정성, 높은 질량, 복잡한 제작 공정, 그리고 곡면과 같은 복잡한 구조에 부착하기 어려운 특성으로 인해 웨어러블 기기나 소형 전자 기기에 적용하는 데 한계가 있었다[17]. 이러한 문제를 해결하기 위해 소재의 유연성이 더욱 요구되며, 이에 따라 유연한 고분자 재료를 활용한 연구가 주목을 받고 있다. 압전 고분자는 뛰어난 유연성을 제공하며, 전기방사나 스핀 코팅과 같은 간단한 공정을 통해 제작할 수 있는 장점이 있다[18]. 또한 고분자를 매트릭스로 활용한 용액을 드롭 캐스팅 방법을 통해 간단한 제작 공정으로 저비용 생산이 가능하다는 특징이 있다[19]. 또한 나노 섬유를 이용한 제작 방법이 제안되면서 유연하고 신축성 있는 새로운 형태의 에너지 하베스터 개발 가능성이 제시되고 있다. 나노 섬유는 기존 벌크 소재와 차별화된 높은 비표면적을 제공하여 에너지 변환 효율을 극대화할 수 있으며, 고유의 유연성과 신축성이 있어 곡면이나 복잡한 형태의 표면에도 쉽게 부착이 가능하다. 이러한 특성은 특히 웨어러블 기기와 같이 다양한 환경에서의 유연성을 요구하는 기술에서 큰 장점이 될 수 있다. 더 높은 출력 밀도를 구현할 수 있는 가능성을 열어주어 다양한 분야에서 폭넓은 활용이 기대된다[20, 21].

단일의 열전 효과나 압전 효과만으로는 충분한 에너지를 확보하는 데 한계가 존재한다. 열전 재료는 낮은 온도차에서 에너지 변환 효율이 떨어지며, 이로 인해 생성되는 출력 전압 역시 낮아지는 문제를 가지고 있다[22]. 반면에 압전 재료는 기계적 에너지를 전기 에너지로 변환할 수 있으며, 높은 출력 전압을 생성하고 내구성도 뛰어나다는 장점을 가지고 있다[23]. 이러한 압전 재료의 우수한

특성을 활용해 더 많은 에너지를 확보하기 위해서는 압전 및 열전 재료를 결합한 하이브리드 에너지 소자의 개발이 필수적이다. 최근 연구자들은 열전과 압전 특성을 결합한 하이브리드 셀을 개발하여, 단일 재료가 가지는 한계를 극복하고 다중 에너지원에서 동시에 에너지를 수확함으로써 출력 성능에서 시너지 효과를 얻었다고 보고하고 있다[24, 25].

본 연구에서는 하이브리드 열전-압전 에너지 하베스터를 이용하여 발전 성능을 향상시킬 수 있음을 확인하였다. 열전 부분에서는 실온에서 뛰어난 효율을 가지는 Bi_{0.5}Sb_{1.5}Te₃ (BST) 및 Bi₂Te_{2.7}Se_{0.3} (BTS) 분말을 선정하였다. 간단하고 저렴한 드롭 캐스팅(Drop-casting)을 이용하여 PVDF에 무기 열전 소재 BTS 및 BST 분말을 분산시켜 열전 복합체를 제조하였다. 압전 부분에는 뛰어난 내화학성, 기계적 안정성, 생체 적합성의 특성을 가져 유연하고 신축성 있는 소자에 적합하게 응용이 가능한 Polyvinylidene fluoride-trifluoroethylene (P(VDF-TrFE))를 선정했고, 유전율이 높은 N,N-Dimethylformamide (DMF) 용매에 용해시켜 전기방사를 이용하여 나노 멤브레인을 제작하였다. 이후 Polydimethylsiloxane (PDMS)를 이용하여 보호층으로 코팅해주고 유연하고 신축성 있는 하이브리드 열전-압전 에너지 하베스터를 제작하였다. 제작된 열전 필름은 열전 특성 평가 장치를 이용하여 제백계수(Seebeck coefficient), 전기전도도, 파워팩터(Power factor)를 평가하였다. 제작된 열전-압전 하이브리드 에너지 하베스터는 순환적인 온도 가열과 냉각에서 굽힘 테스트를 진행하여 출력 전압 및 전류를 측정하였다. 반복적인 굽힘 변형동안 안정적인 전기적 출력을 유지하였고, 최대 4 V의 전압과 0.2 μA의 전류를 확인하였다. 5000번의 반복 굽힘 변형에도 우수한 내구성을 확인하였다.

2. Experimental Section

2. 실험방법

2.1 Bi₂Te₃ 기반의 열전 복합 필름 제조

아세톤(Acetone, >99.8%; Daejung, Korea)과 DMF (>99.5%; Daejung, Korea)를 7:3의 질량비로 혼합한 용매에 n-type의 Bi₂Te_{2.7}Se_{0.3} (BTS, VI Semiconductor Materials Group Co. Ltd, China), p-type의 Bi_{0.5}Sb_{1.5}Te₃ (BST, VI Semiconductor Materials Group Co. Ltd, China) 분말 그리고 PVDF(Kynar Flex-2801-00, Arkema, France)를 첨가하고 교반기를 이용해 24시간 이상 교반시켜 용해하였다. 최적의 열전 성능을 가지는 열전 복합체를 제작하기 위해 열전 분말의 함량(70 - 85 wt%)에 따라 복합체 용액을 제작하였다. 제작된 용액을 드롭 캐스팅(Drop-casting)을 통해 세척된 3 × 3 cm² 크기의 유리 기판위에 각각 도포하고, 70°C 오븐에서 2시간 이상 건조하여 열전 필름을 완성하였다.

2.2 전기방사 공정을 이용한 압전 멤브레인 제조

P(VDF-TrFE) (PVDF:TrFE = 70:30 mol %, Poly-K Inc., USA) 분말을 아세톤과 DMF가 7:3의 질량비로 혼합된 용매에 첨가하고 50 °C에서 24시간 이상 교반하여 15 wt% P(VDF-TrFE) 용액을 제작하였다. 알루미늄 기판에 15 kV 전압을 인가해주고 1 mL · h⁻¹의 유량으로 전기방사 공정을 수행하였으며, 균일한 나노 멤브레인을 얻기 위해 공정 간 습도는 30% 이하로 유지하였다. 이후 전기방사된 나노 멤브레인을 80°C의 오븐에서 24시간 이상 건조하여 잔류 용매를 제거하였으며, 145°C에서 2시간 동안 열처리하여 전기적 특성을 향상시켜 압전 나노 멤브레인을 완성하였다.

2.3 열전-압전 기반의 하이브리드 에너지 하베스터 제작

제작된 열전 필름을 부착하기 위해 압전 나노 멤브레인 위에 6000rpm 30초의 조건으로 PDMS를 코팅했다. 이후 나노 멤브레인 위에 제작한 열전 필름을 n-type 및 p-type 순서로 3쌍을 배열 및 부착해주었다. 알루미늄 호일(Foil)과 전도성 에폭시를 이용하여 열전필름을 전기적으로 연결하였으며, 열전 및 압전 전기 신호를 출력하기 위해 하베스터의 상·하부에 전도성 에폭시(CW2400, Chemtronics Co.)를 이용하여 구리선을 연결하였다. 압전 나노 멤브레인과 열전 필름을 보호해주기 위해 열전-압전 하이브리드 하베스터를 PDMS로 보호(Encapsulation)하였다. 이후 제작된 하이브리드 에너지 하베스터의 압전 성능 향상을 위해 외부 전기장을 통해 압전층 내부의 분극을 한 방향으로 배열을 유발하는 폴링(Poling) 공정을 진행했으며, 100°C에서 200 kV/cm의 전압을 4시간 동안 인가하였다.

2.4 소재 분석 및 특성 평가

X선 회절 분석(X-ray diffraction, XRD; Empyrean, Malvern PANalytical, UK)을 통해 열전 분말의 결정학적 구조를 확인하였으며, 열전 필름 및 압전 나노 멤브레인의 표면 형상과 두께를 확인하기 위해 주사현미경(Scanning Electron Microscopy, SEM; JEOL, JSM-IT700HR, Japan) 분석을 수행하였다. 소스미터(2612 B, Keithley), 다채널 측정 시스템(3706 A, Keithley), 나노볼트미터(3706 A, Keithley) 및 DC 전원 공급 장치(GPP 1326, GW Instek)로 구성된 4-point Probe 기반의 열전 특성 평가 장치(TCH-1, SnM)를 사용하여 열전 필름의 제벡 계수, 컨덕턴스(Conductance) 및 파워팩터(Power factor)를 평가하였다. 열전 필름에 접촉된 4개의 프로브는 펠티어 소자(Peltier device)에 의해 필름에 직접 형성된 온도 차와 전압 차를 측정하며, 이를 통해 열전 필름의 제벡 계수와 컨덕턴스(Conductance)가 실시간으로 계산되어 컴퓨터에 기록된다. 전기전도도는 측정된 컨덕턴스 값에 프로브 간의 거리를 곱한 후 열전 필름의 단면적으로 나누어 산출되며, 파워팩

터는 제벡 계수의 제곱과 전기전도도를 곱하여 계산하였다.

2.5 열전 발전 성능 평가

열전 에너지 하베스터의 전기적 신호를 평가하기 위해 열전 발전 성능 측정 시스템을 구축하였다. 열전 소자의 양단에 온도 구배를 형성하기 위해 핫플레이트(MSH-20D, Daihan Scientific) 및 냉각 칠러(RW3-3025, Lab Companion)를 이용하여 고온부 및 저온부를 형성하였다. 디지털 패치형 온도계를 사용하여 정확한 온도차이를 실시간으로 확인하였으며, 저항박스(RS-200 W, IET Labs, Inc.)를 통해 1k Ω~1 MΩ 범위의 외부저항을 소자에 인가하였다. 소스미터(2612 B, Keithley)를 통해 생성되는 부하 전류와 전압을 평가하였으며, 소자의 출력성능은 부하전압과 전류 값을 곱하여 도출하였다.

2.6 압전 발전 성능 평가

압전 에너지 소자의 압전 효과의 출력 전압 및 전류를 측정하기 위해 제작된 자체 굽힘 측정 시스템(Bending Machine System, SnM)을 활용하여 반복적이고 주기적인 굽힘 변위를 가하여 굽힘 테스트를 진행하였다. 생성된 전기 신호는 전위계측기(Electrometer, 6514E, Keithley, USA)를 이용해 감지되어 실시간으로 기록되었다. 측정된 전기적 신호가 개발 소자의 압전 효과에 의한 결과임을 확인하기 위해 소자와 전위계의 극성 연결을 반대로 연결하여 측정하는 극성 스위칭 테스트(Polarity switching test)를 수행하였다.

2.7 개발 소자의 하이브리드 에너지 하베스팅 성능 평가

제작된 열전-압전 하이브리드 소자의 성능을 평가하기 위해 자체 굽힘 측정 시스템을 활용했다. 반복적이고 주기적인 굽힘 테스트를 10번 진행하며 가열 및 냉각을 동시에 2세트 수행하였다. 이때 생성된 전기 신호는 전위계측기를 통해 감지되어 열전-압전 하이브리드 소자에서 생성된 전류 및 전압이 수집되었다.

3. Results and Discussion

3.1 제조된 열전 복합체 필름과 압전 멤브레인

Fig. 1(a)에 열전 필름의 제조 방법에 대한 모식도를 나타내었다. PVDF와 열전 분말을 혼합하여 열전 복합체 용액을 제작하고, 이를 유리 기판에 균일하게 도포하여 유연한 열전 필름을 제작하였다. Fig. 1(b)는 P(VDF-TrFE) 압전 나노 멤브레인과 열전-압전 하이브리드 에너지 하베스터의 제작 공정에 관한 모식도를 나타내었다. 열전 및 압전 복합소재와 하이브리드 에너지 하베스터의 자세한 제작공정은 실험 방법에 기술하였다.

Fig. 2(a)는 제작된 n-type 및 p-type 열전 필름의 XRD 분석 결과를 나타낸 것이다. 사용된 BST 및 BTS 분말의 패턴은 표준

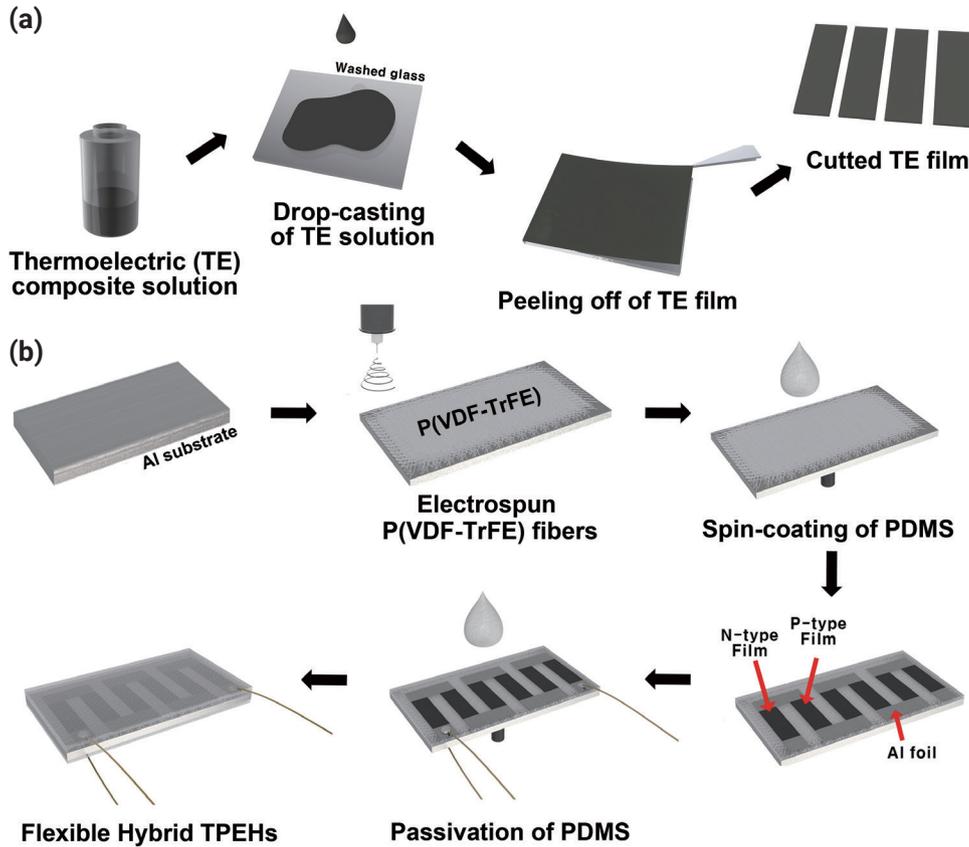


Fig. 1. (a) Schematic illustration of the procedure for fabricating the thermoelectric composite film. (b) Schematic diagrams showing the fabrication process of electrospun P(VDF-TrFE) membranes and hybrid energy harvesters based on thermoelectric films/piezoelectric membranes.

JCPDS 50-0954, JCPDS 49-1713에 기록된 패턴과 일치하였으며, 20° 부근에서 PVDF의 피크가 넓게 나타나는 것을 확인하였다. Fig. 2(b)는 P(VDF-TrFE) 나노 멤브레인의 SEM과 XRD분석 결과를 나타낸 것이다. SEM을 통해 P(VDF-TrFE) 나노 멤브레인의 표면을 관찰한 결과, 균일한 두께의 나노 섬유가 방사되었음을 확인하였다. 압전 나노 멤브레인의 XRD분석 결과, 19-20° 근처에서 β상의 피크를 나타내는데, 이는 (100) 결정면에서 발생하는 회절에 해당한다. P(VDF-TrFE) 나노 멤브레인 제작을 위한 전기방사 공정에서 고전압이 인가되는데, 이는 P(VDF-TrFE)의 분자 사슬을 특정 방향으로 배향 시키기 때문에 β상을 나타내는 피크의 강도가 크게 증가함을 확인할 수 있다. Figs. 2(c)와 2(d)는 SEM 통해 관찰한 열전 필름의 단면 및 표면 이미지를 나타낸다. 제작된 열전 복합 필름은 약 100 μm 두께를 가지는 것으로 확인되었으며, BST 및 BTS 열전 분말이 기상에 전체적으로 잘 분산됨을 확인할 수 있었다.

3.2 열전 복합 필름의 열전 특성

열전 분말 함량에 따른 열전 필름의 성능을 최적화 하기위해

4-point probe 기반의 열전 특성 평가 장치를 이용해 열전 필름의 전기전도도, 제벡계수와 파워팩터를 측정하였다. Figs. 3(a)와 3(b)는 n-type 열전 복합체의 열전특성 측정값을 나타내었다. 최대 251.3 μV/K의 제벡계수와 0.633 S/cm의 전기전도도가 측정되었고, 75 wt%에서 최대 파워팩터를 보였다. Figs. 3(c)와 3(d)는 p-type의 열전 복합체의 열전 특성 측정값을 나타내었다. 최대 -196.4 μV/K의 제벡계수와 0.82 S/cm의 전기전도도가 측정되었으며 p-type 또한 75 wt%에서 최대 파워팩터를 보였다. 열전 분말 함량이 75 wt% 이상의 영역에서 열전 특성이 감소하는 양상을 보인다. 이러한 결과는 높은 질량 분율을 가지는 열전 복합체의 경우 열전 소재의 함량이 증가함에 따라 폴리머 기상의 양이 부족해 분말의 응집이 발생하여 열전 효율이 감소됨을 의미한다.

3.3 하이브리드 에너지 하베스터의 단일 발전 성능 평가 결과

먼저 하이브리드 에너지 하베스터의 열전 발전 성능을 평가하기 위해 온도에 따라 외부 저항을 인가하며 부하 전류, 부하 전압을 측정하고 출력 전력을 도출하였다. 냉각 칀 및 핫플레이트를 사용

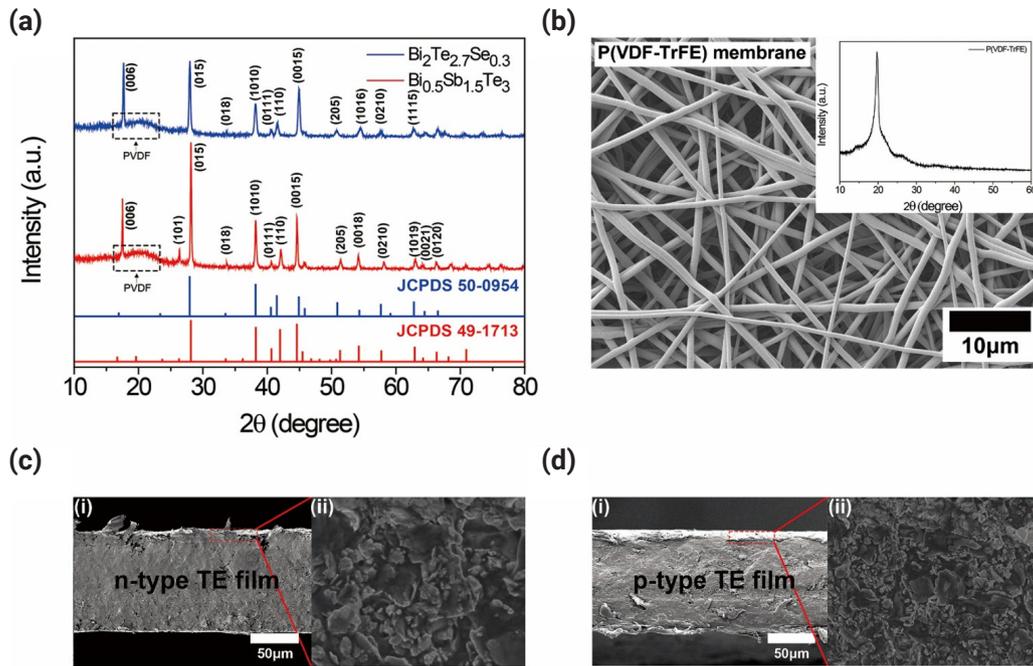


Fig. 2. (a) X-ray diffraction patterns of thermoelectric composite films and inorganic Bi-Te-based particles. (b) Scanning electron microscopy (SEM) image and X-ray diffraction patterns of the electrospun P(VDF-TrFE) fibers-based membrane. (c, d) Cross-sectional SEM images of fabricated n- and p-type thermoelectric composite films.

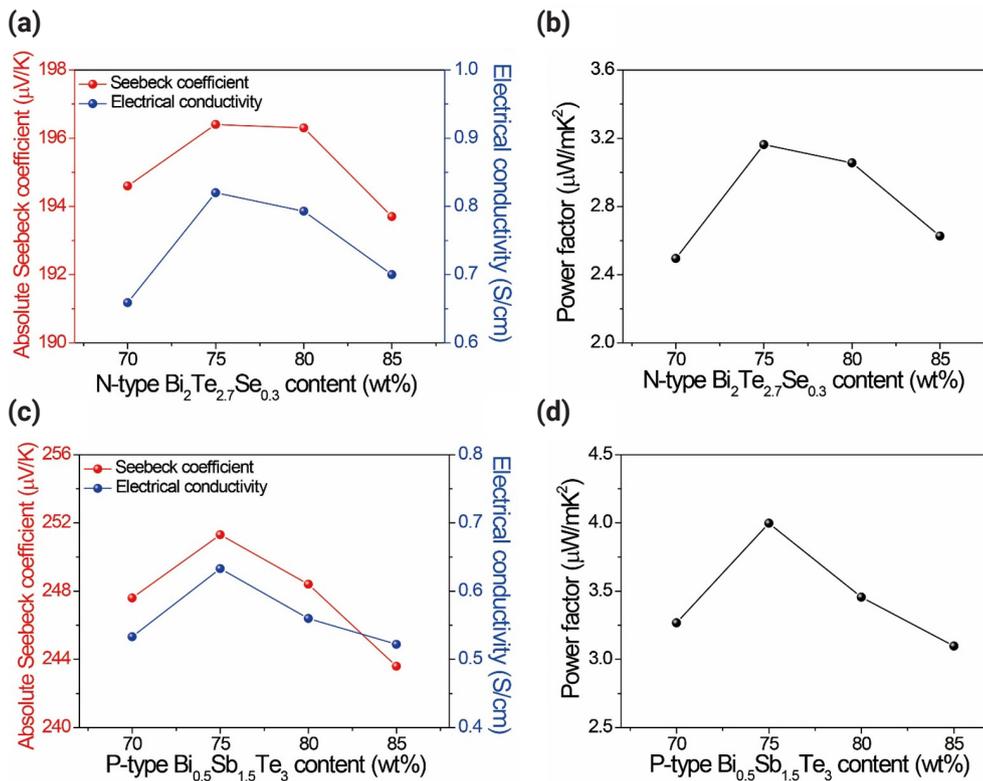


Fig. 3. Absolute Seebeck coefficient, electrical conductivity, and power factor of thermoelectric films with various n-type (a, b) and p-type contents (c, d).

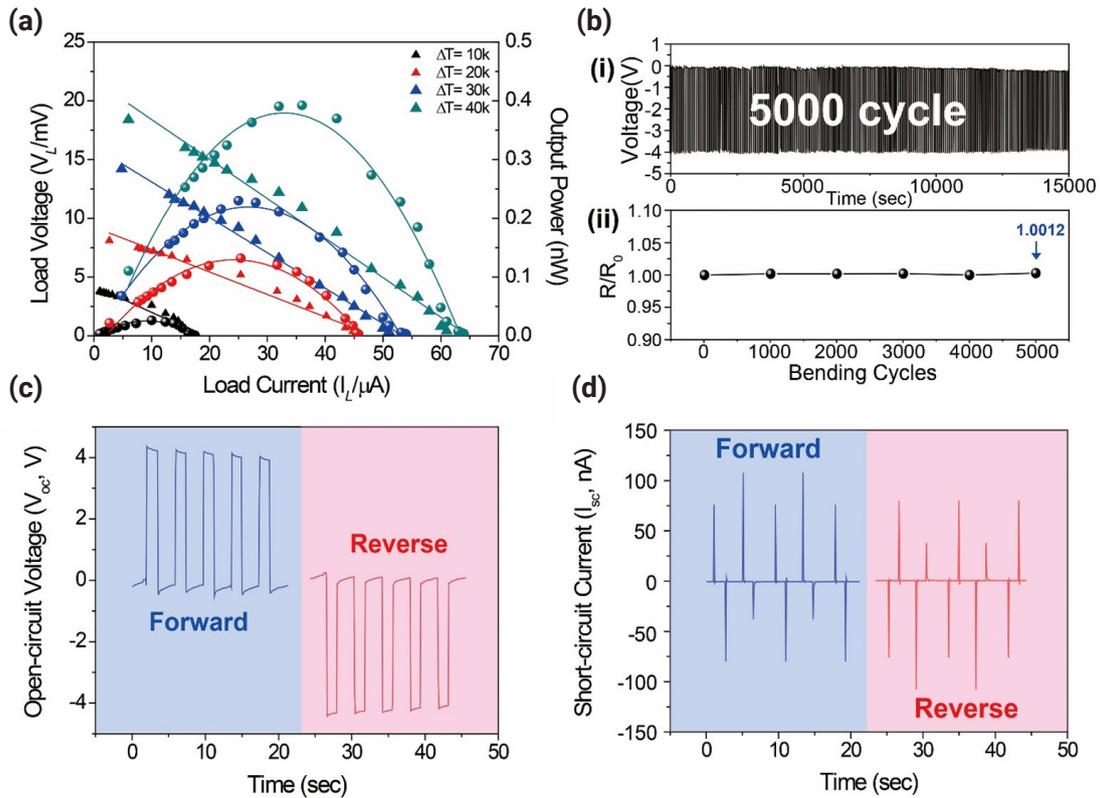


Fig. 4. (a) The voltage-current-power curves of the fabricated devices. (b) The mechanical stability test results of piezoelectric and thermoelectric parts of the flexible energy harvester during bending up to 5,000 cycles. (c, d) Open-circuit voltage (c) and short-circuit current (d) characteristics of the piezoelectric component.

하여 에너지 하베스터의 상부와 하부에 고온부와 저온부를 각각 형성하였으며, 일정한 온도차를 인가하며 하베스터의 발전 성능을 평가하였다. Fig. 4(a)는 제작된 에너지 하베스터의 온도차에 따른 단일 열전 발전 성능 측정 결과를 나타낸 그래프이다. $\Delta T = 40\text{k}$ 에서 18 mV의 최대 전압과 0.65 μA 최대 전류를 나타내었으며, 약 3.8 nW의 출력 전력을 도출하였다. Fig. 4(b)는 하이브리드 에너지 하베스터의 열전 및 압전 내구성을 평가하기 위해 7 mm의 굽힘 변위에서 5000번의 굽힘 변형 후 소자의 내부 저항 그래프 및 전압을 나타낸 것이다. Fig. 4(b)-i)는 열전 내구성을 나타내며 내구성 테스트 결과 하이브리드 에너지 하베스터의 열전층은 5000번의 반복적인 굽힘 변형 인가에도 내부 저항이 약 0.124% 증가한 것을 확인하였으며, 우수한 내구성을 가지는 것을 입증하였다. 입자 네트워크 층의 기계적 및 전기적 신뢰성을 보여준다. Fig. 4(b)-ii)는 압전 내구성을 나타내며 내구성 테스트 결과 하이브리드 에너지 하베스터의 압전층은 5000번의 반복적인 굽힘 변형 동안 생성된 전압 신호가 일정하게 유지됨을 확인할 수 있었다. 이를 통해 제작된 열전-압전 하이브리드 에너지 하베스터는 우수한 기계적 안정성을 가지고 있음을 나타낸다.

하이브리드 에너지 하베스터의 압전 발전 성능을 평가하기 위해 반복적인 굽힘 변형에 의해 형성되는 전류 및 전압 신호를 평가하였다. 자체 제작한 굽힘 변형 인가장치를 통해 7 mm의 굽힘 변위 조건에서 일정한 굽힘을 인가하며 에너지 하베스터의 발전 성능을 평가했다. Figs. 4(c)와 4(d)는 반복적인 굽힘에 의한 소자의 출력 전압과 전류 신호를 측정된 결과로, 제작된 에너지 하베스터는 반복적인 굽힘 변형 동안 안정적인 전기적 출력을 유지했으며 최대 4 V의 전압과 100 nA의 전류를 생성함을 확인하였다. 또한 측정된 전기적 신호가 제작된 소자의 압전 효과에 의한 결과임을 확인하기 위해 소자와 전위계를 반대로 연결해 측정하는 스위칭 테스트를 수행하였다. 측정된 출력 전압 및 전류의 신호가 반전됨을 확인하여 압전 효과에 의한 에너지 하베스터에서 출력된 값임을 입증하였다.

3.4 하이브리드 모드에서 에너지 하베스터의 발전 성능 평가

일반적으로 단일 열전 하베스터는 높은 출력 전류와 낮은 출력 전압을 생성하는 반면 압전 하베스터는 낮은 전류와 높은 전압 신호를 생성한다. 이러한 서로 다른 특성을 결합하여 동시에 상호보완적인 에너지를 수확할 수 있다. Fig. 5(a)는 자체 제작한 하이브

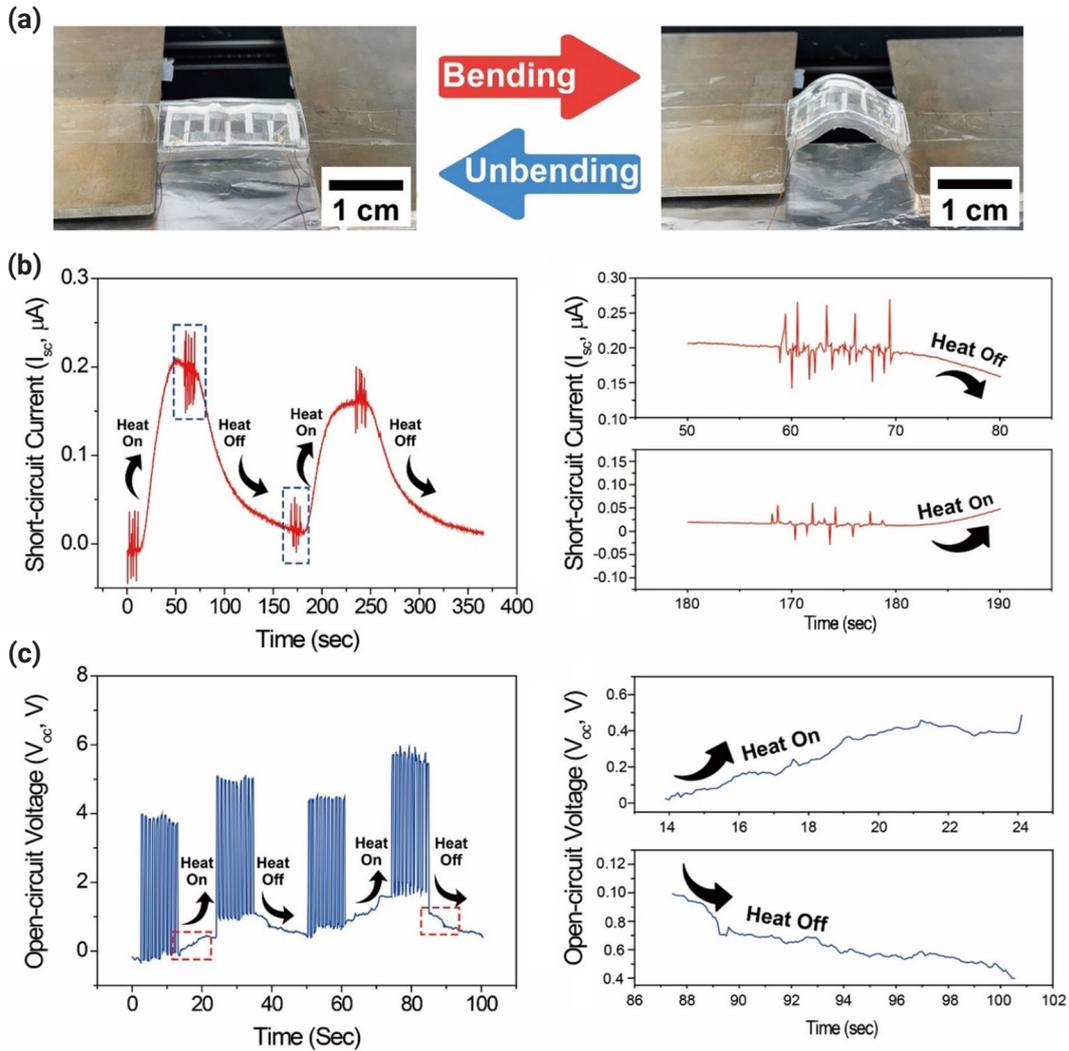


Fig. 5. (a) Schematic diagram of the measurement system for characterizing the thermoelectric and piezoelectric energy conversion efficiency of the fabricated energy harvester in hybrid mode. (b, c) The measured short-circuit current (b) and open-circuit voltage (c) of the hybrid energy harvester under periodical heat input and mechanical bending.

리드 에너지 발전 성능 평가 장치를 이용하여 열전-압전 하이브리드 에너지 하베스터의 발전 성능을 평가했다. 반복적인 굽힘 변형 10회씩 4세트를 진행하고, 두 번의 온도 가열 및 냉각 순환을 실시하였다. Fig. 5(b)는 하이브리드 에너지 하베스터에서 생성된 전류 신호를 나타낸다. 하이브리드 작동 모드에서 열전-압전 하이브리드 소자는 열전 효과로 0.2 μA , 압전 효과로 0.05 μA 의 전류 신호를 생성하였다. Fig. 5(c)는 하이브리드 에너지 하베스터에서 생성된 전압 신호를 나타낸다. 압전부로 4 V가 생성되었으며, 압전부가 열전부보다 훨씬 높아 열전 전압 신호는 무시되었다. 열전 전압 신호는 가열 및 냉각시 전압의 약간의 상승과 하락을 확인할 수 있었으나 하이브리드 작동 모드에서 열전-압전 하이브리드 에너지 하베스터가 생성한 출력 전압, 전류는 별도로 측정된 압전 및 열전 출력 값과 거의 유사하였다. 이러한 출력 전압 및 전류는 하이브리드

화로 인해 각각의 출력을 저하시키지 않고 에너지 생성 성능을 개선하는데 있어 보완적인 방법임을 시사한다.

4. Conclusion

본 연구에서는 열전 및 압전을 이용한 하이브리드 에너지 하베스터를 제작하였다. 다양한 열전 분말 함량에 따라 열전 복합체 필름을 제작하였고, 전기방사를 도입하여 압전 나노 멤브레인을 제작하였다. 플렉서블한 열전 소자 및 압전 소자를 결합한 하이브리드 에너지 하베스터의 발전 성능을 측정하기 위해 자체 제작된 열전 및 압전 발전 성능 측정장치를 이용하였다. 열전부에서는 $\Delta T = 40K$ 에서 18 mV의 최대 전압과 0.65 μA 최대 전류를 나타내었고, 압전부에서는 최대 4 V의 전압과 100 nA의 전류를 생성함을 확인

하였다. 또한 반복적인 굽힘 변형 동안 안정적인 전기적 출력을 유지했으며, 측정된 출력 전압 및 전류의 신호가 반전됨을 확인하여 압전 효과에 의한 에너지 하베스터에서 출력된 값을 확인하였다. 열전-압전 하이브리드 하베스터는 반복적인 굽힘 변형 10회씩 4세트를 진행하고, 두 번의 온도 가열 및 냉각 순환이 수행되었다. 열전부에서 0.2 μA , 압전부에서 0.05 μA 의 전류가 생성되었으며, 압전부에서는 4 V의 전압도 확인되었다. 압전부에서 생성된 전압 값이 열전부에서 생성된 전압에 비해 우수하여 열전부에서 발생한 전압 신호는 무시하였다. 하이브리드 화에도 각각의 출력을 저하시키지 않고 에너지 생성 및 개선으로 웨어러블 기기에 다양하게 활용될 수 있음이 기대된다.

Funding

본 연구는 2024년도 과학기술정보통신부의 재원으로 한국연구재단의 지원을 받아 수행되었습니다. (No. 2022R1A2C1003853, No. RS-2024-00403822)

Conflict of Interest

교신저자는 현재 JPM편집이사로서 봉사 중이지만, 논문 출판과정의 어떤 과정에서도 관여하지 않았습니다. 이 사항을 제외하면 저자들은 잠재적인 이해상충에 관련된 해당사항이 없음을 선언합니다.

Data Availability Statement

The dataset files are available on request.

Author Information and Contribution

전효민: 석사과정 학생; conceptualization, experiment, writing—original draft

김철민: 석사과정 학생; experiment, writing—review & editing

박현준: 석사과정 학생; conceptualization, experiment

배빛나: 석사과정 학생; data curation, formal analysis

최혜정: 석사과정 학생; data curation, formal analysis

박귀일: 교수; writing—original draft, funding acquisition, supervision

Acknowledgments

None.

References

- [1] G. H. Kim, H. J. Park, B. Bae, H. Jang, C. M. Kim, D. Lee and K.-I. Park: *J. Powder Mater.*, **31** (2024) 16.
- [2] S. Kim, D. Y. Hyeon, D. Lee, J. H. Bae and K.-I. Park: *Mater. Today Phys.*, **35** (2023) 101103.
- [3] D. Lee, S. Jeong, H. S. Jang, D. Y. Hyeon, Y. M. Woo, C. Baek, M.-K. Lee, G.-J. Lee, J. H. Park and K.-I. Park: *J. Korean Inst. Electr. Electron. Mater. Eng.*, **37** (2024) 427.
- [4] K.-I. Park, C. K. Jeong, J. Ryu, G. T. Hwang and K. J. Lee: *Adv. Energy Mater.*, **3** (2013) 1539.
- [5] J. M. Kim, S. H. Kim, Y. J. Na and K.-I. Park: *J. Korean Inst. Electr. Electron. Mater. Eng.*, **3** (2022) 119.
- [6] K. H. Lee, J.-Y. Kim and S.-M. Choi: *J. Korean Ceram. Soc.*, **52** (2015) 1.
- [7] J. G. Park and Y. H. Lee: *Curr. Appl. Phys.*, **16** (2016) 1202.
- [8] L. V. Kayser and D. J. Lipomi: *Adv. Mater.*, **31** (2019) e1806133.
- [9] C. Hu, K. Xia, C. Fu, X. Zhao and T. Zhu: *Energy Environ. Sci.*, **15** (2022) 1406.
- [10] J. Shuai, J. Mao, S. Song, Q. Zhu, J. Sun, Y. Wang, R. He, J. Zhou, G. Chen, D. J. Singh and Z. Ren: *Energy Environ. Sci.*, **10** (2017) 799.
- [11] B. Bae, N. R. Alluri, C. M. Kim, J. Ryu, G. H. Kim, H. J. Park, C. Baek, M.-K. Lee, G.-J. Lee, G.-T. Hwang and K.-I. Park: *Mater. Today Phys.*, **48** (2024) 101567.
- [12] H. J. Park, B. Bae, H. Jang, D. Y. Hyeon, D. H. Lee, G. H. Kim, C. M. Kim, N. R. Alluri, C. Baek, M.-K. Lee, G.-J. Lee and K.-I. Park: *Nano Energy*, **131** (2024) 110299.
- [13] J. Gao, D. Xue, W. Liu, C. Zhou and X. Ren: *Actuators*, **6** (2017) 24.
- [14] G. L. Smith, J. S. Pulskamp, L. M. Sanchez, D. M. Potrepka, R. M. Proie, T. G. Ivanov, R. Q. Rudy, W. D. Nothwang, S. S. Bedair, C. D. Meyer, R. G. Polcawich and D. J. Green: *J. Am. Ceram. Soc.*, **95** (2012) 1777.
- [15] L. Lu, W. Ding, J. Liu and B. Yang: *Nano Energy*, **78** (2020) 105251.
- [16] S. Rajala, T. Siponkoski, E. Sarlin, M. Mettananen, M. Vuoriluoto, A. Pammo, J. Juuti, O. J. Rojas, S. Franssila and S. Tuukkanen: *ACS Appl. Mater. Interfaces*, **8** (2016) 15607.
- [17] G. Tan, L. D. Zhao and M. G. Kanatzidis: *Chem. Rev.*, **116** (2016) 12123.

- [18] V. F. Cardoso, G. Minas and S. Lanceros-Méndez: *Sens. Actuators Rep. A: Physical*, **192** (2013) 76.
- [19] Y. Na, S. Kim, S. P. R. Mallem, S. Yi, K. T. Kim and K.-I. Park: *J. Alloys. Compd.*, **924** (2022) 166575.
- [20] M. Baniasadi, Z. Xu, S. Hong, M. Naraghi and M. Mi-nary-Jolandan: *ACS Appl. Mater. Interfaces*, **8** (2016) 2540.
- [21] J. Chang, M. Dommer, C. Chang and L. Lin: *Nano Energy*, **1** (2012) 356.
- [22] Y. Wang, L. Yang, X. L. Shi, X. Shi, L. Chen, M. S. Dargusch, J. Zou and Z. G. Chen: *Adv. Mater.*, **31** (2019) e1807916.
- [23] Y. Wu, Y. Ma, H. Zheng and S. Ramakrishna: *Mater. Design*, **211** (2021) 110164.
- [24] S.-B. Kim, J. Shin, H.-S. Kim, D.-G. Lee, J.-C. Park, J. M. Baik, S. Y. Kim, C.-Y. Kang, W. Choi, H.-C. Song and S. Hur: *Energy Convers. Manag.*, **298** (2023) 117774.
- [25] S. Kumar, H. H. Singh and N. Khare: *Energy Convers. Manag.*, **198** (2019) 111783.

수분 기반 발전기내 셀룰로오스 섬유 간 밀도 변화가 에너지 하베스팅 성능에 미치는 영향

이승환^{1,2}, 백소현^{1,2}, 이현우¹, 권용범¹, 이강혁¹, 박기룡¹, 송요섭¹, 김범성¹, 박지영², 좌용호^{2,*}, 정다운^{1,3,*}

¹한국생산기술연구원 국가희소금속센터

²한양대학교 재료화학공학과

³중앙대학교 기계공학부

Effect of Cellulose Fiber Density Variation on Energy Harvesting Performance in a Hydrovoltaic Generator

Seung-Hwan Lee^{1,2}, So Hyun Baek^{1,2}, Hyun-Woo Lee¹, Yongbum Kwon¹, Kanghyuk Lee¹, Kee-Ryung Park¹, Yoseb Song¹, Bum Sung Kim¹, Ji Young Park², Yong-Ho Choa^{2,*}, Da-Woon Jeong^{1,3,*}

¹Korea National Institute of Rare Metals, Korea Institute of Industrial Technology, Incheon 21655, Republic of Korea

²Department of Materials Science and Chemical Engineering, Hanyang University, Ansan 15588, Republic of Korea

³School of Mechanical Engineering, Chung-Ang University, Seoul 06974, Republic of Korea

Energy harvesting has become a crucial technology for sustainable energy solutions; in particular, the utilization of ambient water movement in hydrovoltaic generators has emerged as a promising approach. However, optimizing performance requires an understanding of structural factors affecting energy harvesting, particularly capillary effects. This study aimed to improve hydrovoltaic generator performance by adjusting internal fiber density, which influences water transport and ion mobility. Using cold isostatic pressing, cellulose acetate (CA) loading in a urethane mold was varied to optimize internal density. As CA loading increased, the fiber arrangement became denser, narrowing capillary pathways and reducing proton mobility. While open-circuit voltage (V_{oc}) remained stable, short-circuit current (I_{sc}) decreased with higher CA mass. The sample with a loading of 0.3 g exhibited the highest energy harvesting efficiency, achieving $I_{sc} = 107.2 \mu\text{A}$, $V_{oc} = 0.15 \text{ V}$, and power (P) = $16.7 \mu\text{W}$. This study provides insights into methods of improving hydrovoltaic generator efficiency through internal structural modifications.

Keywords: Energy harvesting; Hydrovoltaic; Internal density; Capillary; Evaporation

Received: February 13, 2025

Revised: March 18, 2025

Accepted: April 2, 2025

***Corresponding author:**

Da-Woon Jeong

TEL: +82-32-226-1362

E-mail: dwjeong@kitech.re.kr

Yong-Ho Choa

TEL: +82-31-400-5650

E-mail: choa15@hanyang.ac.kr

1. Introduction

전 세계적으로 급속한 산업화와 인구 증가로 인해 에너지 소비량이 꾸준히 증가하고 있으며, 이에 따라 지속 가능한 에너지원 확보가 중요한 연구 과제로 대두되고 있다[1-4]. 전통적인 화석 연료

기반의 에너지 공급 방식은 이산화탄소 및 초미세먼지와 같은 대기 오염 물질을 배출하여 환경 문제를 야기하며, 장기적으로 석유 및 천연가스의 고갈 문제도 심각하게 고려되어야 한다[5]. 이러한 한계를 극복하기 위해 태양광, 풍력, 수력 등 다양한 친환경 에너지원이 개발되고 있으나, 기존 재생에너지 기술은 설치 면적의 제약, 낮은 에너지 변환 효율, 자연환경 변화에 따른 불안정성 등의 문제를 안고 있다[6]. 특히, 태양광 발전은 하루 평균 3~4시간의 제한적인 일조량과 광전효과 기반의 구조적 한계로 인해 대규모 설비가 필요

<https://doi.org/10.4150/jpm.2025.00052>

© 2025 The Korean Powder Metallurgy & Materials Institute

하며[7], 풍력 발전은 지리적 제한과 저주파 소음 발생으로 인해 활용이 제한적이다[8]. 이러한 한계를 극복하기 위한 차세대 에너지 하베스팅 기술이 요구되고 있다.

최근 환경 변화에 대한 적응성과 지속 가능한 에너지원 확보를 목표로, 주변 환경에서 에너지를 직접 수확하는 에너지 하베스팅 (Energy harvesting) 기술이 주목받고 있다. 대표적인 에너지 하베스팅 기술로는 압전 (Piezoelectric), 마찰전기(Triboelectric), 광전 (Photovoltaic), 그리고 수분을 이용한 Hydrovoltaic 등이 연구되고 있다[9-14]. 특히, 수분 기반 발전 기술은 물이 전도성 물질과 상호작용하는 과정에서 전기를 발생시키는 원리를 이용하며, 지구의 70% 이상을 차지하는 풍부한 수자원을 활용할 수 있다는 점에서 차세대 에너지원으로 주목받고 있다[15].

수분 기반 발전기의 연구는 주로 물의 이동 방식과 전하 분포 변화에 따른 전력 생성 메커니즘을 규명하는 데 집중되고 있다. 현재까지 보고된 연구들은 물과 전도성 나노소재 간의 상호작용을 활용한 에너지 생성 메커니즘을 다음과 같이 분류할 수 있다. 첫 번째로, 모세관 효과를 기반으로 한 에너지 생성 방식은 나노 또는 마이크로 기공 내에서 물이 이동하면서 전위차가 형성되고, 이에 따라 전류가 발생하는 원리를 이용한다[16]. 두 번째로, 증발 유도 (Evaporation-induced) 메커니즘에서는 물이 전도성 표면에서 증발하면서 전자 밀도 차이가 발생하고[17], 이로 인해 전하가 이동하며 전류가 형성된다[18, 19]. 마지막으로, 유사 스트리밍(Pseudo-streaming)에서는 모세관 내부의 물 흐름과 함께 양이온 및 음이온이 이동하면서 전기장이 형성되고, 이로 인해 전하 이동이 일어나는 것으로 보고되고 있다[20-23].

기존 연구들에서는 다양한 나노소재(탄소 나노튜브, 그래핀 산화물, 셀룰로오스 유도체 등)[24-27]를 이용하여 발전 성능을 향상시키려는 시도가 이루어져 왔다. 예를 들어, Xue et al. 연구팀은 다공성 탄소 필름을 이용하여 1 V 이상의 유도 전압과 높은 전력 밀도를 갖는 발전기를 보고하였으며[18], Huang et al. 연구팀은 그래핀 산화물 복합체를 활용하여 0.6 V의 출력을 갖는 발전기를 개발하였다[28]. 또한, Hao et al. 연구팀은 종이 기반 발전기를 제작하여 0.25 V의 전압과 15 nA의 전류를 발생시킬 수 있음을 증명하였으며[29], Yoon et al. 연구팀은 산화아연(ZnO) 소재를 이용하여 약 0.4 V의 출력을 얻을 수 있음을 보고하였다[30]. 그러나 현재까지 보고된 연구들은 발전기의 내부 밀집도 변화가 에너지 하베스팅 성능에 미치는 영향에 대한 체계적인 분석이 부족한 실정이다. 특히, 셀룰로오스 아세테이트 파이버로 구성된 수분기반 발전기 내부 섬유 간 구조적 변화에 대한 연구는 거의 이루어지지 않았다.

본 연구에서는 에너지 하베스팅의 성능의 주요 변수인 모세관 효과와 증발 효과를 변화시켜 발전 성능을 최적화하고자 발전기 내부 섬유 간격을 다르게 샘플을 제조하였다. 발전기에 압력을 고르게

가할 수 있도록 냉간등방압(Cold Isostatic Pressing, LOOMIS PRODUCTS COMPANY) 공정을 적용하였고, 이때 몰드내 장입하는 셀룰로오스 아세테이트(Cellulose acetate)의 양을 변화시켜 내부 섬유 간 밀도를 다르게 제조하였다. 연구 결과를 바탕으로 수분기반 발전기 소자를 제조할 때 내부 밀집도를 조절하여 성능을 최적화할 수 있는 기초 연구 결과를 제시하고자 한다.

2. Experimental Section

2.1. 카본 코팅 용액 제조 및 발전기 제작 방법

카본 코팅 용액은 카본블랙(Carbon Black, EC 600 JD, Mitsubishi Chemical Co., Ltd.) 분말과 양이온성 계면활성제(Hexadecyltrimethylammonium bromide, CTAB, Tokyo Chemical Industry Co., Ltd.)를 Deionized water (DI water)에 일정 비율로 첨가하여 제조하였다. 전도성 용액 제조를 위해 카본 블랙과 CTAB의 농도는 각각 0.375 wt. %와 1.5 wt. %로 설정하였으며, 혼합된 용액은 1시간 동안 초음파 처리하여 균일하게 분산되도록 하였다. 해당 조성은 선행 연구의 최적화된 비율을 적용하였고, 추가 검증을 위해 용액 제조 후 카본용액의 제타 전위 분석을 통해 분산도를 확인하였다.

본 연구에서 사용된 수분기반 발전기 제조 공정은 Fig. 1과 같고, 자세한 공정은 다음과 같다. 먼저, 셀룰로오스 아세테이트를 0.3, 0.4, 0.5 g 세 가지 조건으로 나누고, 우레탄 몰드(L: 30 mm, Ø: 7.5 mm)에 삽입하여 2000 bar의 압력으로 냉간등방압 공정을 통해 제조하였다. 이후, 압축 성형된 샘플을 카본 코팅용액에 딥 코팅 하여 제조하였다. 이때 샘플의 균일한 코팅을 위해 양쪽 끝을 10초간 동일하게 담지시켰다. 마지막으로, 코팅된 시편을 80°C에서 10시간 동안 건조하여 잔여 수분을 제거하면 발전기 제조가 완료된다.

2.2. 발전기 성능 평가 및 소재 특성 분석 방법

발전기 발전 성능 평가를 위해 3.3 M의 CaCl₂ 수용액 100 µL를 발전기 한쪽 끝에 도포하였다. CaCl₂ 수용액은 스스로 수분을 흡수하는 흡습성 재료로 초기 주입 이후 추가 주입 없이도 대기중의 수분을 흡수하여 장시간 발전이 가능하도록 만들어준다[20]. 에너지 하베스팅 개방전압(Open-circuit voltage) 및 단락전류(Short-circuit current) 측정을 위해 소스 미터(Keithley 2400)를 활용하였고, 아크릴 챔버 내 환경을 정밀 제어하기 위해 온-습도 센서(SHT10, Arduino Uno, Sensirion Inc.)를 활용하여 온도 25 °C, 상대습도 45-55 %에서 측정하였다(Fig. 2).

발전기 제조에 사용되는 소재 특성을 분석하기 위해 아래의 장비를 활용하여 최적화하였다. 투과전자현미경(Transmission Electron Microscope, TEM, JEM-2100F, JEOL Ltd.)을 통해 전도성

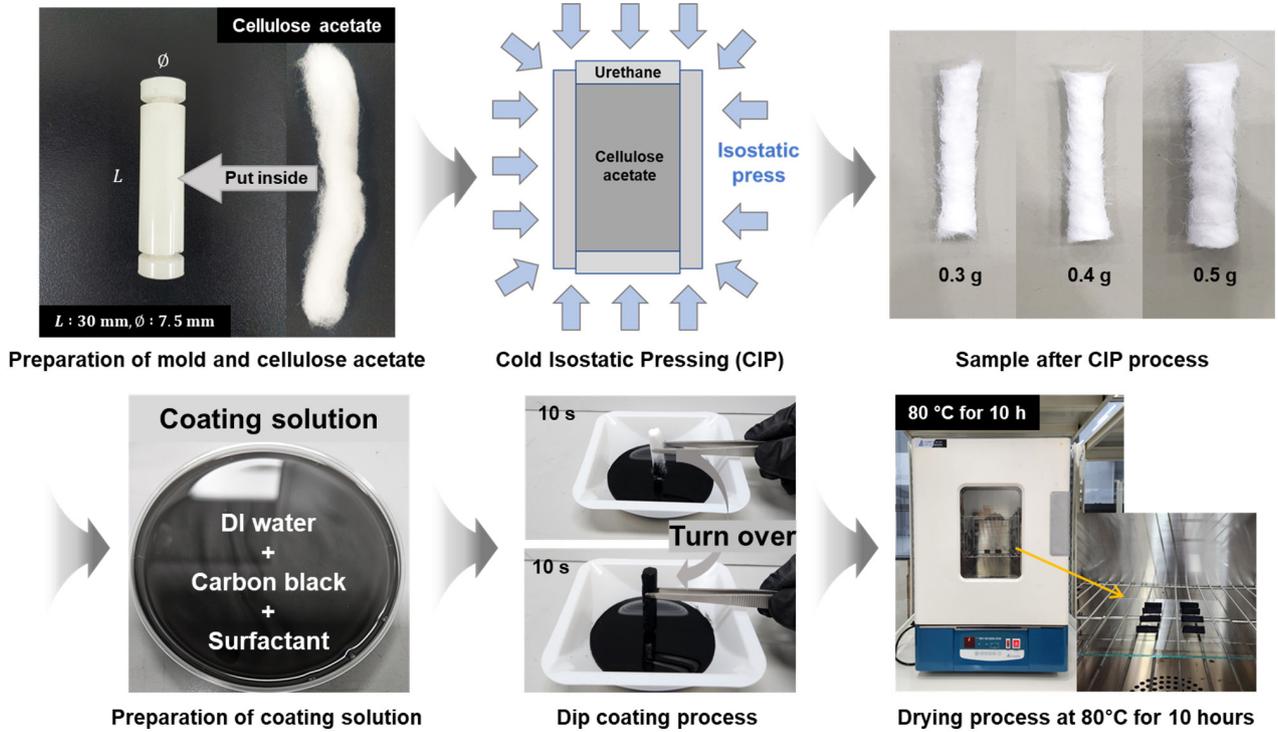


Fig. 1. Schematic of the fabrication process for the cellulose acetate-based hydrovoltaic generator (insertion of cellulose acetate into the urethane mold, cold isostatic pressing (CIP) at different masses, conductive dip coating, and drying at 80°C for 10 hours).

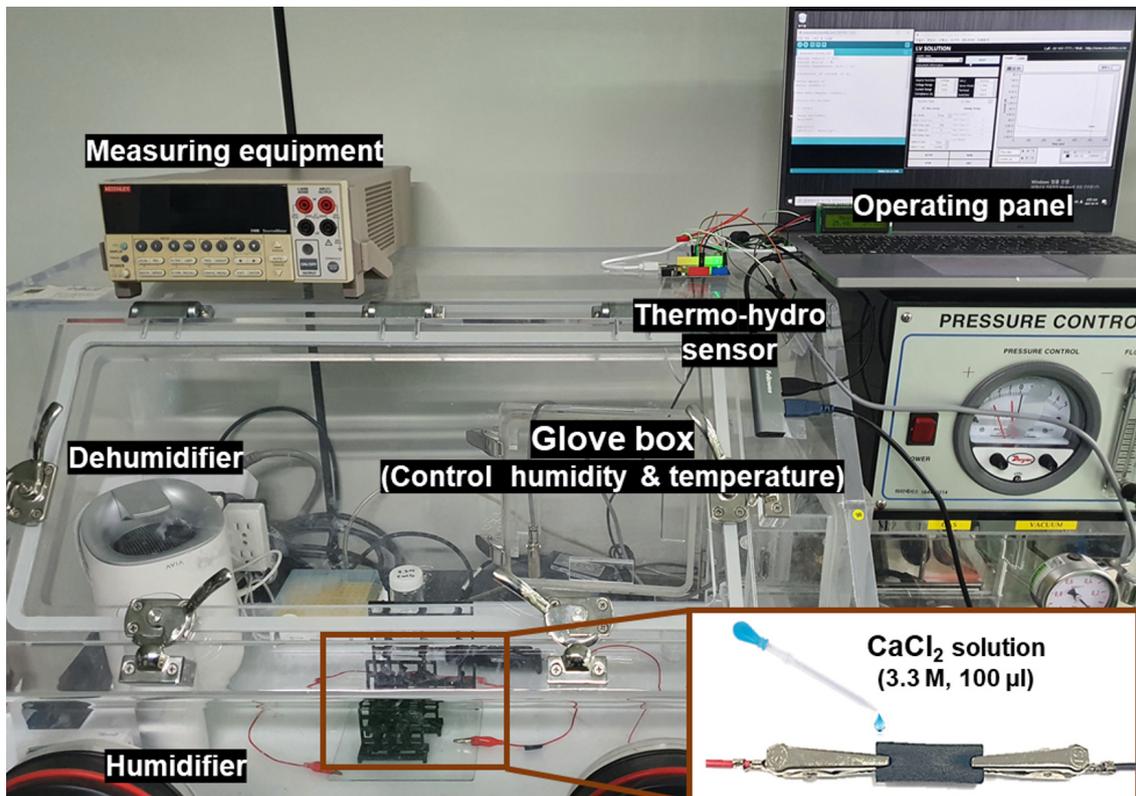


Fig. 2. Experimental setup for measuring the performance of the hydrovoltaic generator.

용액에 사용된 카본 블랙 분말의 미세구조를 분석하였다. 발전기 비표면적을 분석하기 위해 Brunauer–Emmett–Teller (BET) 분석 장비(3Flex, Micromeritics Instrument Co.)를 활용하였다. 셀룰로오스 아세테이트, 카본블랙, 그리고 발전기의 화학 결합 특성을 분석하기 위해 푸리에 변환 적외선 분광기(Fourier Transform-Infrared spectroscopy, FTIR, VERTEX 80V, Bruker)를 활용하였다. 카본용액의 응집도/분산도를 최적화하기 위해 전기적 영동을 분석장비(ELSZ-1000ZS, Otsuka Electric)를 활용하여 제타 전위를 분석하였다. 발전기 내 셀룰로오스 아세테이트 장입량에 따른 내부 미세구조를 분석하기 위해 주사전자현미경(Scanning Electron Microscopy, SEM, JSM-7100F, JEOL Ltd.)을 활용하였다.

3. Results and Discussion

3.1. 수분기반 에너지 하베스팅 메커니즘

수분기반 에너지 하베스팅의 성능을 향상시키는 변수는 다양하게 존재하지만 주요 변수는 발전기 내 젖음성의 차이로 전위차를 생성하는 모세관 효과 및 흡수된 물이 대기중으로 증발하면서 에너지를 생성하는 증발 효과의 복합 작용에 의한 것으로 판단된다. 모세관 현상에 의한 하베스팅 메커니즘은 발전기 소자 내부에서 발생하는 스트리밍 전위를 기반으로 한다. 스트리밍 전류는 마이크로 크기의 채널에서 압력 차이가 발생할 때 전하의 이동에 의해 흐르는 전류를 의미하며, 수용액이 마이크로 또는 나노 크기의 좁은 다공성 채널을 통과할 때, 채널 벽면과의 상호작용으로 인해 용액 내 전하 중성이 깨지게 된다. 채널 벽면에서는 양성자가 용액으로 해리되며, 이에 따라 채널 벽면에는 음전하가 형성된다. 반대로, 용액 내 양이온은 채널 벽면의 음전하를 상쇄하기 위해 이동하게 된다. 이렇게 형성된 양전하와 음전하의 이중층을 전기 이중층(Electrical Double Layer, EDL) 이라고 하며, 고체-액체 계면에서의 전하 분포는 유체역학적 흐름에 의해 전하를 끌어당기면서 전류를 생성한다. 이때 발생하는 전류를 스트리밍 전류라고 하며, 다음 식을 이용하여 계산할 수 있다[31].

$$I_{str} = \frac{A\varepsilon_0\varepsilon_r\Delta P\zeta}{\eta L} \quad (1)$$

마찬가지로, 스트리밍 전위 (Streaming potential)도 다음 식을 통해 정리된다.

$$V_{str} = \frac{\varepsilon_0\varepsilon_r\Delta P\zeta}{\sigma\eta} \quad (2)$$

여기서, σ 는 미세 채널 내 용액의 전도도, η 는 용액의 점성 (Viscosity), 그리고 $\varepsilon_0\varepsilon_r$ 는 주입 용액의 유전율(Dielectric constant)을 의미한다. 발전기 내부에 셀룰로오스 섬유들이 정렬되어 있으며, 그 사이의 빈 공간이 모세관 채널을 형성하는 구조를 가지고 있다.

이때, 채널의 길이는 L , 기공의 단면적은 $A = \pi d^2/4$, 내부 표면의 제타 전위는 ζ 이다. Young–Laplace 방정식을 이용하면, 발전기의 한쪽과 반대쪽 끝 사이에서 발생하는 압력 차이 (ΔP)는 다음과 같이 표현할 수 있다.

$$\Delta P = \frac{4\gamma \cos \theta}{d} \quad (3)$$

여기서, d 는 기공의 직경, θ 는 용액이 표면을 따라 흐를 때의 접촉각(Contact angle), 그리고 γ 는 용액의 표면 장력 (Surface tension)을 나타낸다.

$$I_{str} = \frac{\pi\gamma d\varepsilon_0\varepsilon_r\zeta \cos \theta}{\eta L} \quad (4)$$

$$V_{str} = \frac{4\varepsilon_0\varepsilon_r\gamma\zeta \cos \theta}{\sigma\eta d} \quad (5)$$

또한, 스트리밍 전류는 다공성 (Porosity) 개념을 포함하여 다음과 같은 식으로 표현될 수 있다 [21].

$$I_{str} = \frac{4\gamma A\emptyset^{2.5}\varepsilon_0\varepsilon_r\zeta \cos \theta}{\eta dL} \quad (6)$$

여기서, \emptyset 는 다공성을 나타내며, 기공의 구조적 특성이 스트리밍 전류의 생성에 미치는 영향을 반영한다.

또한, 물 분자와 탄소 소재 간의 상호작용이며, 특히 다공성 탄소 필름 내부에서 물이 증발하면서 발생하는 흐름이 주요 원인으로 작용된다. 따라서 수분기반 에너지 하베스팅 메커니즘은 스트리밍 전류 (I_{str}), 증발에 의한 전류 (I_{evp}) [32], 그리고 실험 습도 및 온도 (α)의 복합작용으로 발전되고, 간단히 정리하면 아래의 식으로 표현할 수 있다.

$$I_{Total} = I_{str} + I_{evp} + \alpha \quad (7)$$

3.2. 발전기 제조를 위한 소재 특성 최적화

본 연구에서는 셀룰로오스 아세테이트를 냉간등방압 공정을 통해 모형을 만들고, 카본용액을 코팅하여 발전기를 제조하였으며, 성능 최적화를 위해 소재의 물리·화학적 특성을 분석하였다. 셀룰로오스 아세테이트는 친수성(Hydrophilic) 소재로서 수분 흡수를 용이하게 하여 발전기 내부에서 자연적인 모세관 흐름을 유도하는 역할을 한다. 카본블랙은 1192 m²/g 매우 큰 비표면적을 갖는 다공성 구조의 전도성 탄소 소재로(Fig. 3c), 발전기의 전기적 특성을 부여하는 데 중요한 요소이다. 또한, 하이드록실기(-OH)를 많이 포함하는 소재이고(Fig. 3e), 입자 간 반데르발스 힘(Van der Waals forces)으로 인해 쉽게 응집되는 특성을 가지므로, CTAB를 첨가하여 분산 안정성을 확보하였다. 이를 통해 코팅 용액내 카본블랙의 균일한 분산을 유도하고, 발전기를 고르게 코팅하여 전기적

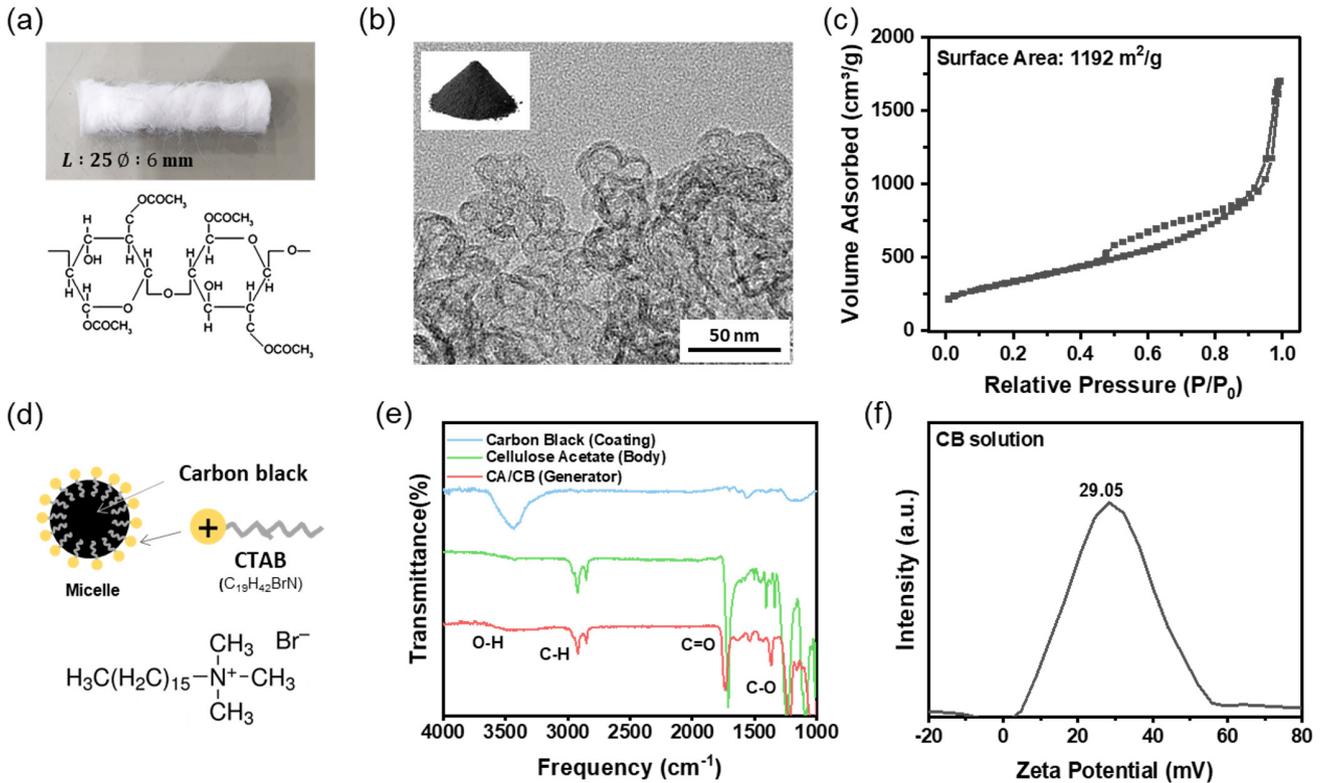


Fig. 3. (a) Photograph of cellulose acetate before processing (L: 25 mm, Ø: 6 mm) and chemical structure of cellulose acetate. (b) Transmission electron microscopy image of black nanoparticles (inset: carbon black powder). (c) Nitrogen adsorption-desorption isotherm of carbon black. (d) Schematic of surfactant-assisted dispersion mechanism and molecular structure of cationic surfactant (CTAB). (e) Fourier transform infrared spectra of cellulose acetate, carbon black, and carbon-coated cellulose acetate (generator). (f) Zeta potential distribution of the conductive solution.

특성을 분석하였다.

냉간등방압 공정 후 제작된 셀룰로오스 아세테이트 크기는 길이 25 mm, 직경 6 mm로 제작되었고(Fig. 3a), 친수성 소재로서 공기 중의 수분을 효과적으로 흡수할 수 있다. 또한, 내부 섬유간 밀도 조절을 통해 흡수된 수분의 모세관 효과를 제어함으로써 수분/이온을 통한 하베스팅 성능을 최적화할 수 있는 소재로 적합하다. FTIR분석을 통해 셀룰로오스 아세테이트의 화학 결합 구조를 확인한 결과(Fig. 3e), 하이드록실기(-OH) 구조가 일정부분 존재하여 물 분자와의 친화성을 갖고 있음을 확인하였다.

전도성 소재인 카본블랙의 TEM 분석을 수행한 결과(Fig. 3b), 카본 블랙은 다공성 구조를 가지며 내부가 중공(Hollow) 형태로 형성되어 있어, 코팅 이후 발전기의 넓은 비표면적을 갖기 위한 코팅 소재로 판단되었다. 또한, 이는 전하 저장 및 이온 이동을 용이하게 하여 발전기의 전도성을 극대화하는 역할을 한다. 또한, 질소 흡착-탈착 등온선(Nitrogen adsorption-desorption isotherm) 분석 결과(Fig. 3c), 카본블랙이 메조다공성(Mesoporous) 및 마이크로다공성(Microporous) 구조를 가지며, 넓은 비표면적을 통해 발

전기의 에너지 변환 성능을 향상시킬 수 있음을 확인하였다.

전도성 용액 내 카본블랙의 균일한 분산을 위해 CTAB를 활용하였고, 이는 양이온성 계면활성제로서 카본블랙 입자의 표면을 감싸면서 양전하(+)를 부여하여, 입자 간 정전기적 반발력을 증가시키고 응집을 방지하는 역할을 한다(Fig. 3d). 일반적으로 콜로이드 입자 간 정전기적 인력을 극복하기 위해 제타 전위의 절대값이 20 mV 이상이면 분산 안정성이 높다고 보고되고 있다[33]. 이는 입자 간 정전기적 반발력이 충분히 커져 응집을 막을 수 있기 때문이고, 본 연구에서 사용된 코팅용액의 제타 전위는 29.05 mV로서 응집 없이 고르게 분산되어 있음을 확인하였다(Fig. 3f).

3.3. 발전기 내부 섬유 간 밀도에 의한 하베스팅 성능 최적화

본 연구에서 개발한 수분 기반 발전기는 식물의 증산 현상을 모방하였으며(Fig. 4a), 발전기 내부 모세관 효과에 의한 수분/양성자 흐름과 증발 현상을 활용하여 에너지를 생성하는 발전기이다. 공기 중의 수분을 스스로 흡수하기 위해 CaCl₂ 용액을 도포하여 외부 조작 없이 연속적으로 수분을 흡수하고 에너지를 생성하는 발전기

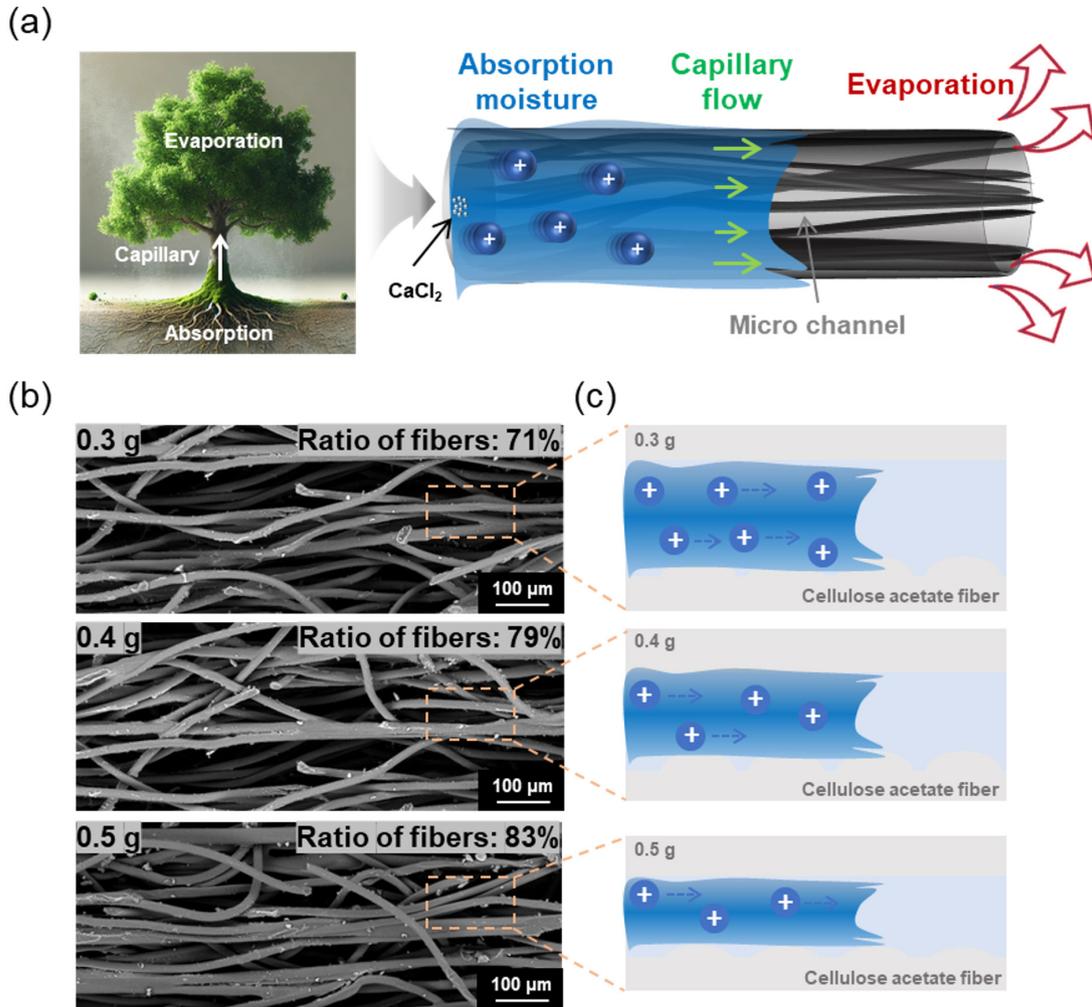


Fig. 4. (a) Schematic illustration of the transpiration mechanism in nature and its application to cellulose acetate fiber microchannels. Water absorption, capillary flow, and evaporation contribute to ion movement and energy generation. (b) Scanning electron microscopy images of cellulose acetate fibers with different mass conditions and ratios of fibers (0.3 g, 0.4 g, and 0.5 g), showing variations in fiber density. (c) Illustration of ion transport within cellulose acetate fiber microchannels under different fiber densities, demonstrating the effect of mass on moisture capillary and charge distribution.

를 구현하였다[20]. 이러한 발전기의 성능을 향상시키기 위해 내부 밀집도 제어를 하였고, 이때 냉간등방압 압력은 동일하게 설정하고, 몰드 내 셀룰로오스 아세테이트 장입량(0.3 g, 0.4 g, and 0.5 g)에 따라 성능을 최적화하였다. Fig. 4b는 장입량에 따른 발전기 내부 구조에 대한 FE-SEM 분석 결과를 나타내며, 장입량이 증가함에 따라 내부 섬유 밀도가 증가하고, 유로의 직경이 작아지므로 모세관 현상이 증가할 수 있다. 하지만 발전기 내부 이미지 처리 결과를 보면, 장입량이 증가할수록 파이버가 차지하는 비율(71→83%)이 증가하여 유로내 이동할 수 있는 양성자(Proton)의 양이 감소하게 된다. Fig. 4c는 유로의 밀도에 따른 수분 및 양성자의 이동을 나타낸 것으로, 장입량이 증가할수록 내부 공간이 감소하면서 이온의 이동량이 저하되는 것을 시각화 하였다. 또한, 섬유간 밀도가 증

가하면 발전기의 비표면적이 작아지고, 이에 따라 대기중으로 증발되는 수분의 양은 감소하게 된다. 이는 비표면적(Specific surface area)의 감소를 초래하고, 결과적으로 수분의 증발 효과를 감소시켜 내부의 압력 차이(ΔP)가 감소하게 된다. 결과적으로 모세관 효과와 증발 효과를 모두 감소시켜 발전 성능이 저하되게 된다.

제작한 수분기반 발전기의 성능을 측정하기 위해 온도/습도 제어 가능한 챔버 내에서 3.3M CaCl₂ 수용액 100 uL를 발전기 한쪽 끝에 도포하고, 단락전류와 개방전압을 500 secs 동안 연속하여 측정하였다. 셀룰로오스 아세테이트 장입량이 0.3 g, 0.4 g, 그리고 0.5 g로 증가함에 따라 발전 단락전류 값은 107.2 μA, 76.4 μA, 그리고 56.1 μA로 감소하는 것을 볼 수 있다(Fig. 5a). 이는 내부 유로가 좁아지면서 수분/양성자 이동성이 저하되고, 이에 따라 스트

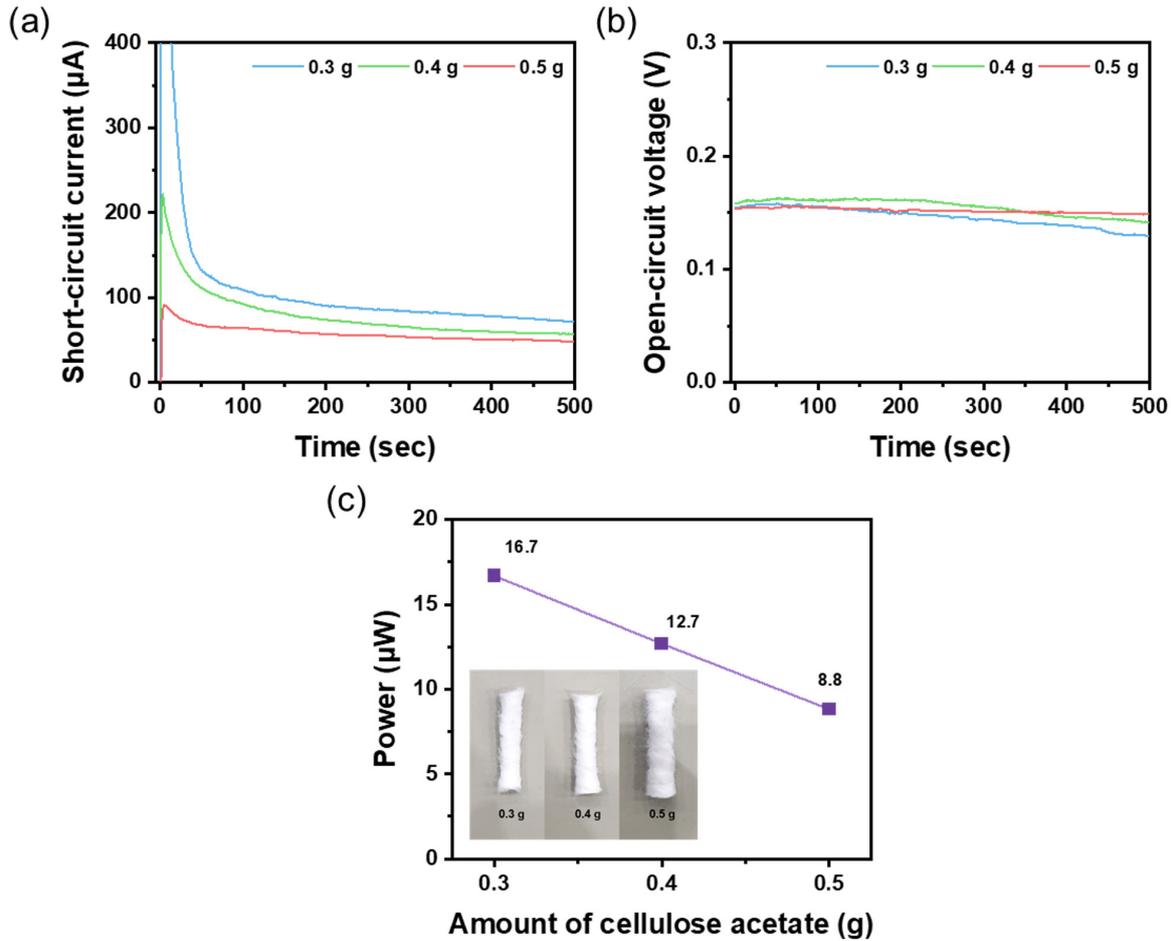


Fig. 5. Electrical performance of the cellulose acetate-based hydrovoltaic generator under different mass conditions. (a) Short-circuit current (I_{sc}). (b) Open-circuit voltage (V_{oc}) measurements over time for different cellulose acetate mass conditions. (c) Effect of cellulose acetate mass on the power of the generator and photographs of samples (0.3 g, 0.4 g, and 0.5 g).

리밍 전류의 생성이 줄어들기 때문으로 판단할 수 있다. 또한 섬유 간 밀집도가 증가하면서 대기중으로 증발하는 수분의 양이 줄어들어 생성되는 전력이 감소하는 복합 현상으로 판단된다. 반면, 개방 전압은 셀룰로오스 아세테이트의 장입량이 증가해도 0.15 V로 일정하게 유지되는 것을 확인할 수 있는데 (Fig. 5b), 이는 동일한 전도성 용액을 사용하고 발전기의 축 방향 길이가 동일하기 때문에 양 끝단의 전위차가 비교적 일정한 것으로 판단된다. 선행 연구 결과에도 농도가 같은 용액으로 코팅을 할 때, 발전기 저항에 지배적인 영향을 주는 변수는 축방향의 길이라는 결과와 일치한다[34]. 결과적으로 동일한 몰드 내 셀룰로오스 아세테이트 장입량이 감소함에 따라 발전 전력은 8.8 µW, 12.7 µW, 그리고 16.7 µW로 증가한다(Fig. 5c). 실험 결과를 정리하면, 수분 기반 에너지 하베스팅의 성능을 최적화하기 위해 내부 밀도는 모세관 효과와 증발 효과를 충분히 발휘할 수 있는 정도의 밀도를 갖는 것이 중요하고, 발전기의 전압을 향상시키기 위해서는 축방향의 최적화가 추가 연구되

어야 하는 것을 확인하였다. 이러한 실험 결과는 발전기의 성능 최적화를 위해 내부 밀집도를 적절히 조절하는 것이 필수적임을 확인하였고, 수분기반 에너지 하베스팅 메커니즘은 모세관 효과와 증발 효과의 복합적 현상에 의한 것이라는 것을 검증하였다.

4. Conclusion

에너지 하베스팅 기술은 지속 가능한 전력 공급을 위한 핵심 연구 분야로 주목받고 있으며, 특히 수분 기반 발전기의 성능 최적화를 위해 내부 밀집도 조절이 필수적이다. 본 연구에서는 냉간등방압 공정을 적용하여 내부 섬유 간 밀도를 변화시킴으로써 증발과 모세관 현상의 최적화를 시도하였다. 이를 위해 동일한 우레탄 몰드 내 셀룰로오스 아세테이트의 장입량을 조절하였고, 성능 분석 결과 셀룰로오스 아세테이트 장입량이 증가할수록 내부 섬유간 밀도가 증가하여 수분/양성자의 이동 채널이 좁아지므로 단락전류

값이 감소하는 것을 확인하였다. 또한, 개방전압은 조건에 관계없이 일정하게 유지되었으므로 발전 전력은 장입량이 증가할수록 감소한 것을 파악하였다. 본 연구는 수분기반 발전기의 내부 섬유 간 밀도 최적화가 발전 성능 향상에 결정적인 역할 하는 것을 확인할 수 있었다. 또한, 발전 전압을 최적화하기 위해서는 발전기 길이 조절이 필요한 것을 검증하였다. 본 연구 결과를 바탕으로 수분기반 에너지 하베스팅 성능을 향상시키기 위한 구조적 변수를 제시하는 기초연구로 기여할 수 있을 것으로 예상된다.

Funding

This work was supported by the Korea Institute of Industrial Technology as Development of Current-Enhanced Moisture-Induced Electrical Power Generators for Sustainable Green Hydrogen Production (KITECH EO- 250017). Additional support was provided by the Hyundai Motor Chung Mong-Koo Foundation as Development of DLE-type carbon-neutral next-generation lithium-ion concentration technology (KITECH IR-24A90).

Conflict of Interest

The authors declare no competing interests.

Data Availability Statement

All dataset files used in this study are already provided in the manuscript.

Author Information and Contribution

Seung-Hwan Lee: PhD candidate; Methodology, formal analysis, investigation, data curation, and writing – original draft. So Hyun Baek: PhD candidate; Methodology, formal analysis. Hyun-Woo Lee: MS candidate; Investigation, data curation. Yongbum Kwon: PhD candidate; Investigation, data curation. Kanghyuk Lee, Kee-Ryung Park, Yoseb Song: Dr.; Investigation and methodology. Bum Sung Kim, Ji Young Park: Dr.; Visualization, and data curation. Yong-Ho Choa: Professor; Supervision, formal analysis, and validation. Da-Woon Jeong: Dr., Professor; Conceptualization, writing - review and editing, supervision, project administration, and funding acquisition. All the

authors discussed the results and commented on the manuscript.

Acknowledgments

None.

References

- [1] M. Szucs, M. L. Vahsen, B. A. Melbourne, C. Hoover, C. Weiss-Lehman and R. A. Hufbauer: *Proc. Natl. Acad. Sci. U.S.A.*, **114** (2017) 13501.
- [2] F. Johnsson, J. Kjärstad and J. Rootzén: *Climate Policy*, **19** (2019) 258.
- [3] A. Qazi, F. Hussain, N. A. Rahim, G. Hardaker, D. Alghazawi, K. Shaban and K. Haruna: *IEEE Access*, **7** (2019) 63837.
- [4] S. Chu and A. Majumdar: *Nature*, **488** (2012) 294.
- [5] A. Mayer: *Energy, Sustainability and Soc.*, **12** (2022) 27.
- [6] J. Khan and M. H. Arsalan: *Renewable and Sustainable Energy Rev.*, **55** (2016) 414.
- [7] C. De Castro, M. Mediavilla, L. J. Miguel and F. Frechoso: *Renewable and Sustainable Energy Rev.*, **28** (2013) 824.
- [8] L.M. Miller and D.W. Keith: *Joule*, **2** (2018) 2618.
- [9] V. Devabhaktuni, M. Alam, S. S. S. R. Depuru, R. C. Green II, D. Nims and C. Near: *Renewable and Sustainable Energy Rev.*, **19** (2013) 555.
- [10] H. Daiguji, P. Yang, A. J. Szeri and A. Majumdar: *Nano Lett.*, **4** (2004) 2315.
- [11] M. S. Aziz, S. Ahmed, U. Saleem and G. M. Mufti: *Int. J. Renewable Energy Res.*, **7** (2017) 111.
- [12] Y. Zou, V. Raveendran and J. Chen: *Nano Energy*, **77** (2020) 105303.
- [13] X. Yue, M. Kauer, M. Bellanger, O. Beard, M. Brownlow, D. Gibson, C. Clark, C. MacGregor and S. Song: *IEEE Internet of Things J.*, **4** (2017) 2092.
- [14] N. Sezer and M. Koç: *Nano Energy*, **80** (2021) 105567.
- [15] X. Wang, F. Lin, X. Wang, S. Fang, J. Tan, W. Chu, R. Rong, J. Yin, Z. Zhang and Y. Liu: *Chem. Soc. Rev.*, **51** (2022) 4902.
- [16] S.-H. Lee, H.-W. Lee, S. H. Baek, J. Yun, Y. Kwon, Y. Song, B. S. Kim, Y.-H. Choa and D.-W. Jeong: *Polymers*, **16** (2024) 433.

- [17] P. I. Dolez: *Sensors*, **21** (2021) 6297.
- [18] G. Xue, Y. Xu, T. Ding, J. Li, J. Yin, W. Fei, Y. Cao, J. Yu, L. Yuan and L. Gong: *Nat. Nanotechnol.*, **12** (2017) 317.
- [19] Y. Wang, S. Gao, W. Xu and Z. Wang: *Adv. Funct. Mater.*, **30** (2020) 1908252.
- [20] J. Bae, T. G. Yun, B. L. Suh, J. Kim and I.-D. Kim: *Energy Environ. Sci.*, **13** (2020) 527.
- [21] S. S. Das, V. M. Pedireddi, A. Bandopadhyay, P. Saha and S. Chakraborty: *Nano Lett.*, **19** (2019) 7191.
- [22] J. Bae, M. S. Kim, T. Oh, B. L. Suh, T. G. Yun, S. Lee, K. Hur, Y. Gogotsi, C. M. Koo and I.-D. Kim: *Energy Environ. Sci.*, **15** (2022) 123.
- [23] Z. Zhang, X. Li, J. Yin, Y. Xu, W. Fei, M. Xue, Q. Wang, J. Zhou and W. Guo: *Nat. Nanotechnol.*, **13** (2018) 1109.
- [24] R. Zhang, S. Wang, M. H. Yeh, C. Pan, L. Lin, R. Yu, Y. Zhang, L. Zheng, Z. Jiao and Z. L. Wang: *Adv. Mater.*, **27** (2015) 6482.
- [25] S. Vinhas, M. Sarraguça, T. Moniz, S. Reis and M. Rangel: *Polymers*, **16** (2023) 20.
- [26] W. Sparreboom, A. van den Berg and J. C. Eijkel: *Nat. Nanotechnol.*, **4** (2009) 713.
- [27] B. Shao, Z. Song, X. Chen, Y. Wu, Y. Li, C. Song, F. Yang, T. Song, Y. Wang and S.-T. Lee: *ACS Nano*, **15** (2021) 7472.
- [28] Y. Huang, H. Cheng, C. Yang, H. Yao, C. Li and L. Qu: *Energy Environ. Sci.*, **12** (2019) 1848.
- [29] X. Gao, T. Xu, C. Shao, Y. Han, B. Lu, Z. Zhang and L. Qu: *J. Mater. Chem. A*, **7** (2019) 20574.
- [30] S. G. Yoon, Y. Yang, J. Yoo, H. Jin, W. H. Lee, J. Park and Y. S. Kim: *ACS Appl. Electron. Mater.*, **1** (2019) 1746.
- [31] G. Xue, Y. Xu, T. Ding, J. Li, J. Yin, W. Fei, Y. Cao, J. Yu, L. Yuan, L. Gong, J. Chen, S. Deng, J. Zhou and W. Guo: *Nat. Nanotechnol.*, **12** (2017) 317.
- [32] Z. Sun, V. Nicolosi, D. Rickard, S. D. Bergin, D. Aherne and J. N. Coleman: *J. Phys. Chem. C*, **112** (2008) 10692.
- [33] Z. Sun, V. Nicolosi, D. Rickard, S. D. Bergin, D. Aherne and J. N. Coleman: *The Journal of Physical Chemistry C*, **112** (2008) 10692–10699.
- [34] S. H. Lee, Y. Kwon, S. Kim, J. Yun, E. Kim, G. Jang, Y. Song, B. S. Kim, C. S. Oh and Y. H. Choa: *Chem. Eng. J.*, **495** (2024) 153411.

백운석에서 $MgSO_4$ 의 추출과 간수에서 $Mg(OH)_2$ 합성 연구심현승¹, 김지연¹, 최아름^{1,2}, 오누리², 김유진^{1,*}¹한국세라믹기술원 엔지니어링 소재 센터²한양대학교 신소재 공학과Extraction of $MgSO_4$ from dolomite and synthesis of $Mg(OH)_2$ in BitternHyunSeung Shim¹, Jiyeon Kim¹, Areum Choi^{1,2}, Nuri Oh², Yoojin Kim^{1,*}¹Engineering Materials Center, Korea Institute of Ceramic Engineering and Technology, Icheon, Republic of Korea²Division of Materials Science & Engineering, Hanyang University, Seoul, Republic of Korea

Synthesis of high-purity magnesium hydroxide using dolomite and bittern is important for use in various applications. We synthesized magnesium hydroxide using bittern and dolomite, which are domestic resources. In Bittern, there is a high concentration of Mg^{2+} ions, but the impurity Ca^{2+} ion content is also significant, requiring a purification process to remove it. There are two main methods for this purification. Firstly, there is a separation method that utilizes the difference in solubility between Mg^{2+} ions and Ca^{2+} ions by using sulfuric acid on dolomite. Adding $MgSO_4$ solution from dolomite to Bittern removes Ca^{2+} ions as $CaSO_4$. This process simultaneously purifies Ca impurities and increases the Mg/Ca ratio by adding extra Mg^{2+} ions. In this study, purified bittern was obtained by using dolomite and sulfuric acid to extract $MgSO_4$, which was then used to purify Ca^{2+} ions. High-purity $Mg(OH)_2$ was synthesized by optimizing the NaOH and NH_4OH ratio as an alkaline precipitant. $Mg(OH)_2$ synthesis technology made by effectively removing Ca ions from dolomite and bittern can contribute to domestic pilot production.

Keywords: Dolomite; Bittern; $MgSO_4$; Sulfuric acid; $Mg(OH)_2$

Received: March 31, 2025

Revised: April 17, 2025

Accepted: April 18, 2025

***Corresponding author:**

Yoojin Kim

TEL: +82-31-645-1427

FAX: +82-31-645-1485

E-mail: yjkim@kicet.re.kr

1. Introduction

수산화마그네슘($Mg(OH)_2$)은 방열 소재와 제약 산업의 원료로 사용되는 무기 재료이며, 연소 시 수화물이 탈수화되면서 흡열반응이 일어나기 때문에 난연제로서 주목받는 물질이다. [1-3]. Mg 원료는 해수와 광물로부터 소성, 화학적 예칭, 침전법 등의 방법을 통해 추출할 수 있다[4, 5]. 먼저 광물 추출원료로는 Magnesite($MgCO_3$)와 Dolomite (백운석, $(CaMg(CO_3)_2)$) 등이 있다. 백운석은 우리나라에서 채굴할 수 있는 비금속 광물자원으로 내화재, 유리,

충전재 등으로 사용되고 있으며, 화학성분은 $CaCO_3$ 와 $MgCO_3$ 가 약 1대 1의 비율로 포함되어 있다[1, 6]. 따라서 백운석 내 Mg^{2+} 성분을 이용하기 위해서 높은 비율의 Ca^{2+} 함량을 제어하는 것이 중요하다. 광물자원의 경우 산을 이용한 예칭 방법이 일반적이기 때문에 산이면서 황산염에 대한 용해도 차이를 이용할 수 있는 H_2SO_4 를 이용하여 Mg^{2+} 을 추출하고자 한다. 이는 정제 및 침전을 동시에 진행시켜 $Mg(OH)_2$ 를 얻을 수 있으나, 백운석에 포함된 Si, Fe이온 등의 불순물 이온 등에 의해 고순도 $Mg(OH)_2$ 를 얻기 힘들다. 불순물들이 포함되어있는 $Mg(OH)_2$ 는 다양한 응용범위 적용이 힘들기 때문에, 이에 가용자원을 이용한 98-99%의 고순도 $Mg(OH)_2$ 의 합성 및 정제기술이 산업에 필요하다. 다른 Mg 공급원인 해수는 Cl^- 과 Na^+ 이온이 가장 많이 포함되어있고 Mg^{2+} 이온

<https://doi.org/10.4150/jpm.2025.00073>

© 2025 The Korean Powder Metallurgy & Materials Institute

의 함량이 적기 때문에 경제적인 공정 개발과 낮은 순도 문제의 해결이 필요하다[7]. 반면에 간수는 해수에서 이온교환막을 통해 Na⁺ 이온을 일부 제거한 용액이며, 해수에 비해 Mg²⁺ 이온이 농축되어 있지만 Ca²⁺ 이온 비율이 해수보다 상대적으로 높아 정제가 필요하다. 이러한 Ca²⁺ 이온을 제거하는 방법으로는 SO₄²⁻을 첨가하여, 간수 내 Ca²⁺ 이온을 SO₄²⁻이온과 반응시켜 이수석고(CaSO₄·2H₂O)로 침전시켜 제거할 수 있다[4]. 이후 Ca²⁺이 제거된 간수에 염기성 침전제(NH₄OH, NaOH 등)를 첨가해 Mg(OH)₂를 얻을 수 있다[7]. 간수 내의 Mg²⁺과 Ca²⁺은 결정화에 있어 pH의 영향을 받는데, 이 두 물질의 침전되는 pH가 다르므로 공정 간 적정 pH의 최적화와 유지가 Mg(OH)₂ 순도에 있어 중요한 요소이다[8].

이번 연구는 Mg²⁺ 이온 전구체로 백운석과 간수를 이용해 효율적으로 Mg²⁺ 추출 및 Ca²⁺ 제거하여 고순도의 Mg(OH)₂ 합성하는 연구를 진행하였다. 백운석과 H₂SO₄를 이용하여 추출된 MgSO₄를 간수에 첨가하여 물에 대한 용해도가 낮은 CaSO₄를 침전시켜(Bittern + MgSO₄ → MgCl₂ + CaSO₄·2H₂O ↓) Ca²⁺ 불순물을 정제하였다. 간수에 백운석에서 추출된 MgSO₄를 첨가하면 H₂SO₄를 첨가할 때 보다 높은 pH 유지를 통해 염기성 침전제 사용량을 줄일 수 있으며, 간수의 Mg²⁺ 이온 함량을 증가시켜 물질의 순도 증가에 기여할 수 있다.

2. Experimental Section

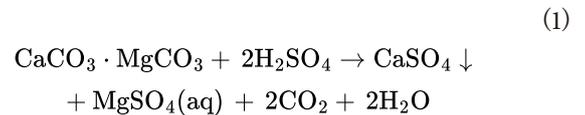
2.1 재료 및 분석기기

백운석은 D사에서 공급받아 괴상의 백운석을 디스크 밀(Pulversette 12, Fritsch, Germany)을 이용해 디스크 간격을 조절하며 입자 크기를 조절하였고, 이를 Particle Size Analysis (PSA, LA-950V2, Horiba, Japan)분석을 통해 확인하였다. 정제염 간수는 성분 및 이온 함량을 분석하기 위해 H사에서 공급받아 사용하였다. H₂SO₄ (대정화급, 95 %)는 증류수를 이용해 다양한 농도로 묽혀서

사용하였다. 침전공정에 사용된 시약은 NaOH (덕산화학, 50 %)와 NH₄OH(덕산화학, 28 %)를 사용하였다. 원료와 합성된 결과물은 X-ray diffraction (XRD, Model D/Max 2500, Rigaku, Japan)을 통해 Cu-Kα radiation (λ = 1.5406 Å)으로 10° - 80°의 2θ 범위에서 4° min⁻¹의 주사율로 결정상을 분석하였으며, X-ray fluorescence (XRF, Model S1 TITAN, Bruker, USA)와 Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES, Model SPECTRO ARCOS, Thermo Fisher Scientific, USA)로 성분을 분석하였고 Transmission Electron Microscope (TEM, Model CM 200, Philips, Netherlands)을 통해 형상을 평가하였다.

2.2 H₂SO₄을 이용한 백운석 내 Ca²⁺ 제거 및 MgSO₄ 추출

백운석의 성분 분석을 위하여 ICP 및 XRF 분석을 실시하였다. 분석 결과 백운석 내 Mg²⁺, Ca²⁺ 이 주성분을 이루고 있었고, Mg²⁺을 얻기 위해 Ca²⁺ 분리가 필요하다. 따라서 효율적인 Ca²⁺ 제거를 위하여 다음과 같은 실험을 진행하였다. 백운석과 H₂SO₄를 반응시키면 석고(CaSO₄)형태가 고체 상태로 침전되어 백운석 내 Ca²⁺을 제거할 수 있다(1).



이는 물에 대한 CaSO₄와 MgSO₄의 용해도 차이를 이용한 방법으로 효율적인 MgSO₄용액 생성을 위해 다양한 실험 조건에서 실험을 진행하였다. Table 1은 백운석에 H₂SO₄의 농도를 조절하여 반응시킨 실험 조건이다. 여러 가지 백운석 중 K사로부터 공급받은 괴상의 백운석을 사용하였다. 괴상의 백운석은 디스크밀(Pulversette 12, Fritsch, Germany)을 통해 100 μm 이하로 분쇄하여 분말 형태로 사용하였다.

Condition I (sample 1~3)에서는 최적의 Ca²⁺ 제거 효율을 나

Table 1. Reaction condition of H₂SO₄ Dolomite

Condition	Sample	Dolomite (g)	H ₂ SO ₄ (%)	Mole ratio (Dolomite:H ₂ SO ₄)	Stirring time (h)
I	1	10	1	1:2	24
	2	10	5	1:2	24
	3	10	10	1:2	24
II	4	5	5	1:4	24
	5	10	5	1:2	24
	6	15	5	1:1.3	24
III	7	10	5	1:2	2
	8	10	5	1:2	4
	9	10	5	1:2	6
	10	10	5	1:2	24

타내는 H₂SO₄ 농도에 대해 찾고자 하였다. 백운석과 H₂SO₄의 몰비율을 1:2로 고정한 상태에서 가하는 H₂SO₄의 퍼센트 농도를 다르게 하여 실험을 진행하였다. 10 % H₂SO₄ 용액을 이용하여 1, 5 % H₂SO₄ 용액을 제조하고 이를 백운석 10 g에 가한 후 24시간 동안 교반하여 MgSO₄ 용액을 제조하였다.

Condition II (sample 4~6)에서는 최적의 Ca²⁺ 제거 효율을 나타내는 백운석과 H₂SO₄의 비율을 찾고자 하였다. H₂SO₄의 농도는 5 %로 고정하고 백운석의 양(5, 10, 15 g)을 조절하여 백운석과 H₂SO₄의 몰비율을 조절하였다. 이 후 24시간 동안 교반하여 MgSO₄ 용액을 제조하였다.

Condition III (sample 7~8)에서는 최적의 Ca²⁺ 제거 효율을 나타내는 백운석과 H₂SO₄의 반응시간을 찾고자 하였다. 백운석 10 g에 H₂SO₄ 수용액 400 ml를 첨가하여 반응시간(2~24 h)을 조절하여 pH에 따른 Mg²⁺이온의 양을 확인하였다. 이 후 24시간 동안 교반하여 MgSO₄ 용액을 제조하였다.

1-8번 샘플 모두 교반속도 300 rpm으로 교반하여 반응시키고 이 후, 8000 rpm으로 10분간 원심분리 하였다. 원심분리를 통해 얻은 MgSO₄ 용액은 ICP-OES로 성분을 분석하였다.

Fig. 1은 백운석과 간수를 활용하여 고순도의 Mg(OH)₂를 수득하는 과정의 모식도이다. 백운석과 간수에 포함되어있는 Ca²⁺을 제거하기 위하여 첫번째로 분말 형태의 백운석을 H₂SO₄ 용액에 넣고 CaSO₄로 침전 시켜 백운석 내의 Ca²⁺을 제거하는 과정과, 두번째로 이후 얻어진 MgSO₄ 용액을 간수와 반응시켜 간수 내의 Ca²⁺을 CaSO₄ 형태로 침전 시켜 제거하는 과정이다. 마지막으로 얻어진 MgCl₂ 용액에 NH₄OH를 첨가하여 Mg(OH)₂를 수득하였다.

2.3 MgSO₄을 이용한 간수 내 Ca²⁺ 정제

간수의 성분 분석을 위하여 ICP 및 XRF 분석을 실시하였다. 분석 결과 해수에 비해 높은 비율의 Mg²⁺, Ca²⁺ 이온이 존재하였고, Mg²⁺을 얻기 위한 Ca²⁺ 분리가 필요하다. 간수 중 Ca²⁺ 이온을 효

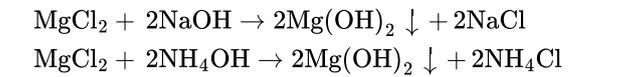
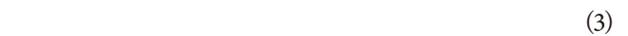
율적으로 제거하기 위해 (H₂SO₄ 및) MgSO₄를 이용하였다. 간수 내 Mg/Ca 비율을 증가시켜 고순도 MgSO₄를 제조하였다. 간수에 MgSO₄를 첨가하게 되면 물에 대한 용해도가 낮은 CaSO₄ (0.255/100 ml)는 침전되어 Ca²⁺ 성분을 감소시킬 수 있다[9] (2).



이때 사용한 MgSO₄ 용액은 앞선 실험에서 최적화한 방법으로, 5 %의 H₂SO₄와 백운석의 몰비율을 1:2로 4시간 교반하여 제조 후 간수와 반응시켜 CaSO₄를 분리하여 디칼슘 간수를 제조하였다. 이를 간수에 첨가하여 300 rpm에서 2시간 동안 교반을 진행하였다. 이후 8000 rpm에서 10분간 원심분리하여 Ca²⁺이 정제된 간수를 제조하였다. Ca²⁺이 정제된 간수는 ICP로 성분을 분석하였다.

2.4 Ca²⁺이 정제된 간수에 염기성 침전제를 첨가하여 Mg(OH)₂ 제조

Mg(OH)₂는 간수에 염기성 침전제를 첨가하면 염기성 물질 내의 OH⁻이온이 간수 내의 Mg²⁺이온과 반응하여 Mg(OH)₂의 형태로 침전된다(3).



Mg(OH)₂의 합성을 위해 Ca²⁺이 정제된 간수에 염기성 침전제인 NaOH와 NH₄OH의 몰비율을 1:2로 하여 각각 투입 후 300 rpm에서 2시간동안 충분히 교반을 진행하였다. 반응이 끝난 생성물은 8000 rpm에서 10분간 원심분리하여 침전물을 얻었다. 침전물은 증류수를 사용하여 2회 세척을 하였다. 세척이 완료된 생성물은 80 °C 건조기에서 24시간 동안 건조 후 백색의 Mg(OH)₂를 분말로 수득하였다. 수득한 Mg(OH)₂는 XRD, ICP를 통해 성분을 분석하였다.

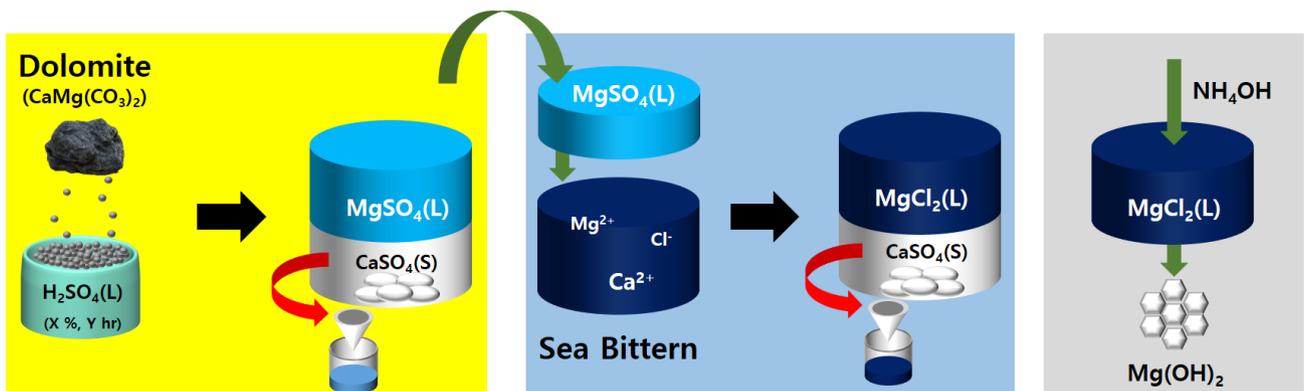


Fig. 1. Schematic diagram of the process of obtaining Mg(OH)₂ with dolomite and sea bittern.

Table 2. ICP-OES data of dolomite provided by 4 companies

Sample	Component (wt %)						Total (Except for Mg, Ca)
	CaO	MgO	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃		
W	30.6	21.3	0.33	0.21	0.17		0.71
K	30.5	21.7	0.22	0.12	0.09		0.43
S	30.9	21.3	0.21	0.18	0.14		0.54
D	30.8	21.6	0.15	0.08	0.08		0.30

Table 3. ICP-OES data of bittern and seawater of company H

Sample	Component (wt %)					
	Cl	SO ₄ ²⁻	Ca ²⁺	Mg ²⁺	K ⁺	Na ⁺
Sea water	1.93	0.27	0.04	0.13	0.04	1.07
Sea bittern	16.82	0.006	1.66	3.30	4.21	2.65
Sea bittern/Sea water	8.72	0.02	41.5	25.4	105	2.48

Table 4. ICP-OES data for MgSO₄ at different sulfuric acid concentrations

Sample (H ₂ SO ₄)	Component (ppm)				Ratio (%)	
	Mg	Ca	Si	S	Mg/Si	Mg/Ca
1 %	1304	529.8	5	2001	260.8	2.46
5 %	3288	651.2	8.6	12110	382.3	5.05
10 %	3357	703.4	9.1	33310	368.9	4.77

3. Results and Discussion

3.1 백운석 성분 분석결과

괴상 상태의 백운석은 디스크밀을 이용하여 1 μm 이하로 분쇄하였다. Table 2 은 분쇄된 백운석의 ICP 분석 결과이다. CaO는 30.5~30.9 wt%, MgO는 21.3~21.7 wt%로 백운석의 이론적 화학조성과 비슷한 수치이다[10]. 4개의 회사로부터 공급받은 백운석에서 공통으로 소량의 금속산화물 불순물 SiO₂, Al₂O₃, Fe₂O₃가 존재하였다. 이 중 D사 백운석의 금속산화물 불순물(SiO₂, Al₂O₃, Fe₂O₃)들의 총합계는 0.3 wt%로 가장 낮게 측정된 것을 확인할 수 있었다. 따라서 고순도 Mg(OH)₂ 제조를 위한 MgSO₄ 용액 제조 실험에는 향후 제거가 어려운 SiO₂ 함량이 가장 적은 D사의 백운석을 사용하였다.

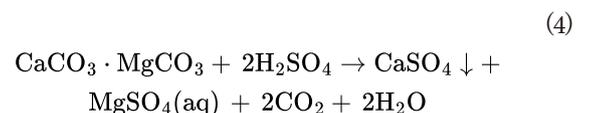
3.2 간수 성분 분석결과

간수는 해수를 이온교환막을 통과시켜 Na⁺를 일부 추출한 용액으로 Mg²⁺ 이온이 주성분이다. 간수의 성분을 알아보기 위하여 ICP 분석 및 이온 함량을 측정하였다. Table 3은 해수 및 간수의 이온 함량과 해수 대비 간수의 농도를 비교한 분석 결과이다. 분석

결과에 따르면, 간수는 Mg²⁺ 이온을 3.3 wt% 가지고 있으며, Ca²⁺, K⁺ 이온 등 다른 불순물 또한 다량으로 포함하는 것을 확인하였다. 이는 해수에 비해 Mg²⁺이온은 25.4배로 농축되어 있어 해수 대비 Mg²⁺ 이온을 효율적으로 추출이 가능하다. 하지만 Ca²⁺ 이온은 해수 대비 41.5배로 높은 비율로 존재하기 때문에 Ca²⁺를 효율적으로 제거해야 고순도의 Mg(OH)₂을 얻을 수 있다.

3.3 백운석과 다양한 H₂SO₄의 농도에 따른 MgSO₄용액 추출

백운석과 H₂SO₄의 화학반응을 통해 고체 상의 CaSO₄를 제거하고 용액 상의MgSO₄를 얻을 수 있다(4).



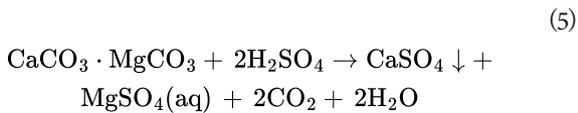
물에 대한 용해도가 낮은 CaSO₄(0.255g/100 ml)는 침전되므로 Ca²⁺ 이온을 백운석과 H₂SO₄ 용액으로부터 제거할 수 있다. 물에 대한 용해도가 상대적으로 높은 MgSO₄ (35.1g/100 ml)는 용액 내 이온상태로 존재하므로 화학 반응에 이용하기 용이하다. 이를 간수 내 Mg²⁺ 이온의 농도를 증가시키기 위한 목적으로 사용할 수 있다.

백운석 내 Ca²⁺ 제거 후 고순도의 MgSO₄ 용액을 얻기 위해 H₂SO₄의 농도, 백운석과 H₂SO₄의 mol 비, 반응시간을 변화하여 3 가지 실험을 진행하였다. Table 4는 H₂SO₄의 농도를 조절하여 얻은 MgSO₄ 용액의 ICP 결과이다. H₂SO₄의 농도에 따른 Mg²⁺ 이온 양과 불순물의 양을 확인하기 위해 해당 실험을 진행하였다. 1 M MgSO₄를 얻기 위해 백운석: H₂SO₄을 1:2로, 24 hr 동안 반응시키고 필터를 이용하여 CaSO₄를 제거하였다. H₂SO₄의 농도가 증가하면 모든 원소의 추출량이 증가하는 것을 확인할 수 있었다. 이는 충분한 SO₄²⁻ 이온이 Ca²⁺ 이온과 침전을 이루기 때문이다. 1 % H₂SO₄을 사용하는 경우, 분석한 전 원소에서 가장 낮은 원소 함량을 보였다. 이는 부족한 H₂SO₄이 백운석과 반응하지 않아 추출이 되지 않았고, 이는 충분한 H₂SO₄이 필요함을 보여준다.

또한 1 % H₂SO₄에 비해 5 % H₂SO₄을 사용하는 경우 Ca, Si 등의 농도가 증가함을 확인할 수 있다. 이는 H₂SO₄의 양의 증가에 의해 백운석에 포함된 Ca, Si 등이 더욱 추출된 것으로 추정되며, 특히 Mg²⁺의 경우 다른 농도 샘플에 비해 약 1/3로 추출 효율이 크게 떨어지는 것을 관찰할 수 있었다. 5 %와 10 % H₂SO₄을 사용한 경우를 보면 두 농도에서 Mg²⁺ 추출량은 비슷하나(3288 ppm, 3357 ppm) 10 % 농도를 사용한 경우 Ca와 Si를 비롯한 불순물의 추출이 소폭 증가함을 확인할 수 있었다. 그 결과, Mg/불순물 비율(Mg/Ca, Mg/Si)이 5 %에서 가장 높았다. 이는 H₂SO₄의 농도가 높아지면서 CaSO₄의 용해도가 상승하기 때문이다[11], 따라서 Mg²⁺이온을 보충하기 위한 목적으로 5 % H₂SO₄ 사용이 적합함을 확인할 수 있었다. 또한, 두 농도에서 황(S) 농도의 큰 차이는 5 % H₂SO₄만으로도 백운석 내 Ca²⁺ 제거에는 충분하다는 것을 뒷받침한다.

3.4 H₂SO₄과 백운석의 몰 비율 변화에 따른 MgSO₄용액 추출

반응식 (5)는 백운석으로부터 MgSO₄를 추출하고 Ca²⁺ 이온을 제거하기 위한 화학반응식이다.



이론적으로는 백운석과 H₂SO₄이 1:2의 비율로 반응한다. 그러

나 백운석 내 불순물과 기타 환경적, 실험적 요인으로 인해 실제 반응비와는 차이가 존재한다. 따라서 H₂SO₄의 양을 조절하는 방식으로 백운석과 H₂SO₄의 비율을 변화시켜 MgSO₄용액 내 Mg²⁺이온 양을 확인하였다. Table 5은 백운석과 H₂SO₄의 몰 비율을 조절하여 얻은 MgSO₄ 용액의 ICP 결과이다. 백운석에 5 % H₂SO₄을 첨가하여 24 hr 동안 반응시켰다. CaSO₄는 필터를 이용하여 제거하였다. H₂SO₄을 과량 첨가한 경우(백운석과 H₂SO₄의 비율 1:4) 가장 낮은 농도의 Mg과 가장 높은 농도의 Ca과 Si 농도를 보였다. H₂SO₄양을 고정하고 백운석의 양을 5 g에서 10 g으로 늘렸을 때(백운석: H₂SO₄의 비율이 1:4에서 1:2로 변화할 때), MgSO₄내 Mg²⁺의 농도도 2배가량 증가하는 것을 보아 해당 MgSO₄ 용액은 Mg²⁺포화상태임을 확인할 수 있다. 백운석과 H₂SO₄의 비율이 1:4 일 때 낮은 Mg²⁺ 이온 대비 높은 금속 불순물 비를 얻었다. 백운석의 양이 10 g에서 15 g으로 증가한 경우, 추출된 Mg²⁺ 이온의 농도는 오히려 감소하였으며, Ca, Si, S의 농도는 증가함을 확인하였다. 이는 백운석과 H₂SO₄의 비율이 1:1.3인 경우는 해당 양의 백운석으로부터 Mg²⁺ 성분을 최대한으로 추출하기에는 황산 이온의 농도가 부족하다고 해석할 수 있다. 또한, 반응에 사용된 백운석 양의 증가 대비 Ca 농도는 소폭 증가한 것을 보아 Ca²⁺ 이온 제거에도 충분하지 않았다고 할 수 있다. 그 결과 Mg 대비 금속 불순물의 비율(Mg/Ca, Mg/Si)은 감소하였다. 따라서 백운석과 H₂SO₄의 비율이 1:2가 되도록 반응시키는 것이 Ca²⁺을 비롯한 불순물 함량을 최소화하는 최적의 MgSO₄ 용액 추출 반응 비율이라고 여겨진다.

3.5 H₂SO₄과 백운석의 반응시간에 따른 MgSO₄용액 추출

H₂SO₄ 용액이 들어있는 비커에 백운석 분말을 넣어 교반을 진행하였다. 일반적으로 반응시간이 길어질수록 생성물로의 전환율은 증가하나, 반응시간의 증가는 생산성 저하로 이어진다. 따라서 pH와 ICP를 통한 원소 농도분석을 통해 MgSO₄용액 추출에 필요한 최적의 반응(교반)시간을 도출하고자 한다. Fig. 2는 H₂SO₄과 백운석의 교반 시간에 따른 pH 변화 그래프이다. MgSO₄와 CaSO₄는 약 염기성을 띠므로 반응하면서 pH가 증가하는 것을 확인할 수 있었다. 반응시간이 증가함에 따라 pH는 1시간에서 1시간 30분까지 급격히 증가하였고, 4시간 이후 pH는 7.1로 일정하게 유지되며, 이는 중성영역 범위에 해당한다. 따라서 MgSO₄ 용액은 중

Table 5. ICP-OES data for MgSO₄ by different molar ratios of sulfuric acid and dolomite

Sample (Dolomite:H ₂ SO ₄)	Component (ppm)				Ratio (%)	
	Mg	Ca	Si	S	Mg/Si	Mg/Ca
1:4	3288	651.2	8.6	12110	382.3	5.05
1:2	6825	468.2	1.0	8039	6825	14.57
1:1.3	6246	514.9	1.7	8814	3674	12.13

성을 띠며, 4시간 교반 시 대부분의 반응이 진행된 것을 확인할 수 있다. Table 6은 교반 시간을 조절하여 얻은 MgSO₄ 용액의 ICP 결과이다. 반응 결과 생성된 CaSO₄는 필터를 이용하여 제거하였다. 반응시간이 2시간에서 24시간으로 증가함에 따라 Si 농도가 증가하였다. 이외의 원소의 경우 교반 2시간 이후 추출된 원소의 농도에 큰 차이가 없다고 판단하였다. Mg/Si 비를 고려하면 2시간 반응하는 것이 최적의 반응시간이나 백운석 내 Si 함량보다 Ca²⁺의 함량이 훨씬 높아 Mg²⁺의 선택도를 떨어뜨리는 가장 큰 방해 요인이므로, Mg/Ca의 비율이 가장 높고, 반응시간에 따른 경제성을 고려한 4시간이 최적의 반응 시간이라고 판단된다. 반응교반 시간에 따른 생성물의 XRD 분석 결과를 Fig. 3에 나타내었다. 교반 시간이 2시간일 경우 아직 백운석(JCPDS 83-1530)이 용해되지 않아 남아있는 것을 XRD peak를 통해 확인할 수 있다. 교반 시간이 4시간 이상부터 백운석의 XRD peak가 사라지고 CaSO₄(JCPDS 37-1496) peak만 존재하는 것을 보아 백운석이 완전히 분해된 것을 확인하였다. 그러나 교반 시간이 증가할수록 불순물 함량이 증가하기 시작하였다. 다양한 실험 변수들을 고려하였을 때 백운석과

H₂SO₄을 4시간 교반 하는 경우가 최적의 MgSO₄ 용액을 추출하는 조건이라고 판단된다.

3.6 MgSO₄을 이용한 간수 내 Ca²⁺ 정제

간수 내 Ca²⁺ 이온을 제거하기 위해 물에 대한 CaSO₄과 MgSO₄의 용해도 차이를 이용하고자 한다. CaSO₄ (0.255/100 ml)에 비해 높은 MgSO₄(35.1g/100 ml)의 용해도는 Ca²⁺ 이온은 CaSO₄고체로 침전되고, Mg 성분은 용액 내 이온 상태로 존재하게 하여 Mg²⁺과

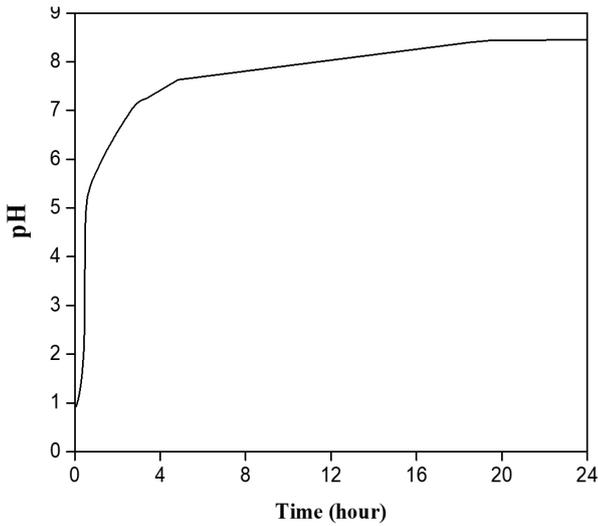


Fig. 2. The pH data of MgSO₄ according to stirring times of sulfuric acid and dolomite.

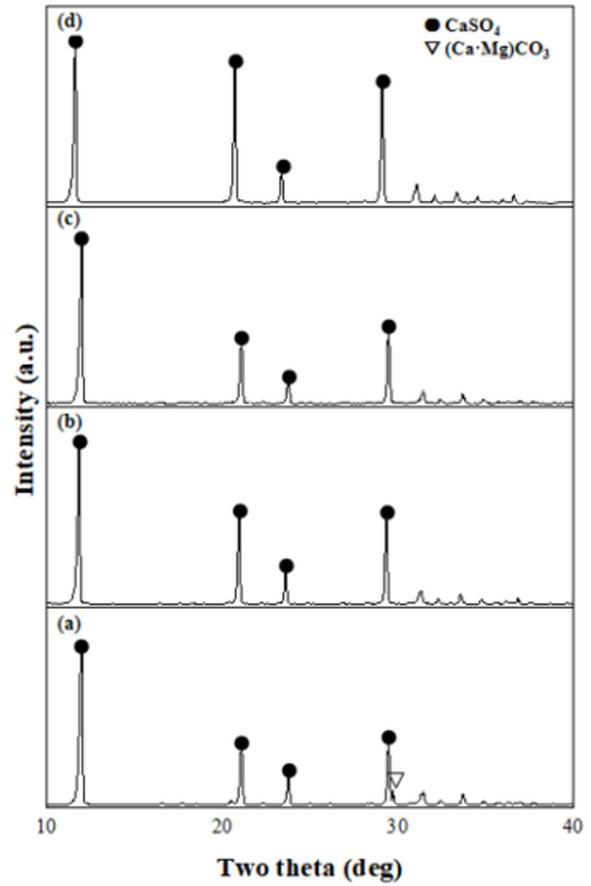


Fig. 3. XRD pattern of precipitate after dolomite and sulfuric acid reaction according to stirring time: (a) 2hr, (b) 4hr, (c) 6hr, (d) 24hr.

Table 6. ICP-OES data for MgSO₄ by different stirring times of sulfuric acid and dolomite

Sample (time)	Component (ppm)				Ratio (%)	
	Mg	Ca	Si	S	Mg/Si	Mg/Ca
2 h	7419	483.3	1.7	8762	4364.1	15.4
4 h	7956	434.6	52.3	9421	152.1	18.3
6 h	6571	571.7	122.8	10070	53.5	11.5
24 h	7326	533.7	160.1	9244	45.8	13.7

Ca²⁺ 이온의 효율적인 분리가 가능하게 한다. MgSO₄을 간수의 황산 이온의 공급원으로 사용하는 경우 Mg(OH)₂ 전구체인 간수 내 Mg²⁺ 함량을 높이는 동시에 Ca²⁺ 함량을 줄일 수 있다. 또한 중성에 해당하는 MgSO₄의 pH는 후속공정에서의 pH조절을 통한 Mg(OH)₂ 생성 시 불필요한 염기성 침전제 사용량을 줄일 수 있다. 위와 같은 이유로 (6)과 같이 간수에 H₂SO₄을 가하지 않고 (7)과 같이 간수에 MgSO₄용액을 가하여 간수 내 Ca²⁺을 정제하고자 하였다.



Table 7은 Ca²⁺을 정제한 간수(디칼슘 간수)와 Ca²⁺을 정제하지 않은 간수의 ICP 결과이다. MgSO₄ 용액은 5 %의 H₂SO₄용액을 사용하였으며, 백운석과 H₂SO₄의 몰비율이 1:2가 되도록 4시간동안 교반 반응 시켜 제조 하였다. 이후 제조한 MgSO₄를 간수와 반응시켜 생성된 CaSO₄를 분리하여 디칼슘 간수를 제조하였다. 실험 결과 Mg²⁺이온은 4.63에서 5.65로 증가한 반면, Ca²⁺이온은 1.71에서 0.03으로 급격히 감소하였다.

3.7 Ca²⁺이 정제된 간수에 염기성 침전제를 첨가하여 Mg(OH)₂ 제조

디칼슘 간수에 염기성 침전제를 첨가하면 염기성 물질 내의 OH⁻이온이 간수 내의 Mg²⁺이온과 결합하여 Mg(OH)₂의 형태로 침전된다. Mg(OH)₂는 50°C 이하에서 pH가 10.5~11.5 사이일 때 침전이 잘 일어나는 것을 확인할 수 있다[12]. 고순도의 Mg(OH)₂를 제조하기 위해서는 용액의 pH가 9.5~12.5 범위 내에서 합성해야 한다[7]. 분말 평가를 위해 디칼슘 간수와 염기성 침전제(NaOH와 NH₄OH)의 반응 비를 1:2로 하여 Mg(OH)₂를 합성하였다(8-1, 8-2).

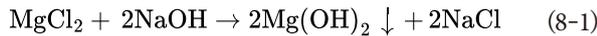


Table 7. ICP-OES data of decalcium bittern and bittern

Sample	Component (wt %)		
	Mg	Ca	SO ₄
Bittern	4.63	1.71	0.0056
Decalcium bittern	5.65	0.03	1.32

Table 8. ICP-OES data of Mg(OH)₂ synthesized using NH₄OH, NaOH

Sample	pH	Component (wt %)							
		Mg(OH) ₂	CaO	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	K ₂ O	Na ₂ O	SO ₂
2M NH ₄ OH	11	99.1	-	0.2	0.2	-	0.1	-	0.7
2M NaOH	13.8	96.0	3.8	-	0.1	-	-	0.1	-

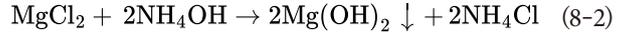


Table 8는 디칼슘 간수와 NH₄OH를 이용하여 합성한 Mg(OH)₂의 ICP 결과이다. 염기성 침전제로 NaOH를 첨가한 샘플의 용액 pH는 13.8, NH₄OH를 첨가한 샘플의 pH는 11로 측정되었다. 간수에 녹아 있는 중탄산 이온과 백운석, H₂SO₄ 반응 후 분해된 CO₂가 물속에 녹아 잔존 Ca²⁺이온이 Ca(HCO₃)₂로 존재한다. 간수에 NaOH를 가하는 경우 용액 pH는 13.8로 Ca²⁺ 이온이 CaCO₃로 침전된다(9).



따라서 간수에 NaOH를 가하는 경우 탄산칼슘(CaCO₃)등의 Ca²⁺가 포함된 불순물 또한 같이 침전되어 96 %의 낮은 Mg(OH)₂ 순도를 보인다. 그러나 NH₄OH를 이용하여 합성한 경우, 99.1 %의 고순도 Mg(OH)₂가 합성된 것을 확인할 수 있다. 이러한 실험 결과는 Fig. 4의 XRD 결과에서도 잘 드러난다. NaOH를 이용하여 합성한 경우 CaCO₃(JCPDS 05-0586)의 peak가 관찰된 반면, NH₄OH를 이용하여 합성한 경우에는 XRD 분석 결과 Mg(OH)₂ (JCPDS 44-1482) peak만이 존재함을 확인할 수 있었다. 따라서 간수를 이용한 Mg(OH)₂ 제조 과정에서 염기성 침전제로 약염기인 NH₄OH를 사용하여 pH를 11이하로 유지하고, Ca(OH)₂ 생성을 억제하고 고순도 Mg(OH)₂를 얻을 수 있다.

4. Conclusion

국내 자원인 백운석과 간수를 이용해 50 nm 급 Mg(OH)₂를 합성을 진행하였다. 본 연구에 사용되는 백운석과 간수에는 Ca²⁺ 이온이 공통으로 다량 존재하며, 효율적인 Ca²⁺ 이온을 제거하기 위해 H₂SO₄을 활용해 CaSO₄를 침전시킬 수 있다. 백운석에 H₂SO₄을 가해 Ca²⁺이 제거된 고순도 MgSO₄ 용액을 제조하였다. 이는 CaSO₄와 MgSO₄의 물에 대한 용해도 차이를 이용한 방법으로 고순도의 MgSO₄ 용액은 5 %의 H₂SO₄을 이용하여 백운석과 H₂SO₄의 반응비가 1:2 일 때 얻을 수 있었다. MgSO₄ 용액의 pH는 반응 시간 4시간 이후부터 pH가 7.1로 일정하게 유지되며, Mg, Ca 및 S 이온의 양은 반응 시간에 큰 영향을 받지 않는 것을 확인하였다.

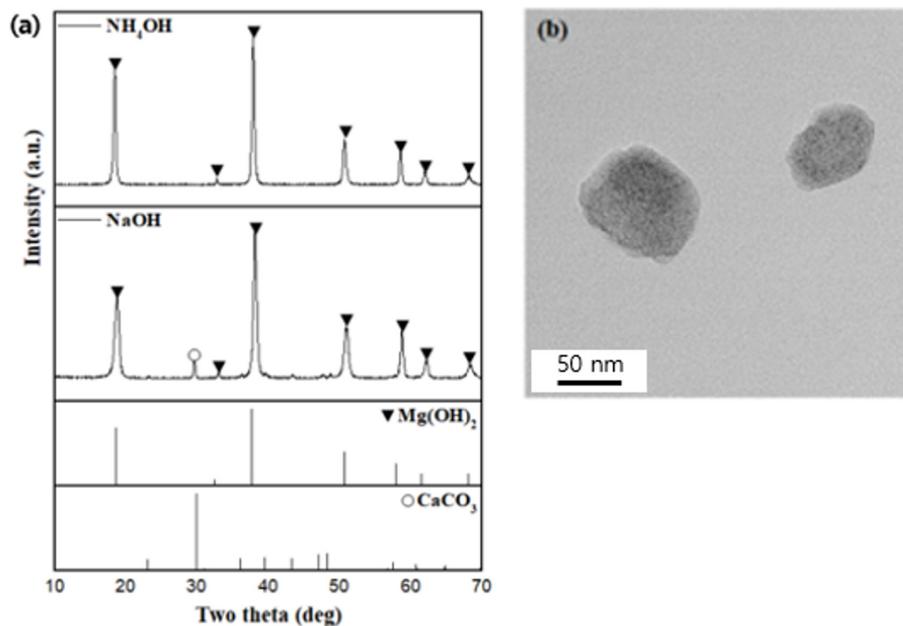


Fig. 4. XRD pattern and TEM image of $\text{Mg}(\text{OH})_2$ by basic catalyst.

Ca^{2+} 이온이 제거된 MgSO_4 는 간수의 Ca^{2+} 를 제거하는데 사용되며, 간수에 MgSO_4 를 첨가하는 경우 Ca^{2+} 제거와 간수 속 Mg^{2+} 농도가 증가하며, 후속공정에서의 pH 조절을 위한 염기성 침전제의 양을 줄일 수 있다. 앞선 실험을 통해 최적의 MgSO_4 용액 추출 조건을 바탕으로 제조한 MgSO_4 용액을 이용하여 간수 내 Ca^{2+} 이온을 CaSO_4 형태로 제거하였다. 그 결과 Ca^{2+} 이온은 약 98 % 제거되었으며, 마지막으로 간수에서 Ca^{2+} 이온을 제거한 MgCl_2 용액에 염기성 침전제를 가해 육각판상형태의 $\text{Mg}(\text{OH})_2$ (크기 약 50 nm)을 얻었다. 고순도의 $\text{Mg}(\text{OH})_2$ 가 합성되는 pH 조건은 MgCl_2 용액에 염기성 침전제를 첨가하여 확인하였다. 약염기인 NH_4OH 를 이용하였을 때 pH가 11로 순도 99.1 %의 $\text{Mg}(\text{OH})_2$ 를 얻을 수 있었다. 국내 자원인 백운석, 간수에서 Ca^{2+} 이온의 효율적 제거를 통해 고순도 육각판상 형태의 $\text{Mg}(\text{OH})_2$ 을 얻었다.

Funding

This work was supported by a grant from “A pilot project for domestic production of magnesium based ceramic raw material” (20016812) funded by the Ministry of Trade, Industry and Energy (MOTIE), Republic of Korea.

Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

All dataset files used in this study can be available on request.

Author Information and Contribution

HyunSeung Shim: researcher; validation, writing–review & editing. Jiyeon Kim: researcher; Investigation, writing–original & draft. Areum Choi: Master’s degree student; Investigation, Data curation. Nuri Oh: professor; supervision. YooJin Kim: chief researcher; writing–original draft, funding acquisition, project administration, supervision.

Acknowledgments

None.

References

- [1] H. Gui, X. Zhang, W. Dong, Q. Wang, J. Gao, Z. Song, J. Lai, Y. Liu, F. Huang and J. Qiao: *Polymer*, **48** (2007) 2537.
- [2] A. S. Bhatti, D. Dollimore and A. Dyer: *Clay Miner.*, **19** (1984) 865.
- [3] L. Qiu, R. Xie, P. Ding and B. Qu: *Compos. Struct.*, **62**

- (2003) 391.
- [4] J. Chen, L. Lin, Y Song and L Shao: *J. Cryst. Growth*, **311** (2009) 2405.
- [5] N. Um and T. Hirato: *Hydrometallurgy*, **146** (2014) 142.
- [6] J. Jakić, M. Labor and V. Martinac: *J. Chem. Biochem. Eng. Q*, **30** (2016) 373.
- [7] T. Y. Cho and M. J. Kim: *J. of Korean Inst. of Resources Recycling*, **25** (2016) 32.
- [8] J. Shukla, V. P. Mohandas and A. Kimar: *J. Chem. Eng.*, **53** (2008) 2797.
- [9] Y. Zhang, Z. Yang, D. Guo, H. Geng and C. Dong: *Procedia Environ. Sci.*, **18** (2013) 84.
- [10] Y. H. Yu, D. J. Hwang, Y. J. Ahn, K. H. Cho, J. W. Ahn and J. S. Choi: *J. Korean Soc. Miner. Energy Resour. Eng.*, **58** (2021) 107.
- [11] G. Azimi, V.G. Papangelakis, J.E. Dutrizac : *Fluid Phase Equilib.*, **260** (2007) 300.
- [12] J. C. Yu, A. Xu, L. Zhang, R. Song and L. Wu: *J. Phys. Chem.*, **108** (2004) 64.

Laser Powder Bed Fusion 공정으로 제조된 Hastelloy X 합금의 인장 특성에 미치는 적층 방향의 영향

윤성준^{1,2}, 노구원³, 손석수², 나영상^{1,*}, 김영균^{1,*}¹한국재료연구원, 극한재료연구소²고려대학교 미래융합소재학과³(주)이엠엘

Effect of Building Orientation on Tensile Properties of Hastelloy X alloy Manufactured by Laser Powder Bed Fusion

Seong-June Youn^{1,2}, GooWon Noh³, Seok Su Sohn², Young-Sang Na^{1,*}, Young-Kyun Kim^{1,*}¹Korea Institute of Materials Science (KIMS), Changwon 51508, Republic of Korea²Department of Advanced Future Convergence Materials, Korea University, Seoul 02841, Republic of Korea³EML Co., Ltd., Suwon 16229, Republic of Korea

In this study, the effect of build orientation on the mechanical properties of Hastelloy X fabricated by laser powder bed fusion (LPBF) process was investigated. Initial microstructural analysis revealed an equiaxed grain structure with random crystallographic orientation and annealing twins. Intra-granular precipitates identified as Cr-rich $M_{23}C_6$ and Mo-rich M_6C carbides were observed, along with a dense dislocation network and localized dislocation accumulation around the carbides. Mechanical testing showed negligible variation in yield strength with respect to build orientation; however, both ultimate tensile strength and elongation exhibited a clear increasing trend with higher build angles. Notably, the specimen built at 90° exhibited approximately 22% higher tensile strength and more than twice the elongation compared to the 0° specimen.

Keywords: Laser powder bed fusion; Ni-based alloy; Hastelloy X; Microstructure; Mechanical properties

Received: April 3, 2025

Revised: April 20, 2025

Accepted: April 21, 2025

***Corresponding author:**

Young-Sang Na

E-mail: nys1664@kims.re.kr

Young-Kyun Kim

TEL: +82-55-280-3514

E-mail: ykkim@kims.re.kr

1. Introduction

Hastelloy X (HX)는 고용 강화형 Ni 기반 초합금으로, 우수한 강도-연성 조합과 산화 및 부식 저항성을 갖고 있다[1-3]. 이러한 특성으로 인해 HX는 가스터빈, 항공기 엔진 연소실 구성품, 가스 냉각 원자로 부품 등 다양한 산업 분야에서 널리 활용되고 있다[4-6]. 그러나 고성능·경량화된 HX 부품을 제작하기 위해서는 복잡한 형상이 요구되며 기존의 가공 방식으로는 이러한 형상을 구현하는

데 한계가 있다[7, 8]. 이러한 한계를 극복하기 위해 다양한 방안이 제시되고 있으며, 그 중에서도 복잡한 형상을 정밀하게 구현할 수 있는 적층 제조(additive manufacturing, AM) 공정이 HX의 차세대 제조 공정으로 주목받고 있다[9-11].

AM 공정은 3차원 CAD (Computer-Aided Design) 모델을 기반으로 복잡한 형태의 근사정형 부품을 제조하는 기술이다[12, 13]. 복잡한 형상을 제어하기 위해서 후가공이 요구되는 주요 공정과 달리 AM 공정은 뛰어난 기하학적 자유도를 제공할 수 있다[14, 15]. 이러한 AM 공정들 중 laser powder bed fusion (LPBF) 공정은 금속 및 합금에 가장 널리 상용화된 기술로, 높은 치수 정밀도와 균일한 미세조직 제어가 가능해 산업적으로 많이 활용되고 있

<https://doi.org/10.4150/jpm.2025.00080>

© 2025 The Korean Powder Metallurgy & Materials Institute

다[16]. LPBF 공정은 층별로 적층되는 공정 특성 상 방향성을 가진 미세조직이 형성되며, 이로 인해 재료의 기계적 특성이 방향에 따라 달라지는 이방성이 발생한다[17, 18]. 이런 이방성 거동은 대부분의 AM 금속 및 합금에서 공통적으로 관찰되며, 특히 적층 방향 (Build Direction, BD)은 LPBF로 제조된 재료에서 기계적 특성에 큰 영향을 미치는 중요한 인자로 작용한다[19, 20]. 현재까지 LPBF 공정 변수 최적화를 통해 HX 합금 제조 조건을 개선하려는 다양한 연구가 수행되어 왔다[9, 10, 13, 21, 22]. 그러나 적층 방향에 따른 기계적 특성 변화에 관한 연구는 대부분 수직 및 수평 방향의 비교에 한정되어 있으며 다양한 적층 방향에 따른 분석은 부족한 실정이다[23, 24].

본 연구에서는 LPBF 공정의 적층 제조 방향을 0°, 45°, 60°, 90°로 제어하여 HX 합금을 제조하고 각 방향에 대한 상온 인장 특성을 조사하였다. 이와 함께 LPBF 공정으로 제조된 HX 합금의 기계적 성능에 적층 방향이 미치는 영향을 고찰하였다.

2. Experimental Section

LPBF 공정으로 Hastelloy X (HX)를 제조하기 위해 EML사의 분말을 이용했으며, 공정 조건은 다음과 같다: Laser power: 370W, scan speed: 950 mm/s, Hatch spacing: 110 μm 및 Layer thickness: 30 μm. LPBF 공정에서 체적 에너지 밀도(Volumetric Energy Density, VED)는 공정 안정성과 미세조직 형성에 중요한 인자로 간주되며 다음 식 (1)으로 정의된다[19]:

$$VED = \frac{P}{v \cdot h \cdot t} \tag{1}$$

여기서, P 는 laser power, v 는 scan speed, h 는 hatching spacing,

t 는 layer thickness를 의미한다. 본 연구에서 적용된 체적 에너지 밀도는 118.0 J/mm³으로 계산되었다. 시편 형상은 ASTM E8 규격의 판상 시편 형태로 제조하였다(LPBF-built HX). 추가적으로 LPBF-built HX의 기계적 특성에 미치는 적층 방향의 영향을 알아보기 위해 적층 방향의 각도를 제어하여 시편을 제조하였다. 각도는 0°, 45°, 60° 및 90°로 각각 제어되었으며, 0°는 시편이 빌드 플레이트에 대해 수평으로, 90°는 수직으로 제조된 경우를 의미한다.

초기 미세조직 관찰을 위해 SiC papers (#100~2000) 및 1 μm diamond suspension을 이용하여 기계적 연마하였다. 이후 전계 방출형 주사전자현미경(field emission scanning electron microscopy, FE-SEM, MYRA 3 XMH, Tescan, Czech) 및 전자 채널링 콘트라스트 이미지 기법(electron channeling contrast image, ECCI, voltage of 30 kV with a BSE detector, working distance of 7 mm), 에너지 분산 분광기(energy dispersive spectrometer, EDS, ultim max, oxford, United Kingdom) 및 전자 후방 산란 회절(electron backscatter diffraction, EBSD, Nordlys CMOS detector, Oxford, United Kingdom)을 이용하여 미세조직을 관찰하고 분석하였다. EBSD 분석의 경우, 저배율 조건에서는 2 μm의 step size를, 고배율 조건에서는 약 180 nm의 step size를 적용하였다.

상온 인장 특성은 만능재료시험기(universal testing machine, Instron-5982, Instron, USA)를 활용하여 평가되었다. 이때, 초기 변형률 속도는 10⁻³/s로 설정했으며, 각 소재 별로 3회 반복하여 시험을 진행하여 신뢰성을 확보하였다.

3. Results and Discussion

그림 1은 LPBF 공정으로 제조된 HX의 적층 방향에 대해 90°로 회전된 시편의 미세조직을 EBSD로 분석한 결과이다. 일반적인 주

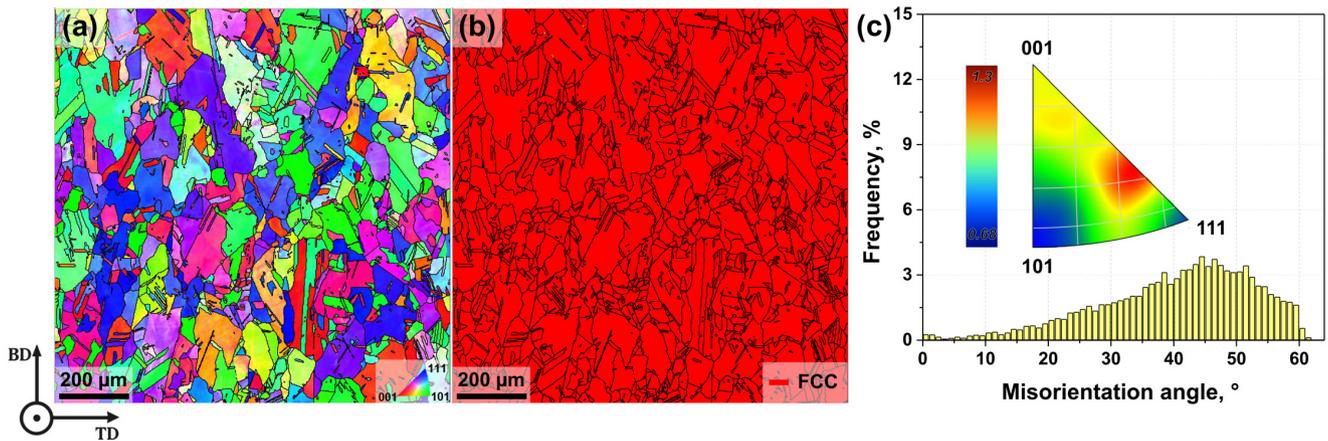


Fig. 1. EBSD analysis results of LPBF-built HX: (a) inverse pole figure map, (b) phase map, (c) misorientation distribution map.

조공정으로 제조된 wrought HX는 polygonal 결정립이 주로 형성되는 것으로 알려져 있다[22]. 이와 달리, LPBF-built HX의 결정립은 IPF map (그림 1(a))을 통해 불규칙한 형상과 함께 고온에서 결정립계 미끌림을 방지함으로써 고온 물성을 향상시키는 것으로 알려진 톱니 모양의 결정립계(serrated grain boundary) 역시 확인되었다[25]. 또한 다량의 어닐링 쌍정(annealing twin)이 관찰되었다. 이때, 평균 결정립의 크기는 80.2 μm 로 측정되었다. Phase map (그림 1(b))에서는 조대한 석출상이 확인되지 않았으며, FCC 단상을 가지는 것으로 나타났다. 추가적으로 misorientation distribution map (그림 1(c))을 통해서도 결정립은 특정 방향으로 집합조직을 형성하지 않은 무작위적인 결정 배향을 보이는 것으로 확인되었다. 일반적으로 LPBF 공정으로 제조된 금속 및 합금 소재는 공정 중 반복되는 용융 및 응고 과정에 의해 결정립이 적층 방향을 따라 성장하며 epitaxial grain growth 형태의 미세조직을 형성하고 특정 방향성을 갖는 집합조직을 나타내는 것으로 알려져 있다 [26, 27]. Liu 등[28]은 적층 제조 공정 조건에 따라 재료의 결정립 형태를 조절할 수 있다고 보고하였다. 특히, LPBF 공정에서 에너지 밀도가 감소할 경우 epitaxial 성장이 충분히 이루어지지 않아 columnar 결정립의 중첩비가 낮아지고, 결과적으로 불규칙한 형태의 결정립이 나타나는 경향을 보인다[29]. 또한, 높은 에너지 밀도에서는 적층 방향을 따라 FCC 구조를 갖는 재료의 경우 $\langle 001 \rangle$ 집합조직이 형성되는 반면, 에너지 밀도가 낮아지면 $\langle 100 \rangle + \langle 110 \rangle$ 또는 $\langle 101 \rangle + \langle 111 \rangle$ 방향의 무작위적인 결정 배향이 관찰된다고 알려져 있다[28]. 따라서, 본 연구에서 사용된 LPBF-built HX는 상대적으로 낮은 에너지 밀도 조건에서 제조되어 불규칙한 형상의 결정립과 무작위 결정 배향을 갖는 것으로 이해될 수 있다.

그림 2는 LPBF-built HX의 초기 미세조직에 대한 고배율 EBSD 분석 결과를 보여준다. 먼저 band contrast image (그림 2(a))를 통해 결정립 내부에 수 백 nm 수준의 석출물이 존재하는

것으로 확인되었다. 이때 석출물은 특정 방향성을 따라 정렬된 형태로 나타났으며, 이러한 석출물의 배열은 적층 제조 공정 중 발생하는 방향성 응고(directional solidification) 및 그에 따른 용질 원소 분리(solute element segregation) 현상에 의해 형성된 것으로 사료된다[30]. IPF map (그림 2(b))에서는 nm 스케일의 annealing twin이 관찰되었으며, annealing twin들은 인접하고 있는 결정립과 특정 방위 관계를 갖는 것으로 나타났다. 추가적으로 GND map (그림 2(c))을 통해 기하학적 필수 전위(geometrically necessary dislocation, GND) 밀도는 소재 전반에 걸쳐 낮은 것으로 분석되었다. 일반적으로 LPBF 공정은 약 $10^3 - 10^8$ K/s의 냉각속도로 인해 제조 공정 중 열응력이 발생해 as-built 상태에서 높은 전위 밀도를 갖는 것으로 알려져 있다[31-33]. Zhang 등[34]은 LPBF 공정으로 제조된 HX 합금에서 에너지 밀도가 감소함에 따라 GND 밀도가 감소하는 경향을 확인하였으며, 이는 에너지 밀도가 증가할수록 더 큰 열응력이 유발되고, 이에 따라 GND 밀도 또한 증가하기 때문이라고 설명하였다. 즉, GND map (그림 2(c))에서 확인할 수 있듯이, LPBF-built HX가 낮은 GND 밀도를 갖는 것은 낮은 에너지 밀도로 인해 발생하는 열응력의 축적이 제한되어, 이에 따라 결정 내 전위의 축적 또한 제한되었기 때문으로 해석될 수 있다.

그림 2(a)에서 관찰된 결정립 내부 석출물을 보다 정밀하게 분석하기 위해 SEM/EDS 분석을 수행하였으며, 그 결과를 그림 3에 제시하였다. SEM 이미지를 통해 해당 석출물은 수백 nm에서 수 μm 에 이르는 크기 분포를 갖는 것으로 나타났으며 어두운 영역(point 1)과 밝은 영역(point 3)으로 구분되었다. EDS mapping을 통해 대부분의 석출물은 기지(matrix) 대비 Cr원소의 함량이 높게 분포하고 있는 것으로 나타났다. 석출상의 정확한 조성을 분석하기 위해 EDS point 분석을 수행하였다. 먼저 어두운 석출물(point 1) 내부의 Cr 및 C 원소 함량은 각각 약 33.3% 및 11.5%으로 분석되었으며 이는 기지의 Cr 및 C 원소 함량보다 높은 수준인 것으로 확

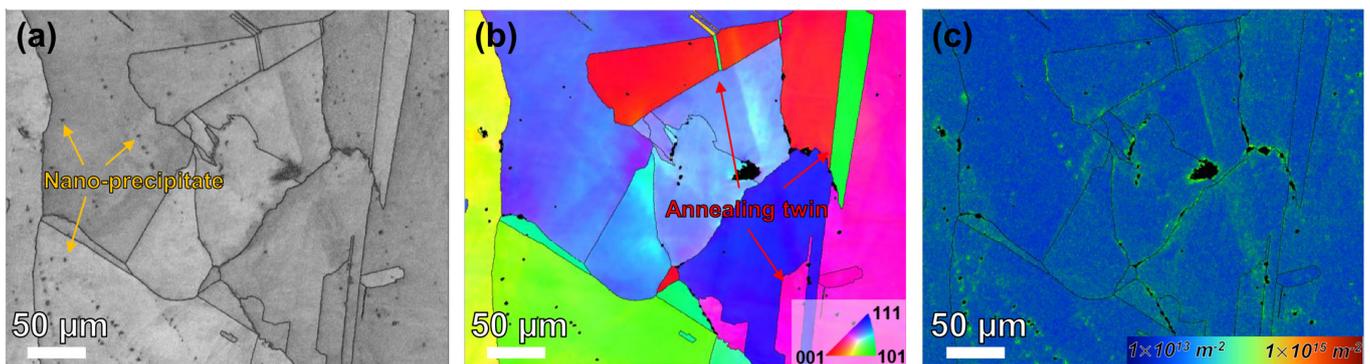


Fig. 2. High resolution EBSD analysis results of LPBF-built HX: (a) band contrast map, (b) inverse pole figure map, (c) geometrically necessary dislocation map.

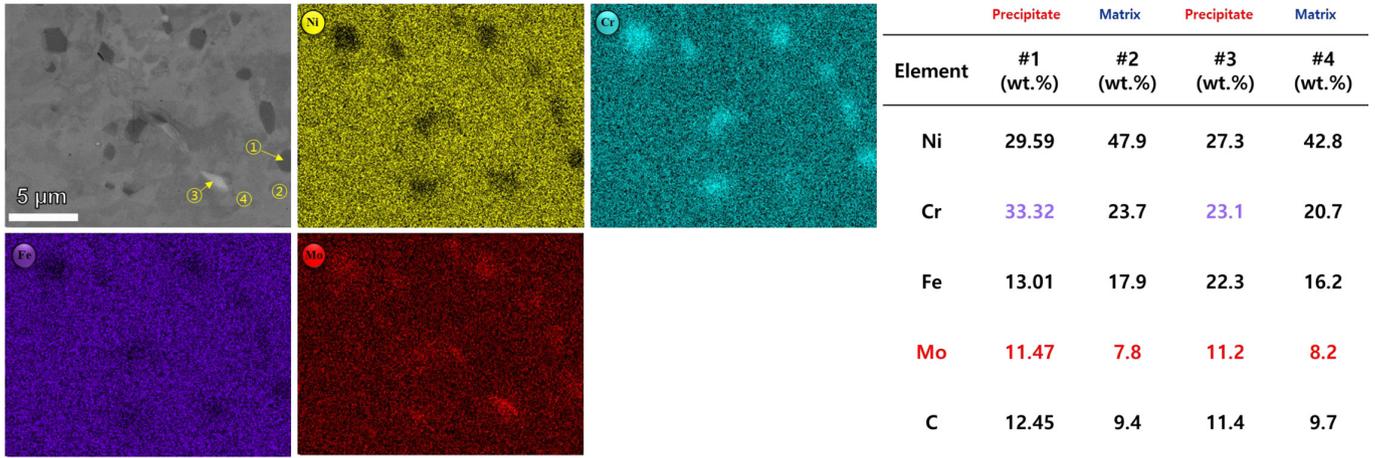


Fig. 3. SEM image and the corresponding energy dispersive X-ray spectroscopy (EDS) mapping results of LPBF-built HX.

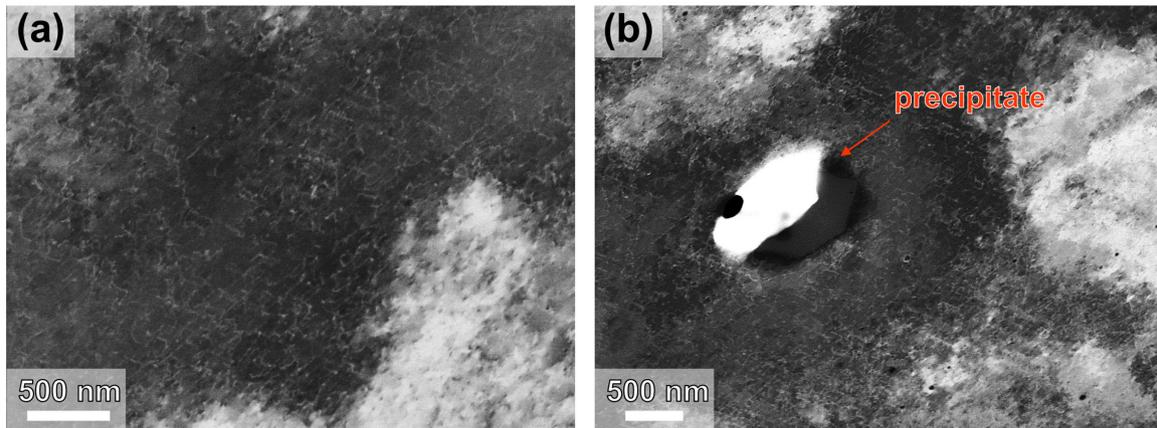


Fig. 4. Electron channeling contrast image of LPBF-built HX: (a) dislocation networks within the grain, (b) dislocation pile-up around a carbide.

인되었다. 이를 통해 해당 석출물은 Cr-rich $M_{23}C_6$ 상으로 추론되었다[35]. 반면, 상대적으로 밝은 석출물(point 3)에는 Mo 원소의 함량이 기지 대비 높은 것으로 분석되었다. 즉, 석출물의 명암 차이는 원소의 구성 차이에 기인하는 것으로 추측되며 상대적으로 밝은 석출물은 Mo-rich M_6C 로 판단되었다[36]. 여기서 LPBF-built HX에서 형성되는 탄화물은 LPBF 공정의 빠른 응고 과정에서 발생하는 원소 분리에 의해 형성된다고 보고된 바 있다[24].

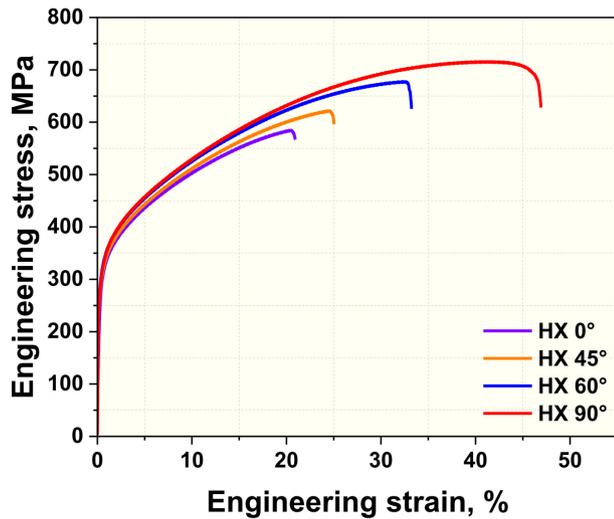
LPBF-built HX의 결정립 내부를 면밀히 분석하기 위해 ECC 이미지 분석을 수행하였다(그림 4). 그림 4(a)에는 결정립 전반에 걸쳐 미세한 전위 네트워크가 형성되어 있는 것이 확인되었다. 이는 앞선 EBSD GND map(그림 2(c))의 경향과는 다소 다른 양상을 보였다. 이러한 차이는 EBSD 기반 GND 분석은 수백 nm 수준의 step size (180 nm)를 이용해 분석된 반면 ECC 이미지는 수십 nm 이하의 미세한 전위 구조까지 시각화가 가능하여 국부적인 전위 농축을

보다 명확히 관찰할 수 있기 때문으로 판단된다. 즉, 낮은 에너지 밀도로 인해 전반적인 GND 밀도는 낮지만, 여전히 급속 응고로 인한 국부적인 열응력 집중으로 인해 결정립 내에 고밀도의 전위를 생성할 수 있으며, 이는 ECC 이미지에서 뚜렷하게 관찰되는 전위 구조의 원인으로 해석될 수 있다. 그림 4(b)에서는 Cr-rich 및 Mo-rich 탄화물 주변에 전위가 집적되는 현상이 뚜렷하게 나타났다. 이는 탄화물이 열응력에 의해 발생한 전위의 이동을 억제함으로써, 그 주변에 전위가 축적되었기 때문으로 사료된다.

그림 5는 LPBF-built HX의 적층 방향(0° , 45° , 60° , 90°)에 따른 상온 인장 시험 결과를 나타낸 것이며, 표 1에는 각 시편의 0.2% offset 항복강도, 최대 인장 강도 및 연신율을 정리하였다. 항복강도는 각각 296 MPa, 287 MPa, 297 MPa 및 298 MPa로 측정되어 적층 방향에 따른 차이는 미미한 수준임을 확인할 수 있었다. 반면, 최대 인장 강도 및 연신율은 적층 각도가 증가함에 따라 뚜렷한 증

Table 1. Tensile properties of LPBF-built HX by build orientation

Specimen	Yield strength [MPa]	Ultimate tensile strength [MPa]	Elongation [%]
0°	296 ± 5	585 ± 8	21.1 ± 1.0
45°	287 ± 6	622 ± 10	26.2 ± 1.2
60°	297 ± 4	678 ± 7	33.3 ± 1.5
90°	298 ± 3	716 ± 6	47.0 ± 2.0

**Fig. 5.** Tensile stress-strain curves of LPBF-built HX tested along different building directions (0°, 45°, 60° and 90°).

가 경향을 보였다. 최대 인장 강도는 0°에서 585 MPa, 90°에서 716 MPa로, 약 22% 향상되었으며, 연신율 또한 각각 21.1%, 26.2%, 33.3% 및 47.0%로 확인되어 90° 시편이 0° 시편 대비 두 배 이상의 연신율을 나타냈다. 선행 연구들에 따르면 적층 제조 공정에서 적층 방향은 합금의 기계적 특성에 유의미한 영향을 미치는 것으로 보고되어 왔다. Ozer 등[23]은 LPBF-built HX 합금에서 적층 방향을 90°로 제어했을 때, 0° 시편 대비 연신율이 현저히 향상된다고 보고하였다. Chen 등[37]은 LPBF 공정으로 제조된 IN-738LC 합금을 대상으로 상온 및 고온 인장 특성을 평가한 결과, 모든 온도 범위에서 90° 시편이 0° 시편 대비 유사하거나 우수한 인장 강도 및 연신율을 보인다고 제시하였다. 즉, LPBF 공정에서 적층 방향은 인장 특성의 방향 의존성을 나타낸다. 일반적으로 LPBF 공정에서 적층 방향을 90°로 설정하면, 0° 시편에 비해 공정 중 열 축적이 더 용이해져 결정립 성장에 유리하고, 전위 밀도도 낮아지는 것으로 알려져 있다[38]. 이러한 미세조직적 특성으로 인해 LPBF-built HX의 90° 시편은 0° 시편보다 연성이 우수하게 나타난다. 결과적으로, 동일한 공정 조건 하에서도 적층 방향을 90°로 제어할 경우 연신율과 인장 강도가 향상되는 경향을 보이며, 이는

LPBF 공정에서 적층 방향 제어를 통해 기계적 성능을 조절할 수 있음을 시사한다.

4. Conclusion

본 연구에서는 LPBF 공정을 통해 제조된 HX의 미세조직을 분석하였으며 기계적 특성에 미치는 적층 방향에 대해 조사하였다. 미세조직 분석 결과 불규칙한 형태의 결정립과 무작위적인 결정 배향이 관찰되었으며 이는 비교적 낮은 에너지 밀도 조건에서 epitaxial 성장이 억제되었기 때문으로 판단된다. 결정립 내부에는 Cr-rich $M_{23}C_6$ 및 Mo-rich M_6C 탄화물이 존재하며 탄화물 주변에 전위가 집중되는 현상이 확인되었다. 이는 급속 응고로 인한 국부적인 열응력 집중과 탄화물의 전위 이동 억제 효과에 기인한 것으로 사료된다. 상온 인장 특성 결과 적층 방향의 각도가 증가함에 따라 최대 인장 강도 및 연신율은 증가하는 경향을 나타냈다.

Funding

This study was supported financially by Fundamental Research Program of the Korea Institute of Materials Science (No. PNKA320); and the Nano Material Technology Development Program (No. RS-2024-00445038) through the National Research Foundation of Korea).

Conflict of Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data Availability Statement

All dataset files used in this study are already provided in the manuscript.

Author Information and Contribution

Seong-June Youn: Ph.D student: writing–original draft
 GooWon Noh: Senior Researcher: Conceptualization, Methodology, Investigation
 Seok Su Sohn: Professor: Methodology, Investigation
 Young-Sang Na: Principal Researcher: Supervision
 Young-Kyun Kim: Senior Researcher: Writing–original draft, Supervision, Conceptualization,

Acknowledgments

None.

References

- [1] S. Zhang, J. Liu, X. Lin, Y. Huang, M. Wang, Y. Zhang, T. Qin and W. Huang: *J. Alloys Compd.*, **878** (2021) 160395.
- [2] W. Zhang, Y. Zhemg, F. Liu, D. Wang, F. Liu, C. Huang, Q. Li, X. Lin and W. Huang: *Mater. Sci. Eng. A*, **820** (2021) 141537.
- [3] A. Malekan, M. Farvizi, S.E. Mirsalehi, N. Saito and K. Nakashima: *J. Manuf. Process.*, **47** (2019) 129.
- [4] S.-H. Jeong, S. H. Kang, C.-H. Han, T.-K. Kim, D.-H. Kim and J. Jang: *J. Powder Meter.*, **18** (2011) 456.
- [5] D. Yoon, I. Heo, J. Kim, S. Chang and S. Chang: *Int. J. Precis. Eng. Manuf. Manuf.*, **20** (2019) 147.
- [6] F. Mevissen and M. Meo: *Mater. Charact.*, **191** (2022) 112099.
- [7] B. Guo, Y. Zhang, F. He, J. Ma, J. Li, Z. Wang, J. Wang, J. Feng, W. Wang and L. Gao: *Mater. Sci. Eng. A*, **823** (2021) 141716.
- [8] C. Li, Y. Liu, T. Shu, W. Guan and S. Wang: *J. Mater. Res. Technol.*, **24** (2023) 1499.
- [9] M. Muhammad, R. Ghiaasiaan, P. R. Gradl, A. Schobel, D. Godfray, S. Shao and N. Shamsaei: *J. Manuf. Process.*, **136** (2025) 123.
- [10] X. Cheng, Z. Du, S. Chu, J. Wu, J. Dong, H. Wang and Z. Ma: *Mater. Charact.*, **186** (2022) 111799.
- [11] B. Guo, Y. Zhang, Z. Yang, D. Cui, F. He, J. Li, Z. Wang, X. Lin and J. Wang: *Addit. Manuf.*, **55** (2022) 102792.
- [12] Y. W. Kim, S. Lee, K. T. Kim, J.-H. Yu, J. G. Kim and J. M. Park: *J. Powder Meter.*, **30** (2023) 140.
- [13] J. Hu, X. Lin and Y. Hu: *Appl. Surf. Sci.*, **648** (2024) 159004.
- [14] D.-H. Yang, Y.-K Kim, Y. Hwang, M.-S. Kim and K.-A. Lee: *J. Powder Mater.*, **26** (2019) 471.
- [15] J.-U. Lee, Y.-K. Kim, S.-M. Seo and K.-A. Lee: *Mater. Sci. Eng. A*, **841** (2022) 143083.
- [16] L. Dowling, J. Kennedy, S. O'Shaughnessy and D. Trimble: *Mater. Des.*, **186** (2020) 108346.
- [17] P. Li, Y. Kim, A. C. Bobel, L. G. Hector Jy, A. K. Sachdev, S. Kumar and A. F. Bower: *Acta Mater.*, **220** (2021) 117346.
- [18] J. Ding, J. Fu, M. Fu and X. Song: *Addit. Manuf.*, **59** (2022) 103082.
- [19] Y.-K. Kim, J. Choe and K.-A. Lee: *J. Alloys Compd.*, **805** (2019) 680.
- [20] M. Ni, C. Chen, X. Wang, P. Wang, R. Li, X. Zhang and K. Zhou: *Mater. Sci. Eng. A*, **701** (2017) 344.
- [21] Q. Han, Y. Gu, S. Soe, F. Lacan and R. Setchi: *Opt. Laser Technol.*, **124** (2020) 105984.
- [22] X. Ni, D. Kong, L. Zhang, C. Dong, J. Song and W. Wu: *J. Mater. Eng. Perform.*, **28** (2019) 5533.
- [23] S. Ozer, M. A. Yalçın, G. M. Bilgin, K. Davut, Z. Esen and A. F. Dericioglu: *J. Alloys Compd.*, **1012** (2025) 178465.
- [24] Y. Sun, H. Zhao, R. Huang, L. Liu, C. Tan, D. Lin, B. Chen, X. Song and R. Ma: *J. Mater. Res. Technol.*, **27** (2023) 703.
- [25] Q. Ren, J. Chen, J. Lu, X. Cheng, Y. Zhang and Z. Zhang: *Mater. Sci. Eng. A*, **900** (2024) 146452.
- [26] X. Zhou, K. Li, D. Zhang, X. Liu, J. Ma, W. Liu and Z. Shen: *J. Alloys Compd.*, **631** (2015) 153.
- [27] T. Niendorf, S. Leuders, A. Riemer, H. A. Richard, T. Tröster and D. Schwarze: *Metall. Mater. Trans. B*, **44** (2013) 794.
- [28] S.Y. Liu, H.Q. Li, C.X. Qin, R. Zong and X.Y. Fang: *Mater. Des.*, **191** (2020) 108642.
- [29] C. Li, Z. Liu, X. Liang, J. Zhao, Y. Cai and B. Wang: *Metals*, **15** (2025) 267.
- [30] S.-H. Sun, Y. Koisumi, T. Saito, K. Yamanaka, Y.-P. Li, Y. Cui and A. Chiba: *Addit. Manuf.*, **23** (2018) 457.
- [31] W. Li, J. Liu, Y. Zhou, S. Wen, Q. Wei, C. Yan and Y. Shi: *Scr. Mater.*, **118** (2016) 13.
- [32] J. Suryawanshi, K. G. Prashanth, S. Scudino, J. Eckert, O. Prakash and U. Ramamury: *Acta Mater.*, **115** (2016) 285.
- [33] T. Vilaro, C. Colin, J. D. Bartout, L. Nazé and M. Sennour: *Mater. Sci. Eng. A*, **534** (2012) 446.

- [34] S. Zhang, Y. Lei, Z. Chen, P. Wei, W. Liu, S. Yao and B. Lu: *Materials*, **14** (2021) 4305.
- [35] Y. Yin, J. Zhang, J. Gao, Z. Zhang, Q. Han and Z. Zan: *Mater. Sci. Eng. A*, **827** (2021) 142076.
- [36] S. Wu, S. B. Dai, M. Heilmaier, H. Z. Peng, G. H. Zhang, S. Huang, X. J. Zhang, Y. Tian, Y. M. Zhu and A. J. Huang: *Mater. Sci. Eng. A*, **875** (2023) 145116.
- [37] J. Chen, J. Xu, J. Moverare and L. A. Barrales-Mora: *Mater. Sci. Eng. A*, **909** (2024) 146756.
- [38] R. S. Thanumoorthy, J. K. Chaurasia, V. A. Kumar, P. I. Pradeep, A. S. S. Balan, B. Rajasekaran, A. Sahu and S. Bontha: *J. Mater. Eng. Perform.*, **33** (2024) 7930.

침상코크스-핏치 탄화블록의 초기 기공률이 함침 후 물성 향상에 미치는 영향

윤우상, 이상혜, 노재승*

금오공과대학교 신소재공학과

Effect of the Initial Porosity of Needle Coke-Pitch Carbonized Blocks on Impregnation-Related Physical Properties

U-Sang Youn, Sang-Hye Lee, Jae-Seung Roh*

School of Materials Science and Engineering, Kumoh National Institute of Technology, Gumi, Gyeongbuk 39177, Republic of Korea

Carbonized blocks with different porosities were prepared by varying the particle size of the filler and subsequent impregnation. The impregnated carbonized blocks were re-carbonized. The use of smaller particles in the filler in the carbonized block was associated with larger porosity, smaller pore size, and a higher impregnation ratio. The block with the smallest average particle size (53 μm), CB-53, had a porosity of 35.9% and pores of approximately 40 μm , while the block with the largest average particle size (413 μm), CB-413, had a porosity of 30.5% and pores of approximately 150 μm . CB-53 had the highest bulk density, electrical resistivity, flexural strength, and impregnation ratio. This is due to the large porosity, which is believed to be due to the presence of more interfaces between particles during the re-carbonization of the impregnated carbonized block, resulting in a better pore-filling effect.

Keywords: Needle Coke; Carbonized Block; Impregnation

Received: February 3, 2025
Revised: February 21, 2025
Accepted: February 25, 2025

***Corresponding author:**
Jae-Seung Roh
E-mail: jsroh@kumoh.ac.kr

1. Introduction

인조흑연블록은 열 및 전기 전도성, 내식성, 내열성, 낮은 열팽창 계수, 높은 기계적 강도 등 특성을 가지고 있다. 인조흑연블록은 이런 특성으로 인해 제철용 전극봉, 단열재, 엔지니어링 재료 등으로 사용된다[1-6]. 2022년 기준 제철용 전극봉의 전 세계 시장 규모는 약 81억 달러로 평가되며 이후 이산화 탄소 배출 감소 정책에 의해 더 크게 성장할 것으로 예상되고 있다[7].

제철용 전극봉의 제조는 원료 분쇄 및 분급, 혼련, 성형, 탄화, 함침, 흑연화 등의 공정으로 제조된다. 충전재는 수 μm 부터 수 cm까지의 입도를 가진 침상 코크스를 혼합하여 사용한다[8]. 탄화 공정 동안 바인더 핏치에 포함된 휘발 물질이 방출되어 내부에 다량의 기공이 생성된다[9]. 생성된 기공은 탄화블록의 밀도, 전기적, 기계

적 물성의 저하를 유발하므로 기공을 채우기 위한 함침 공정이 필요하다[10, 11].

함침 공정은 함침기 챔버 내부를 우선 감압하여 탄화블록 내부 기공에 존재하는 공기 및 불순물을 제거해 함침재가 침투할 공간을 확보하고, 이후 가압을 하여 탄화블록 내부까지 기공에 함침재를 침투시킨다[9, 12]. 함침공정에서 변수로는 함침재의 점도, 표면장력, 함침 시 접촉각, 탄화 수율 등이 있다[13].

Kim et al.은 함침 시 함침 압력이 탄화블록의 기공 크기 변화에 미치는 영향 대해 연구하였다[14]. 함침 압력이 증가할수록 부피밀도 및 함침률이 높아지며 밀도는 최대 2.4% 증가하였고, 기공률은 24.5% 감소한다고 보고하였다. 그리고 Cho et al.은 피치의 점도가 함침 후 물성 향상에 미치는 영향을 연구하였다[15]. 함침 핏치의 점도가 낮을수록 탄화블록 내부로 핏치가 침투가 쉬워 기공률이 최대 7.7% 감소하였다고 보고하였다. 하지만 탄화블록의 기공률을 다르게 하여 제조한 후 함침 전후로 물성 변화를 관찰한 연구는 찾아볼 수 없었다. 상기 보고된 연구결과들을 살펴보면 탄화블록의

<https://doi.org/10.4150/jpm.2025.00038>

© 2025 The Korean Powder Metallurgy & Materials Institute

함침 전후 부피밀도 및 기공률의 변화만 확인하였고 전기적 및 기계적 특성에 대한 분석 및 평가를 진행하지 않았다.

따라서 본 연구팀은 함침 공정의 변수가 아닌 탄화블록의 초기 기공률이 함침물에 미치는 영향과 전기적 및 기계적 특성에 미치는 영향에 대해 확인하고자 하였다. 상용 제철용 전극봉의 직경은 200 ~ 600 mm이지만 연구에 사용되는 성형체 크기가 10 × 10 × 50 mm³ 인 것을 고려하여 충전재의 최소와 최대 입도를 선정하였다. 탄화블록의 기공률은 충전재인 코크스의 입도를 조절하여 제어하였다. 함침 전후 탄화블록의 미세조직 및 물성의 변화를 관찰하여 기공률이 함침 후 물성 향상에 미치는 영향을 확인하고자 하였다.

2. Experimental Procedure

2.1 원료 준비

본 연구에 사용한 충전재는 상업용 침상 코크스이며(POSCO MC Materials社), 결합재와 함침재는 석탄계 핏치(Raincarbon社)를 사용하였다.

침상 코크스는 분쇄 후 5조건의 (-75µm ~ +25 µm, -125 µm ~ +75 µm, -212 µm ~ +125 µm, -300 µm ~ +212µm, -425 µm ~ +300 µm) 입도 범위로 분급을 진행하였다. 분급한 코크스는 입도 분석기(Malvern Ins. GB. MASTERSIZER 3000)를 이용하여 평균 입도와 입도 분포를 확인하였다.

Fig. 1과 Table 1에 입도별 분급한 코크스의 입도 분포 결과를 나타내었다. 입도 분포 분석 결과 각 분급 범위 별 D50은 -75µm ~ +25 µm의 입도 범위에서 53 µm, -125 µm ~ +75 µm 에서 109 µm, -212 µm ~ +125 µm에서 187 µm, -300 µm ~ +212µm에서 329 µm, -425 µm ~ +300 µm 에서 413 µm로 분급되었다. 입도에 따른 CB 및 RCB는 CB-D50와 RCB-D50과 같이 명명하였다.

결합재용 핏치는 연화점 110°C, Quinoline Insoluble(QI) 4~8%, Toluene Insoluble (TI) 22~28%이며, 함침재용 핏치는 연화점 90°C, QI 3%, TI 16%를 사용하였다. 시중에서 판매되는 석탄계 함침 핏치는 연화점 80 ~ 100°C, QI 0 ~ 3%, TI 16 ~ 24%으로 상용으로 판매되는 석탄계 함침 핏치의 특성에 적합하다고 판단하였다. Table 2에 결합재 및 함침재로 사용한 핏치와 상용 함침 핏치의 spec을 나타내었다.

Table 1. Particle size distribution data for coke

Sample name		Sieving range	Coke particle size		
Carbonized block	Re-Carbonized block		D ₁₀ (µm)	D ₅₀ (µm)	D ₉₀ (µm)
CB-53	RCB-53	-75 µm ~ +25 µm	25.8	53.0	94.4
CB-109	RCB-109	-125 µm ~ +75 µm	5.9	109.0	175.0
CB-187	RCB-187	-212 µm ~ +125 µm	25.4	187.0	306.0
CB-329	RCB-329	-300 µm ~ +212 µm	179.0	329.0	527.0
CB-413	RCB-413	-425 µm ~ +300 µm	304.0	413.0	560.0

분급 된 충전재와 결합재는 80 : 20의 무게비율로 준비하여 볼밀링기를 이용하여 100 rpm에서 24 hr 혼합하고, 혼합한 분말은 170°C에서 30 분 혼련하였다.

혼련물은 일축가압법으로 120°C에서 100MPa로 열간 성형하여 10 × 10 × 50 mm³의 green body를 제조하였다. 탄화는 질소 분위기에서 1000°C까지 2°C/min으로 승온 후 60분 유지하였다 [16]. 함침 전후 탄화블록의 물성 변화를 확인하기 위하여 조건 당 5개의 탄화블록을 물성분석에 사용하였다.

2.2 함침 및 재탄화

함침은 함침기 챔버에 함침 핏치와 입도별로 제조한 탄화블록을 장입 후 200°C까지 승온하였다. 이후 5×10⁻³ torr로 60 분 감압하여 챔버 내 공기를 제거하고 5 bar로 60 분 가압하였다. 해당 함침 조건은 우리 연구팀에서 선행 연구로 함침 온도는 150, 200, 250°C로 수행해 함침 온도 200°C에서 부피밀도는 12.5% 향상, 기공률은 26.0% 감소하였다. 선정된 온도에서 가압시간을 30, 60, 90 분으로 수행하여 60분에서 부피밀도는 14.3% 증가, 기공률은 24.0% 감소하여 최적 함침 조건을 함침 온도 200°C, 가압시간 60분으로 선정하였다[17].

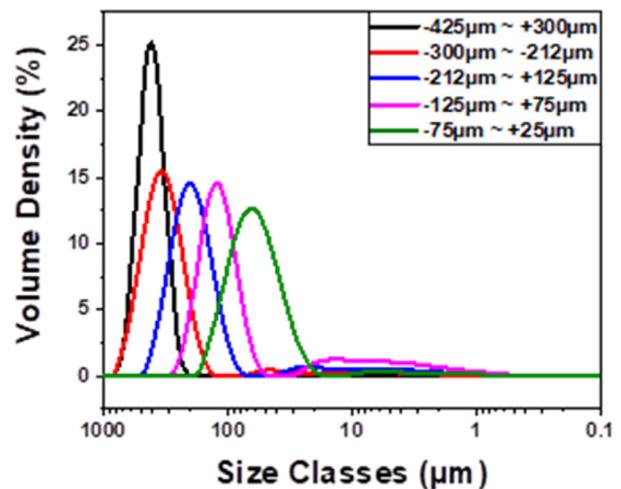


Fig. 1. Particle size distribution of coke.

Table 2. Coal-based binder pitch and impregnation pitch specifications

	Binder pitch	Commercial impregnation pitch	Impregnation pitch
Softening point (°C)	110	80 ~ 100	90
T.I. (wt.%)	22~28	0 ~ 3	16
Q.I. (wt.%)	4~8	16 ~ 24	3
Coking value (wt.%)	54	42 ~ 46	47
Ash (wt.%)	0.3	0.05	0.1

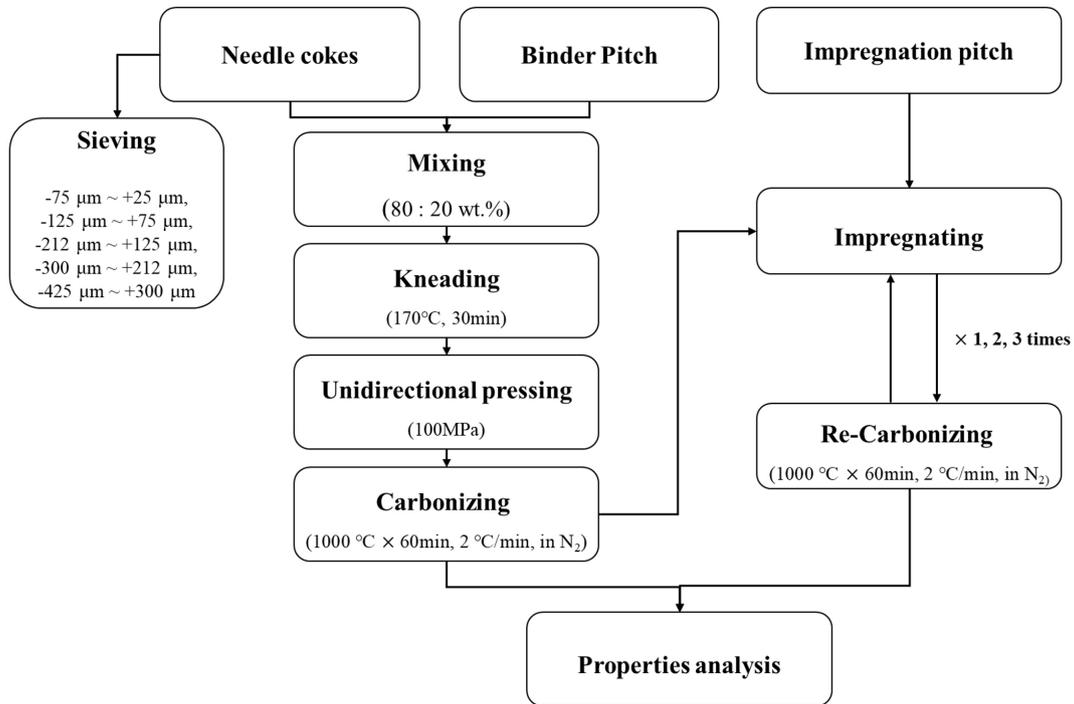


Fig. 2. Experimental Procedure.

함침이 끝난 시편은 탄화와 동일 조건으로 재탄화를 하였다. 탄화 후 성형체는 CB(carbonized blocks), 함침 후 재탄화 한 성형체는 RCB(Re-carbonized blocks)로 명명하였다. CB와 RCB의 열린 기공률을 측정하여 아래 식을 이용해 함침률을 계산하였다[14].

$$\text{Impregnationrate\%} = \frac{\text{OpenPorosityRCB} - \text{OpenPorosityCB}}{\text{OpenPorosityRCB}} \times 100 \quad (1)$$

본 연구의 전체적인 실험 순서는 Fig. 2에 나타내었다.

2.3 부피밀도 및 기공률 측정

CB 및 RCB의 부피밀도와 기공률은 ISO 18754:2020으로 측정하였다[18]. CB와 RCB를 증류수에서 3 시간 끓이고 상온으로 냉각한 뒤 수중 무게를 측정한다. 수중 무게를 측정 후 젖은 천으로 표면

을 닦아 물기를 제거한 뒤 포수 무게를 측정하였다. 이후 110°C 오븐에서 24 시간 건조하고 건조 무게를 측정하여 아래 식을 이용해 부피밀도와 열린 기공률을 계산하였다.

$$\text{Bulkdensity/g/cm}^3 = \frac{\text{Weighdry}}{\text{Weightsaturated} - \text{WeightUnderwater}} \quad (2)$$

$$\text{OpenPorosity\%} = \frac{\text{WeightSaturated} - \text{WeightDry}}{\text{WeightSaturated} - \text{WeightUnderwater}} \times 100 \quad (3)$$

2.4 전기비저항 측정

ASTM C 611을 참고하여 전기비저항을 측정하였다. CB 및 RCB의 단면적을 측정하고 전압단자 사이 길이를 16 mm로 고정하여 0.5 A단위로 0.5~3.0 A의 전류에 대한 전압단자 사이의 전압강

하를 측정해 아래 식을 이용하여 전기비저항을 계산하였다[18, 19].

$$ER=VA/IL \tag{4}$$

ER = Electrical resistivity ($\mu\Omega$ m), V = Voltage drop between voltage terminals (V),

A = Cross-sectional area (mm^2), I = Magnitude of electrical current (A),

L: Distance between contact points (mm)

2.5 굽힘강도 측정

ASTM D 7972를 참고하여 CB와 RCB의 굽힘강도를 만능재료 시험기로 측정하였다. 굽힘강도 측정은 일축가압성형시의 가압면을 하중이 가해지는 면으로 하여 측정하였다. CB 및 RCB의 정 중앙에 하중이 가해지도록 탄화블록을 위치하고 초점거리 40 mm, 가압속도 0.5 mm/min으로 측정하였다[18, 19].

$$\sigma=3PL/(2bd^2) \tag{5}$$

σ : Flexural strength (N/mm^2), P: Maximum load (N), L: Support span(mm)

b: Specimen width (mm), d: Specimen thickness (mm)

2.6 미세조직 분석

CB와 RCB의 함침 전후 미세조직 변화 관찰은 가압면에 평행한 면을 연마하여 광학현미경으로 관찰하였다. 미세조직 관찰 위치는 Fig. 3에 나타내었다.

3. Results and Discussion

3.1 입도에 따른 탄화블록의 함침 전후 물성 변화

Fig. 4 (a), (b)에 CB와 RCB의 부피밀도 및 기공률을 나타내었다. 입도가 가장 큰 CB-413의 함침 전 부피밀도와 기공률은 $1.43 \text{ g}/\text{cm}^3$, 30.5 %이며 함침 후 $1.53 \text{ g}/\text{cm}^3$, 24.7 %이다. 입도가 작아질수록 부피밀도는 감소하고 기공률은 증가하였다. 가장 작은 입도로 제조된 CB-53의 함침 전 부피밀도와 기공률은 $1.33 \text{ g}/\text{cm}^3$, 35.9 %이며 함침 후 $1.50 \text{ g}/\text{cm}^3$, 26.5 % 였다. 충전재의 입도가 작을수록 부피밀도가 작고 기공률이 컸다.

Sun et al과 Liu et al은 입도가 작을수록 비표면적이 증가한다고

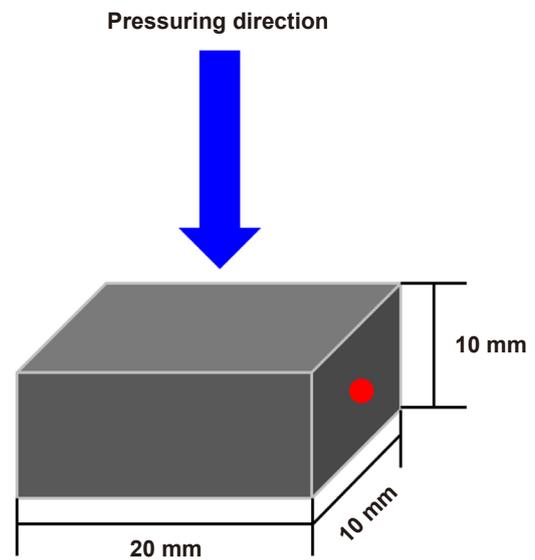


Fig. 3. Microstructure observation position.

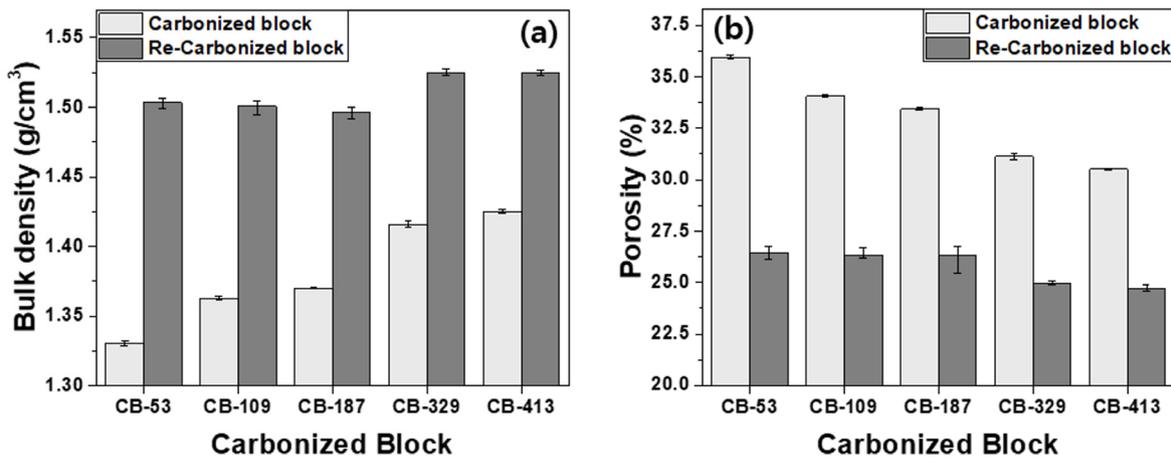


Fig. 4. Properties of carbonized and re-carbonized blocks by particle size. (a) Bulk density and (b) porosity.

보고하였다[20, 21]. 입도가 작을수록 충전재와 바인더의 접촉 표면이 많아져 더 많은 양의 바인더가 필요하다. 따라서 동일 바인더 함량인 20 wt%로 제조된 CB-53은 부피밀도가 작고 기공률이 컸다.

Fig. 5에 입도 별 CB의 함침률을 나타내었다. CB-413의 함침률은 18.9 %이며 기공률이 높은 탄화블록일수록 함침률이 증가하여 CB-53의 함침률은 26.4 %로 가장 높았다.

이는 입자가 작을수록 비표면적은 증가하므로 CB-53이 함침되었을 때 기공에 함침재의 침투가 용이하고, 재탄화 공정 시 입자 사이의 계면이 CB-413 대비 더 많이 존재하여 기공 채움 효과가 더 좋은 것으로 판단된다. 또한 An et al.은 탄화블록 함침 시 핏치가 닫힌 기공에 침투하기 어렵다고 보고하였다[22]. 따라서 본 연구에서 측정된 기공률은 열린 기공이므로 기공률이 더 큰 CB-53의 함침률이 CB-413보다 더 높았다.

Fig. 6의 CB의 전기 비저항 측정 결과는 기공률과 거의 동일한 경향을 나타내었다. CB-413의 전기 비저항은 함침 전 57.8 $\mu\Omega\text{m}$ 에서 함침 후 45.3 $\mu\Omega\text{m}$ 였고, CB-53의 전기 비저항은 함침 전 74.8 $\mu\Omega\text{m}$ 에서 함침 후 54.9 $\mu\Omega\text{m}$ 였다. CB-413의 전기 비저항 감소율은 21.6% 이고 CB-53의 전기 비저항 감소율은 26.6% 였다. 탄화블록 내부의 기공은 전자의 이동을 방해할 수 있다고 보고되었다[22]. Sun et al.은 전기 비저항과 다공성 사이의 모델을 이용하여 탄화블록의 열린 기공이 40% 증가하면 전기 비저항이 250% 증가하지만 닫힌 기공이 40% 증가했을 때 전기 비저항이 25% 증가한다고 보고하였다[23]. 따라서 CB-53의 함침률이 CB-413보다 높아 CB-53의 열린 기공이 더 많이 감소하여 전기 비저항의 감소율이 높은 것을 설명이 가능하다.

탄화블록 내부의 전자의 이동은 입자 간 이동과 입자 내 이동을 통해 이루어지며 이 중 입자 내 전자의 이동이 더 원활하다고 여러 논문에서 보고되었다[24, 25]. 따라서 CB-413은 전자가 이동해야 하는 계면이 적어 전기 비저항이 낮은 것으로 설명이 가능하다.

Fig. 7은 입도 별 CB의 굽힘 강도 변화이다. CB-413의 함침 전 굽힘강도는 7.70 MPa에서 함침 후 13.5MPa였다. 입도가 작을수록 굽힘강도가 증가하여 CB-53은 함침 전 10.0 MPa에서 함침 후 18.0MPa로 증가하였다. Kim은 흑연블록의 압축 강도에서 열린 기공보다 닫힌 기공의 영향을 더 크게 받는다고 보고하였다[26]. Oshida et al.은 등방성 흑연블록의 기공 형상, 크기, 수 그리고 모양이 굽힘강도에 미치는 영향에 대해 연구하였고 기공 크기가 작고 수가 많을수록 기공이 균열 전파를 방해하여 흑연블록의 굽힘강도가 높다고 보고하였다[27].

Heo et al 은 흑연 강화 전도성 고분자 복합재 (CPC)의 기계적 특성은 흑연 입자와 페놀수지의 경계면에서 파단이 발생하여 입자가 작을수록 굽힘강도가 증가한다고 보고하였다[28]. 또한 Kim and Hahn 은 입자 크기 별 복합재의 응력 분포에 관해 연구하여 응력 집중은 보강재와 기지의 경계에서 변형이 발생한다고 보고하였다[29].

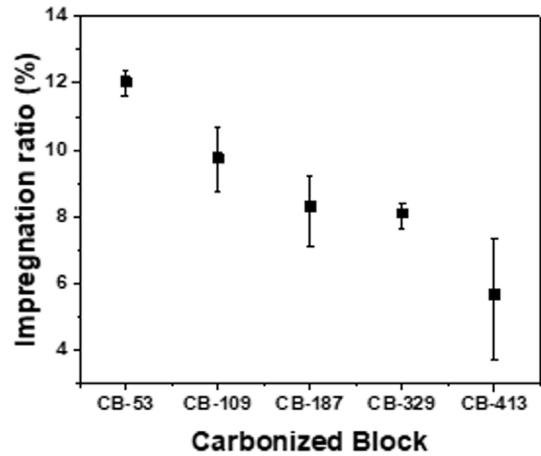


Fig. 5. Impregnation ratio of carbonized blocks by particle size.

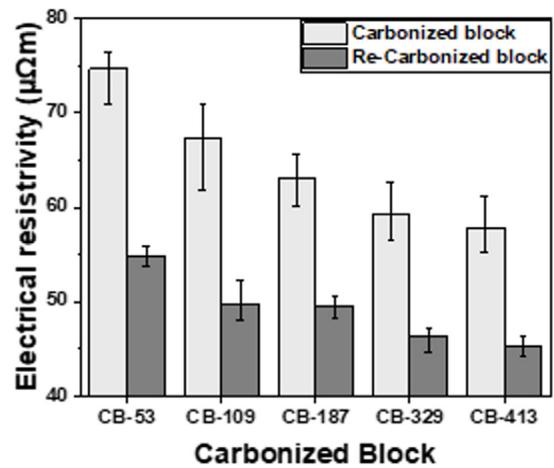


Fig. 6. Electrical resistivity of carbonized and re-carbonized blocks by particle size.

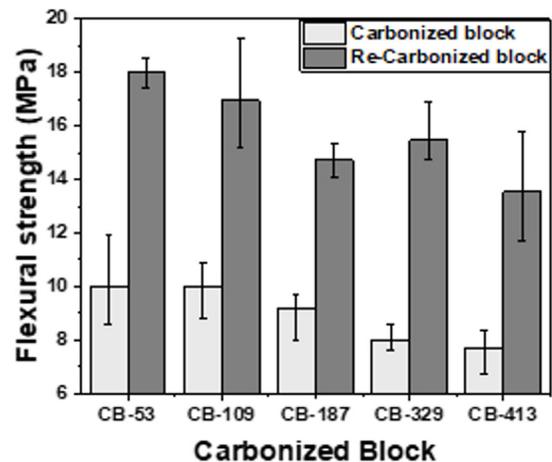


Fig. 7. Flexural strength of carbonized and re-carbonized blocks by particle size.

따라서 입도가 작은 CB 일수록 기공률이 높고 내부 기공 크기가 작아 균열 전파를 방해하는 기공이 더 많이 존재하고 코크스 입자의 경계면을 따라 파단이 발생하여 함침 전후 굽힘강도가 높은 것을 설명할 수 있으며, 그 효과는 함침 후 더 크게 나타났다. 따라서 탄화블록의 굽힘강도는 닫힌 기공의 영향보다 열린 기공률과 입자의 크기의 효과가 더 큰 것으로 생각된다. Table 3에 Figs. 4, 5, 6, 7에 대한 결과 데이터를 정리하였다.

3.2 입도에 따른 탄화블록의 함침 전후 미세조직 변화

Fig. 8에 CB 및 RCB의 평행한 면의 정중앙 부분을 관찰하였다. 미세조직을 나타내었다. 미세조직 관찰 결과 CB-53은 약 40 μm의 작은 기공이 다수 존재하며 약 100 μm 크기의 큰 기공이 일부 형성되었고 CB-413은 입자 사이에 약 150 μm 크기의 기공이 형성되어 있었다. 함침 후에 기공이 채워지는 것을 확인하여 아arki 메테스로 측정된 기공률 경향과 동일하였다.

4. Conclusion

침상 코크스와 석탄계 핏치로 입도 별로 탄화블록을 제조하여 기공률이 다른 CB를 제조하였다. 기공률이 다른 CB를 함침하여 함침 전후로 부피밀도, 기공률, 전기비저항, 굽힘강도 그리고 미세조직 변화에 대해 연구한 결과 다음과 같은 결론을 얻었다.

CB-413은 CB-53 대비 부피밀도가 높고 기공률, 전기 비저항 굽힘강도가 낮았다. 부피밀도와 기공률은 입도에 따라 비표면적의 차이에 의한 필요한 바인더 함량이 다르기 때문이다. 전기 비저항과 굽힘강도는 CB-413의 계면이 CB-53대비 적어 전기 비저항과 굽힘강도가 낮았다.

CB-53에서 26.4 %로 함침률이 가장 높았으며 CB-413에서 18.9 %로 함침률이 가장 낮았다. 이는 기공률이 높아 함침된 탄화블록 재탄화 시 입자 사이의 계면이 더 많이 존재하여 기공 채움 효과가 더 높은 것으로 판단된다.

CB의 기공 크기는 충전제로 사용된 침상 코크스의 입도가 작을 수록 작았다. CB-413 내부에 형성된 기공 크기 대비 CB-53에 형성된 기공 크기가 작고 함침 후에 기공이 채워져 기공률이 감소하는 것을 확인할 수 있었다.

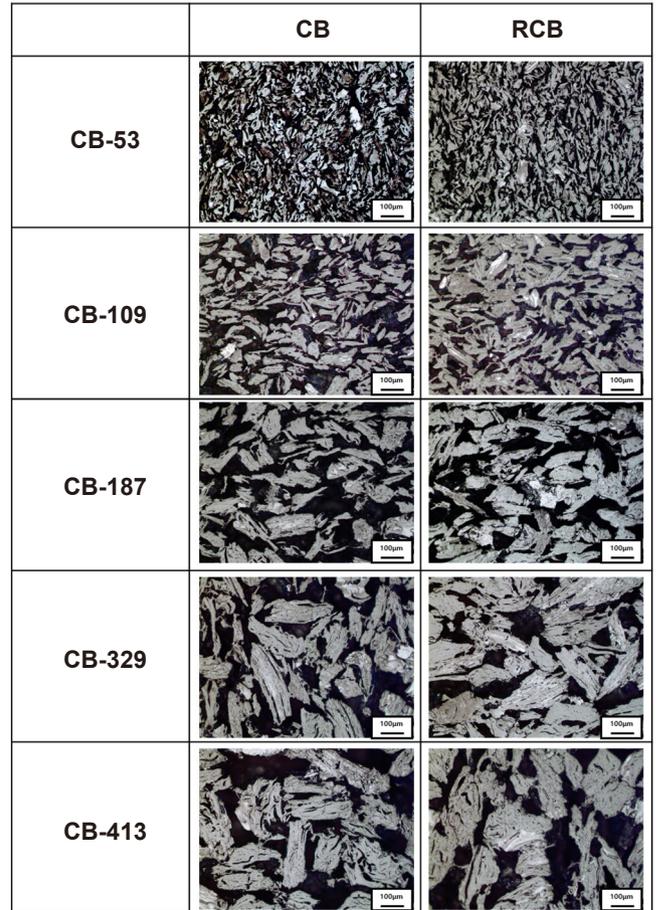


Fig. 8. Microstructure of CB and RCB by particle size (x100).

Table 3. Impregnation property changes of particle size-specific carbonized blocks

Samples	Bulk density (g/cm ³)		Open porosity (%)	Impregnation ratio (%)	Electrical resistivity (μΩm)		Flexural strength (MPa)	
CB-53	1.33	13.00%	35.9	-26.40%	74.8	-26.60%	10	81.30%
RCB-53	1.503		26.4		54.9		18	
CB-109	1.362	10.20%	34.1	-22.70%	67.3	-26.10%	10	69.70%
RCB-109	1.501		26.3		49.8		16.9	
CB-187	1.37	9.20%	33.4	-21.30%	63.1	-21.60%	9.2	60.80%
RCB-187	1.496		26.3		49.5		14.7	
CB-329	1.416	7.70%	31.1	-19.80%	59.3	-21.80%	8	93.70%
RCB-329	1.525		25		46.4		15.5	
CB-413	1.425	7.00%	30.5	-18.90%	57.8	-21.60%	7.7	75.60%
RCB-413	1.525		24.7		45.3		13.5	

Funding

이 연구는 국립금오공과대학교 학술연구비로 지원되었음(2022).

Conflict of Interest

저자들은 이해상충관련 해당사항 없음을 선언합니다.

Data Availability Statement

The data shown in this article are available from the corresponding authors upon a reasonable request.

Author Information and Contribution

윤우상: 박사과정 학생; Specifically performing the experiments, writing original draft
 이상혜: 박사과정 학생; review & editing
 노재승: 교수; Supervision

Acknowledgement

None.

References

- [1] S. H. Chung, K. W. Kim, M. S. Kim and Y. S. Lim: *J. Res. Inst. Ind. Technol.*, **18** (1999) 365.
- [2] Y. S. Ko: *Ceramist.*, **9** (1994) 18.
- [3] Z. Hu, S. Jin, W. Lu, S. Tang, C. Guo, Y. Lu and M. Jin: *Fullerenes, Nanotubes and Carbon Nanostructures*, **25** (2017) 637.
- [4] W. Feng, M. Qin and Y. Feng: *Carbon*, **109** (2016) 575.
- [5] M. Inagaki, Y. Kaburagi and Y. Hishiyama: *Adv. Eng. Mater.*, **16** (2014) 494.
- [6] J. Y. Hsu, C. J. Su, Y. L. Yen and C. Y. Lee: *Carbon Lett.*, **32** (2022) 797.
- [7] Graphite Electrode Market Size, Share, Industry, Forecast and outlook 2024-2031 DataM Intelligence (Published February 2025) URL : <https://www.datamintelligence.com/research-report/graphite-electrode-market>
- [8] S. Ragna and H. Marsh: *J. Mater. Sci.*, **18** (1983) 18.
- [9] S. M. Lee, D. S. Kang and J. S. Roh: *Carbon Lett.*, **16** (2015) 135.
- [10] W. Y. Shin: *Journal of Power System Engineering*, **9** (2005) 143.
- [11] P. D. Matzinos, J. W. Patrick and A. Walker: *Carbon*, **34** (1996) 639.
- [12] H. N. Youm, K. J. Kim, J. M. Lee and Y. J. Chung: *Yoop Hakhoechi*, **30** (1993) 852.
- [13] S. M. Lee, D. S. Kang, H. S. Kim and J. S. Roh: *Carbon Lett.*, **16** (2015) 132.
- [14] C. Kim, W. Kwon, M. H. Lee, J. S. Woo and E. Jeong: *Materials*, **15** (2022) 561.
- [15] J. H. Cho, H. I. Hwang, J. H. Kim, Y. S. Lee, J. S. Im and S. C. Kang: *Applied Chemistry for Engineering*, **32** (2021) 569.
- [16] S. M. Lee, S. H. Lee, D. S. Kang and J. S. Roh: *Compos. Res.*, **34** (2021) 569.
- [17] U. Youn, S. Lee, J. Kim and J. Roh: *Korean J. Chem. Eng.*, **41** (2024) 2153.
- [18] S. H. Lee, Y. M. Hwang, T. S. Byun, J. H. Ko and J. S. Roh: *Carbon*, **208** (2023) 443.
- [19] S. H. Lee, J. H. Kim, W. S. Kim and J. S. Roh: *Materials*, **15** (2022) 3259.
- [20] S. J. Sun, X. J. Liu, T. Q. Li, Z. Fan and Z. H. Feng: *Key Eng. Mater.*, **609** (2014) 238.
- [21] Z. Liu, Q. Guo, J. Shi, G. Zhai and L. Liu: *Carbon*, **46** (2008) 414.
- [22] D. An, K. H. Kim, H. C. Lim and Y. S. Lee: *Carbon Lett.*, **31** (2021) 31.
- [23] T. M. Sun, L. M. Dong, C. Wang, W. I. Guo, L. Wang and T. Liang: *New Carbon Mater.*, **28** (2013) 349.
- [24] P. Wagner, J. A. O'rourke and P. E. Armstrong: *J. Am. Ceram. Soc.*, **46** (2008) 414.
- [25] C. García-Rosales, N. Ordas, E. Oyarzabal, J. Echeberria, M. Balden, S. Lindig and R. Behrisch: *J. Nucl. Mater.*, **307** (2002) 115.
- [26] J. H. Kim: *Carbon Lett.*, **33** (2023) 1757.
- [27] K. Oshida, N. Ekinaga, M. Endo and M. Inagaki: *Tanso*, **173** (1996) 142.
- [28] S. I. Heo, J. C. Yun, K. S. Oh and K. S. Han: *Adv. Compos. Mater.*, **15** (2006) 115.
- [29] S. H. Kim and H. T. Hahn: *Adv. Compos. Mater.*, **15** (2006) 175.

A Review of Recent Developments in CoCrFeMnNi High-Entropy Alloys Processed by Powder Metallurgy

Cheenepalli Nagarjuna¹, Sheetal Kumar Dewangan¹, Hansung Lee¹, Eunhyo Song², K. Raja Rao^{1,3}, Byungmin Ahn^{1,2,*}

¹Department of Materials Science and Engineering, Ajou University, Suwon 16499, Republic of Korea

²Department of Energy Systems Research, Ajou University, Suwon 16499, Republic of Korea

³Department of Mechanical Engineering, Mandsaur University, Mandsaur, Madhya Pradesh 458001, India

Received: November 25, 2024

Revised: January 27, 2025

Accepted: February 12, 2025

***Corresponding author:**

Byungmin Ahn

TEL: +82-31-219-3531

FAX: +82-31-219-1613

E-mail: byungmin@ajou.ac.kr

In recent years, high-entropy alloys (HEAs) have attracted considerable attention in materials engineering due to their unique phase stability and mechanical properties compared to conventional alloys. Since the inception of HEAs, CoCrFeMnNi alloys have been widely investigated due to their outstanding strength and fracture toughness at cryogenic temperatures. However, their lower yield strength at room temperature limits their structural applications. The mechanical properties of HEAs are greatly influenced by their processing methods and microstructural features. Unlike traditional melting techniques, powder metallurgy (PM) provides a unique opportunity to produce HEAs with nanocrystalline structures and uniform compositions. The current review explores recent advances in optimizing the microstructural characteristics in CoCrFeMnNi HEAs by using PM techniques to improve mechanical performance. The most promising strategies include grain refinement, dispersion strengthening, and the development of heterogeneous microstructures (e.g., harmonic, bimodal, and multi-metal lamellar structures). Thermomechanical treatments along with additive manufacturing techniques are also summarized. Additionally, the review addresses current challenges and suggests future research directions for designing advanced HEAs through PM techniques.

Keywords: High entropy alloys; Powder metallurgy; Mechanical alloying; Microstructure; Mechanical properties

1. Introduction of high entropy alloys

The development of advanced materials has greatly impacted human civilization. Metals and alloys, such as bronze, iron, aluminum, and titanium, have been crucial throughout history. Bronze was used for over 1,000 years starting in the Shang Dynasty, the Iron Age spanned about 3,000 years, and aluminum and titanium alloys have been developed for over a century and sixty years, respectively [1, 2]. Metals and alloys are crucial in many areas of life, including agriculture, housing, and defense. Conventional alloys are typically composed of one main element, with minor amounts of other elements added to enhance specific properties. For instance, steel is based on iron, and al-

loying elements like carbon or chromium are introduced to improve strength, hardness, or corrosion resistance. The principal element defines the alloy's fundamental characteristics, while the additional elements fine-tune its performance for specific applications. The conventional alloy design applies to alloys like Fe, Cu, and Al, modern alloys, such as Inconel 718, feature more complex compositions. The principle of bulk amorphous alloys requires at least three elements [3, 4]. Although traditional methods face limitations, the complexity of alloy compositions continues to increase, as illustrated in Fig. 1.

Unlike conventional alloy designs, the novel class of high entropy alloys (HEAs) have been independently developed by J. Wei and Cantor et al. in 2004 [5, 6]. Though the chemical composition of HEAs is complex, HEAs show thermodynamically stable solid solution phases such as face centered cubic (FCC), body centered cubic (BCC), and hexagonal close packed (HCP)

<https://doi.org/10.4150/jpm.2024.00430>

© 2025 The Korean Powder Metallurgy & Materials Institute

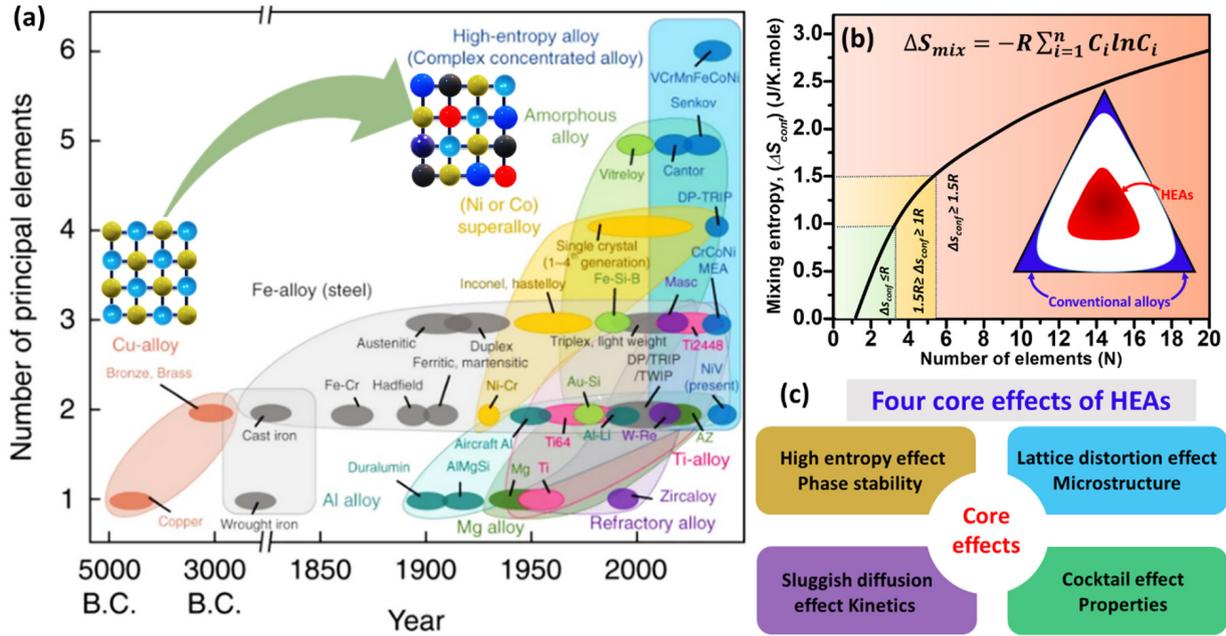


Fig. 1. (a) Historical development of alloy systems. (b) Classification of materials by mixing entropy and number of elements. (c) Core effects of HEAs [18].

phases, resulting in high configurational entropy [7, 8]. The phase composition, microstructure and mechanical properties are influenced by the four core effects of HEAs including the high entropy effect, sluggish diffusion effect, lattice distortion effect, and cocktail effects [9, 10]. As a result of those four core effects, HEAs often show attractive properties such as high strength-ductility, high fracture toughness, good thermal stability, excellent corrosion, and wear resistance, as a result, HEAs have been applied in various emerging applications [11]. Among various HEAs, the CoCrFeMnNi HEA, also known as the Cantor alloy, which has garnered significant attention due to its unique combination of mechanical properties, such as excellent strength, ductility, and toughness, especially at cryogenic temperatures. The enhanced mechanical properties of this HEA at cryogenic temperatures are mainly attributed to the FCC HEAs usually possess low stacking fault energy, leading to a transition in the deformation mechanism from the conventional dislocation plasticity at room temperature to deformation-induced twinning at cryogenic temperatures [12]. However, this alloy system exhibits relatively low yield strength and hardness at room temperature, which limits their engineering applications. Therefore, numerous strengthening mechanisms including precipitation strengthening, twinning-induced plasticity (TWIP), phase transformation strengthening (TRIP), and grain boundary strengthening have been developed to enhance

the strength and ductility of FCC-based HEAs [13, 14]. It is worth noting that the mechanical properties of HEAs are strongly influenced by their microstructural characteristics, which depend on the processing route, understanding the evolution of microstructure in powder metallurgy (PM) processed CoCrFeMnNi HEA is crucial. Therefore, the present study focused on highlighting recent developments in the microstructure of CoCrFeMnNi HEA and their effects on mechanical properties, aiming to enhance performance for advanced engineering applications.

1.1. Definition of HEAs

In general, HEAs can be defined based on composition and entropy. Here’s a definition based on composition:

1.1.1 Composition based definition

In terms of composition, HEAs consist of five or more principal elements with nearly equi-atomic concentrations ranging between 5% and 35 at. %. It is defined as follows.

$$n_{major} \geq 5, 5 \text{ at \%} \leq c_i \leq 35 \text{ at \%} \tag{1}$$

$$n_{minor} \geq 0, c_j \leq 5 \text{ at \%} \tag{2}$$

where n_{major} and n_{minor} represent the number of major and minor

elements in an alloy system, respectively. Additionally, c_i and c_j denote the atomic percentages of these elements. Additionally, minor elements (<5%) were added to enhance the mechanical properties such as the ductility, toughness, strength, creep, oxidation, etc. [15]

1.1.2. Entropy based definition

Based on the definition of entropy, HEAs or medium entropy alloys (MEAs) are determined by high mixing entropy, which includes configurational, vibrational, magnetic dipole, and electronic randomness entropy. The total entropy change due to mixing can be expressed as the sum of these contributions as follows [16].

$$\Delta S_{mix} = \Delta S_{mix}^{conf} + \Delta S_{mix}^{vib} + \Delta S_{mix}^{mag} + \Delta S_{mix}^{ele} \quad (3)$$

For equimolar alloys, configurational entropy increases with the number of elements, which can be estimated using the following equation.

$$\Delta S_{conf} = R \ln n \quad (4)$$

where n is the number of components and R is the universal gas constant. When the alloys with ΔS_{conf} greater than $1.61 R$ classified as HEAs, while those with ΔS_{conf} falling within the range of $0.69 R$ and $1.61 R$, the alloy system is categorized as medium entropy alloy. From the entropy definition, the alloys with less than five elements, such as quaternary alloys, can also exhibit high-entropy characteristics if the ΔS_{conf} exceeds this threshold. It is important to note that a higher number of elements in the alloy results in a higher mixing entropy, which lowers the Gibbs free energy of mixing and stabilizes solid solution phases over secondary or intermetallic compounds [17].

1.2. Core effects of HEAs

1.2.1. High entropy effect

The high-entropy effect in HEAs plays a crucial role in stabilizing solid-solution phases, primarily by reducing the Gibbs free energy and suppressing the formation of ordered phases, particularly at elevated temperatures. This phenomenon arises from the significant mixing entropy due to the multiple principal elements in the alloy, leading to atomic structural disorder and randomness. As dictated by the second law of thermodynamics, the equilibrium state is achieved when Gibbs free energy is minimized, and higher entropy has been shown to in-

crease the stability of solid-solution phases. Consequently, the high-entropy effect enhances the mechanical properties of HEAs, including improved strength, hardness, and resistance to deformation through solid-solution strengthening. Furthermore, it contributes to enhanced thermal stability, as well as increased resistance to corrosion and oxidation [19].

1.2.2. Sluggish diffusion

The sluggish diffusion effect in HEAs results in slower atomic movement within the crystal lattice than that of conventional alloys. As a result, HEAs have been widely used for high temperature applications considering their exceptional strength and structural stability. In addition, sluggish diffusion effect promotes the formation of a stable phases, increases the recrystallization temperature, restricts the phase transformation and intermetallic compounds, and enhances resistance to grain growth, thereby improving the stability and durability of HEAs [20]. While sluggish diffusion has been commonly observed in many HEAs due to the high configurational entropy, recent studies have highlighted that the diffusion behavior can be influenced by specific elements within the alloy. For example, Mn-containing alloys such as CoCrFeMnNi HEA exhibit a typical behavior as Mn does not significantly promote sluggish diffusion due to its similar atomic radius with other elements like Fe, Cr, and Ni, resulting in less lattice distortion [21]. Additionally, Mn stabilizes the FCC phase, which typically allows faster diffusion compared to BCC structures. Furthermore, the relatively high self-diffusion coefficient of Mn element enhances atomic mobility, diminishing its contribution to the sluggish diffusion effect [22]. It is worth mentioning that the diffusion behavior in HEAs is more complex than previously thought and is influenced not only by the configurational entropy but also by the atomic size, electronic structure, and bonding interactions of the individual elements. Therefore, the role of sluggish diffusion effect in particular HEAs remains a subject of debate and may vary depending on the specific composition and microstructure of the alloy. Therefore, further research is required to better understand the sluggish diffusion effect, especially in the case of Mn-containing HEAs.

1.2.3. Severe lattice distortion effect

Lattice distortion in HEAs arises from the presence of multiple elements with different atomic sizes and valance electron concentration [23]. The greater atoms push away their neighbors and smaller atoms have enough space around them, as a result, strain energy associated with lattice distortion raises the

overall free energy of the HEA lattice. The variations in crystal structure and bonding energies among the elements further amplify lattice distortion, as the electronic structure and asymmetric bonding differ from site to site within the lattice. In addition, the severe lattice distortion effect impedes dislocation movement and improved solid solution strengthening, leading to improve the strength and hardness of HEAs. Furthermore, the severe lattice distortion effect increased the electron and phonon scattering, as a result, reduces the electrical and thermal conductivity [24].

1.2.4 Cocktail effect

Professor Ranganathan initially proposed the "cocktail effect," which describes how the inclusion of diverse elements in HEAs impacts their microstructure and properties. Altering the composition of these elements can significantly enhance the alloy's performance [25]. This enhancement is due to the synergistic interactions between the various elements, which result in improved thermal stability, corrosion resistance, and overall strength and toughness [26].

2. Fabrication of HEAs by powder metallurgy route

The fabrication route of HEAs plays a significant role on the microstructure and mechanical properties. Traditionally, Most of the HEAs are processed through conventional methods such as arc melting and vacuum induction melting [27]. Since the processing temperature of these methods like arc melting can exceed 3,000°C, elements with low melting points, such as Mg and Zn, may evaporate. This evaporation complicates the precise control of the composition of the HEAs. Additionally, coarse-grained microstructures, and lack of compositional homogeneity is challenging during the processing of HEAs. For example, Cu tends to segregate from other elements because of its positive mixing enthalpy with many elements. Moreover, this processing method may not be suitable for current industrial practices due to the high cost of equipment and constraints on product shape and size. It is worth mentioning that microstructural characteristics can adversely affect the mechanical properties and performance of the alloys. Therefore, an additional thermo-mechanical process becomes a necessary step to optimize the microstructures and enhance the mechanical properties. These additional methods are cost-expensive and high maintenance [28]. Therefore, PM is an effective method to produce high performance HEAs, and fabrication techniques

of PM were schematically represented in Fig. 2.

2.1 Mechanical alloying

To address these challenges, PM associated mechanical alloying (MA) has emerged as a powerful technique for the fabrication of nanocrystalline HEAs [29]. Mechanical alloying is a solid-state PM process, which can be used to prepare the alloy powders using either a high or low-energy ball miller. During MA, powder particles experience fracturing, cold welding, and rewelding behavior, thereby deforming the powder particles and inducing structural defects (i.e., grain boundaries, dislocations, and stacking faults) [30]. In recent years, MA has been widely utilized to produce nanocrystalline HEA powders, and uniformly distribute the oxide nanoparticles into base HEAs. Compared to conventional HEAs, PM HEAs show superior mechanical properties resulting in the grain boundary strengthening and dislocation strengthening induced by SPD during MA. It is found that most of the solid solution phases formed in HEAs after milling within 15–40 h. However, the formation of amorphous HEAs occurs often because of prolonged milling hours. For example, complete amorphization was observed in AlBCFeNiSi and AlBCeFeNiSi alloys after 140 h and 240 h of MA, respectively [31]. Therefore, PM associated mechanical alloying is an effective method to produce nanocrystalline HEAs with uniform chemical composition with less fabrication cost. Additionally, PM can be used to process elements with different melting points, thereby preventing the evaporation of low melting point elements. Despite its advantages, PM faces challenges such as prolonged milling time for alloying and possible contamination of the powder from sources such as process control agents (PCA) and grinding media.

2.2. Gas atomization

The second most common method for preparing HEA powder is gas atomization, which is ideal for additive manufacturing applications. This rapid solidification technique produces powders with excellent compositional homogeneity, precise particle size, and controlled morphology. It can be able to produce mass scale production and improves the quality of the resultant HEAs, making it a promising approach for industrial-scale applications [32]. Atomization has recently become a significant technique for producing pre-alloyed powders. In this process, high-pressure gas, water, or plasma is used to break liquid metal streams into droplets, which then cool and solidify into spherical particles. By optimizing the process conditions, it is possible to produce powders with the desired par-

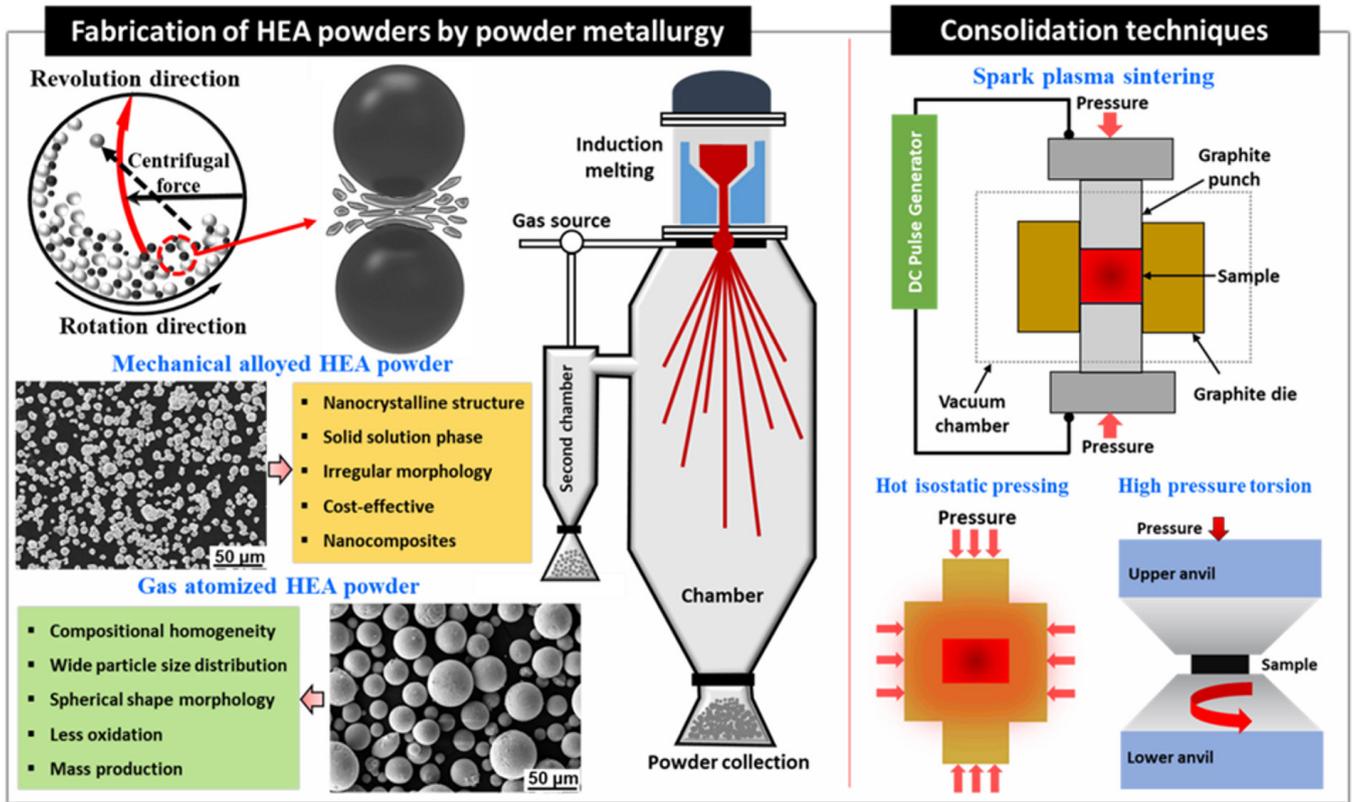


Fig. 2. The process of producing HEA powders through mechanical alloying and gas atomization, followed by their consolidation using various sintering techniques [24].

ticle size, uniform distribution, and excellent sphericity. For example, employing high cooling rates is effective in preventing compositional segregation and minimizing atomic ordering, which helps in avoiding the formation of intermetallic compounds. Water atomization is similar to gas atomization, but it uses water jets instead of high-pressure gas. Powders produced through water atomization typically have a lower degree of sphericity compared to those made by gas atomization. This is because large droplets with high surface tension tend to form nearly spherical particles, while smaller droplets with lower surface tension result in more irregularly shaped particles [33]. Due to unique advantages such as excellent morphology, flowability and homogeneous chemical composition, gas-atomized HEA powders are particularly well-suited for additive manufacturing applications.

2.3. Sintering techniques

In PM route, sintering involves heating metal powders below their melting point to form a dense material. Initially, particles bond at contact points by forming small necks through surface

and grain boundary diffusion. As sintering progresses, necks grow, and pores begin to shrink due to material transport via mechanisms such as bulk and grain boundary diffusion. In the final stage, pores are largely eliminated, grain growth occurs, and the material approaches its theoretical density. Thus far, most HEAs utilized spark plasma sintering (SPS) to produce high performance HEA bulks with excellent density in short durations by applying temperature and pressure. Owing to the less holding time for the sintering, effectively prevents grain growth [34]. For example, Joo et al. [35] investigated the structure and properties of CoCrFeMnNi HEA by systematically controlling the MA time and SPS temperature. They demonstrated that the FCC phase remained stable after SPS, although carbon contamination led to the formation of Cr carbides near the surface. Additionally, they observed that increasing the MA time enhanced the phase stability, while higher SPS temperatures and reduced contamination levels were necessary to achieve improved tensile ductility. Wei Ji et al. [36] synthesized an equiatomic CoCrFeNiMn HEA using MA and SPS. They observed the formation of a solid solution with a refined mi-

microstructure (~10 nm) consisting of both FCC and BCC phases during MA. After SPS consolidation, only the FCC phase remained, with the HEA bulks exhibiting a compressive strength of 1987 MPa. Additionally, a magnetic transition, associated with structural coarsening and phase transformation, was observed during the SPS process. In addition, PM is an effective method for preparing composite structures, especially for homogeneous distribution of nanoparticles into HEA matrix and refine the microstructure. Dai et al. [37] fabricated Al₂O₃ reinforced CoCrFeMnNi HEA composites using MA and SPS. The addition of Al₂O₃ refined the grain size by approximately 48.5% and enhanced the hardness by 56.7% compared to the original HEA matrix. Additionally, the compressive yield strength increased by 74.7% due to grain boundary strengthening combined with Orowan strengthening mechanisms. Kang et al. [38] investigated the effects of varying MXene weight percentages (0–10 wt.%) on the microstructure, wear behavior, and mechanical properties of CrMnFeCoNi HEA. The addition of MXene led to grain refinement, forming FCC and HCP phases in the composites, significantly improving hardness from 205.8 HV to 617.6 HV and yield strength from 390 MPa to 1403 MPa. Furthermore, the addition of MXene enhanced wear resistance and reduced the coefficient of friction.

On the other hand, high-pressure torsion (HPT) has been widely utilized to enhance the strength and hardness of HEAs via deforming the microstructure of cast or sintered products. In this process, reduce the grain size of the HEAs with an increasing number of turns and increase the dislocation density. Indeed, HPT enables us to show gradient deformation in terms of grain size and dislocation densities from the center to the edge of the sample. For example, Liu et al. [39] noticed that MEA bars have high strength at the edges because of the high dislocation density and a high-volume fraction of nano twins. The center of MEA bars is ductile because of a low dislocation density and a low volume fraction of nano twins. These gradient microstructures enable simultaneously improved strength and ductility. Shahmir et al. [40] reported a CoCrFeMnNi HEA was processed by HPT under 10 GPa at room and cryogenic temperature. It shows that increased straining and decreased deformation temperature caused deformation-induced martensitic transformations. Moon et al. [41] reported the deformation-induced phase transformation in FCC Co₂₀Cr₂₆Fe₂₀Mn₂₀Ni₁₄ HEA during cryogenic HPT and the results showed the FCC to HCP. To achieve a superior combination of strength and ductility, many works have developed post-annealing and deformation methods to modify the phase and structural char-

acteristics.

The present review focuses on the fabrication of HEAs by PM techniques. The primary goal of this review is to explore advancements in microstructural tailoring of HEAs through PM and their effects on improving mechanical properties. Furthermore, it also covers recent literature on grain refinement, dispersion strengthening, and various heterogeneous structures such as harmonic, bimodal, multi-metal lamellar composites and thermomechanical methods have been discussed.

3. Microstructural evolution in CoCrFeMnNi alloy using powder metallurgy techniques

Indeed, extensive research has focused on improving the strength of CoCrFeMnNi HEA through microstructural tailoring and optimized processing routes. Recent developments include grain boundary strengthening, dispersion strengthening, and the design of heterogeneous structures such as harmonic, bimodal, multimetal-lamellar composites and hierarchical structures. Additionally, thermomechanical methods have been employed to tailor the microstructure and optimize the mechanical properties. These advancements make CoCrFeMnNi HEA highly effective for demanding structural applications.

3.1 Grain boundary strengthening

Grain boundary strengthening is achieved by grain refinement that can enhance strength and hardness of HEAs. As the grain size decreases, the number of grain boundaries increases, which impedes dislocation movement. This increased resistance to dislocation slip results in greater strength and hardness, as smaller grains act as barriers to deformation and improve the overall mechanical properties [42]. Originally, FCC-structured CoCrFeMnNi HEA exhibits low yield strength and hardness, therefore grain refinement is an effective strategy to enhance its properties by Hall-Petch strengthening effect. For example, Otto et al. [43] observed the Hall-Petch effect in CoCrFeMnNi HEA through reducing the grain size from 155 μm to 4.4 μm, which significantly increased the yield strength from approximately 180 MPa to about 350 MPa at room temperature, with only a slight impact on ductility. Further decreasing the grain size to around 50 nm through severe plastic deformation resulted in a dramatic increase in yield strength, up to 1.95 GPa, although this improvement was accompanied by a significant loss in ductility [44]. Most of the HEAs strengthened by conventional techniques such as accumulative roll bonding, HPT, and equal channel angular extrusion, as well

as surface mechanical attrition and grinding, are used to achieve nano- or ultrafine-grain structures through thermomechanical processing and severe plastic deformation [45]. In contrast to the costly and time-consuming techniques, PM is widely used to produce ultrafine-grained structures. Nowadays, the rapid solidified gas atomization method has been widely used to produce HEAs with high quality, spherical shape, less oxidation and mass production applications. Despite gas atomization being suitable for large-scale production, it has limitations in precise size control, which can result in lower strength and hardness. In contrast, the subsequent milling process allows for fine-tuning of grain size by adjusting milling time and speed, enabling effective grain size reduction and enhancing mechanical properties via grain boundary strengthening. It is worth mentioning that milling process offers a significant advantage over gas-atomization when it comes to controlling par-

ticle size and shape, which are crucial for grain boundary strengthening. With the aim of enhancing the strength of gas-atomized CoCrFeMnNi HEA, Nagarjuna et al. [46] conducted high-energy mechanical milling on the gas-atomized powder at different intervals to refine the grain size. The particle refinement of the HEA powder with milling time was confirmed by the surface morphology and cross-sectional microstructure of the HEA powders at various milling times (Fig. 3). The as-atomized powders are spherical with smooth surfaces and a dendritic microstructure (Fig. 3(a) and 3(a1)). After 5 minutes of high-energy mechanical milling, the powders start to deform, showing signs of fracturing and flattening (Fig. 3(b) and 3(b1)). After 10 minutes, the powders transform into flake-shaped particles due to severe plastic deformation, with fracturing further refining these flakes (Fig. 3(c) and 3(c1)). After 30 minutes of milling, the powders particles showed irregular

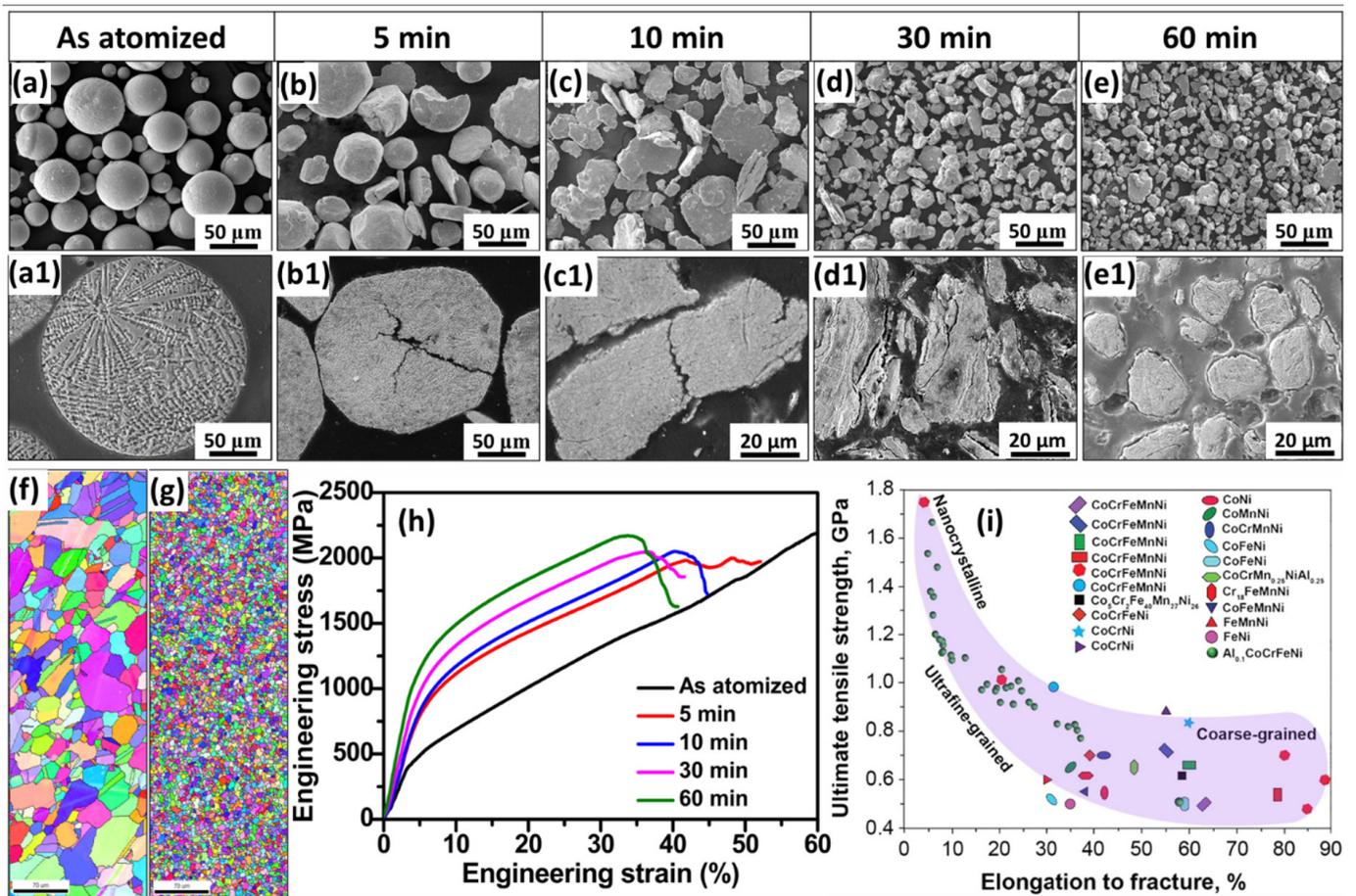


Fig. 3. Scanning electron microscopy images of CoCrFeMnNi high-entropy alloy (HEA) powders (a) as atomized and milled for 5, 10, 30, and 60 min (b-e). The corresponding cross-sectional microstructures are shown in Fig. 3(a1-e1), respectively, Fig. (f and g) are the EBSD inverse pole figure images of as atomized and 60 min milled HEAs, respectively. (h) Compressive stress-strain curves [46] and (i) Strength-ductility trade-off observed in various HEAs [50].

shapes from continuous flattening and fracturing (Fig. 3(d)). Fig. 3(d1) reveals that severe plastic deformation has led to the formation of lamellar cracks, signaling the beginning of powder refinement. After 60 minutes of milling, the particle size effectively reduced and partially turns into a spherical shape due to surface deformation, and the particle size seems to stabilize, likely due to cold-welding (Fig. 3(e) and 3(e1)). This refinement process led to a significant reduction in grain size, which contributed to improved mechanical properties, including enhanced strength and hardness, by promoting grain boundary strengthening. Further, the grain refinement was investigated using the electron backscatter diffraction (EBSD) analysis in Fig. 3(f and g). It shows that average grain size of atomized HEA and 60 minutes milled HEAs were 30 μm and 6 μm , respectively. The typical reduction in grain size by milling caused to increase the density of grain boundaries or interfaces, which effectively blocked the dislocation motion, thereby enhancing the strength and hardness of HEAs. To realize the effect of grain size on mechanical properties, compressive stress-strain curves were presented in Fig. 3(h). It shows that compressive yield strength (CYS) of HEA bulks increased significantly with milling time. For instance, the CYS of atomized HEA bulk is 370 MPa with a fracture strain over 60%. With milling times extended up to 60 minutes, the CYS increases to 1050 MPa, though the compressive strain reduces to 30%. Based on these results, it has been observed that grain refinement by milling is a cost-effective approach to enhance the mechanical performance of HEAs. Similarly, the typical enhancement in strength of CoCrFeMnNi HEA by refining the microstructure was observed in previous literature [47-49]. Fig. 3(i) displays the ultimate tensile strength versus elongation to fracture in CoCrFeMnNi based alloys system with grain sizes. It has been reported that HEAs with coarse grained structures exhibit low strength with high elongation, while the nanocrystalline structures exhibit high strength with low elongation. Therefore, optimum grain size for better strength and ductility is always challenging research for advanced structural applications.

3.2. Dispersion strengthening

Dispersion strengthening is a highly effective method for enhancing the mechanical properties of HEAs by incorporating fine, stable particles or reinforcements into the matrix. This technique boosts hardness and strength by restricting dislocation movement and refining the microstructure [51]. The fabrication of HEA composites is influenced by the processing route. Conventional melting methods, such as casting and arc

melting, are often unsuitable for producing oxide dispersion-strengthened (ODS) composites due to issues with compositional inhomogeneity and coarse grains. In contrast, PM is preferred method for producing composite HEAs due to its benefits, including uniform reinforcement distribution, prevention of elemental segregation, fine grain sizes, and achieving full density without porosity [52]. For instance, Hadraba et al. [53] achieved up to 70% strength improvement in CoCrFeMnNi/yttria composites at 800°C. Rogal et al. [54] increased the compressive yield strength of an Al_2O_3 -strengthened CoCrFeMnNi HEA from 1180 MPa to 1600 MPa using MA and HIP. Xiao et al. [55] found that PM significantly improved the wear resistance and hardness of CoCrFeNiMnCx by precipitating hard M7C3 carbides and reducing porosity. Ravi et al. [56] observed that adding 2 wt.% carbon nanomaterials, such as graphite flakes, graphene nanoplatelets, and carbon nanotubes, increased carbide precipitation, enhancing wear resistance. Yim et al. [57] prepared TiC-reinforced CoCrFeMnNi HEA composites by mixing TiC nanoparticles into water-atomized HEA powder, followed by low-energy mixing and SPS sintering. They compared the morphology of original HEA powders (Fig. 4a) with TiC-reinforced HEA powders (Fig. 4b) after milling. The HEA-TiC powders exhibited a flaky morphology, while the HEA powders showed an irregular shape. This difference suggests that TiC addition causes localized hardening and results in a distinct morphological change during milling. Further, the grain size of HEA and HEA-TiC composite bulks was studied by the EBSD inverse pole figure (IPF) maps (Fig. 4(c and d)). It was observed that the HEA-TiC composite has a smaller average grain size (5.1 μm) compared to the HEA without TiC (10.6 μm). Fig. 4(e) shows the compressive stress-strain curves of HEA and HEA-TiC composite bulks, indicating the addition of TiC content increased the yield strength from 508 MPa to 698 MPa and the fracture strength from 1527 MPa to 2215 MPa. The true stress-strain and strain hardening rate curves shown in Fig. 4f, suggesting that strain hardening rate decreases after yielding for both materials, it remains higher in the HEA-TiC composite. To realize the effect of TiC NPs in the strain hardening behavior, TEM analysis was carried out for the 2% strained composite HEA (Fig. 4g and h). It reveals dislocation pile-up at the TiC/FCC matrix interface and bowing of dislocation along the TiC interface. It is evident that TiC nanoparticles enhance strain hardening by impeding dislocation movement. These results demonstrate that incorporating reinforcements into HEAs via PM is an effective approach for strengthening HEAs with controlled microstructure and achieve the required

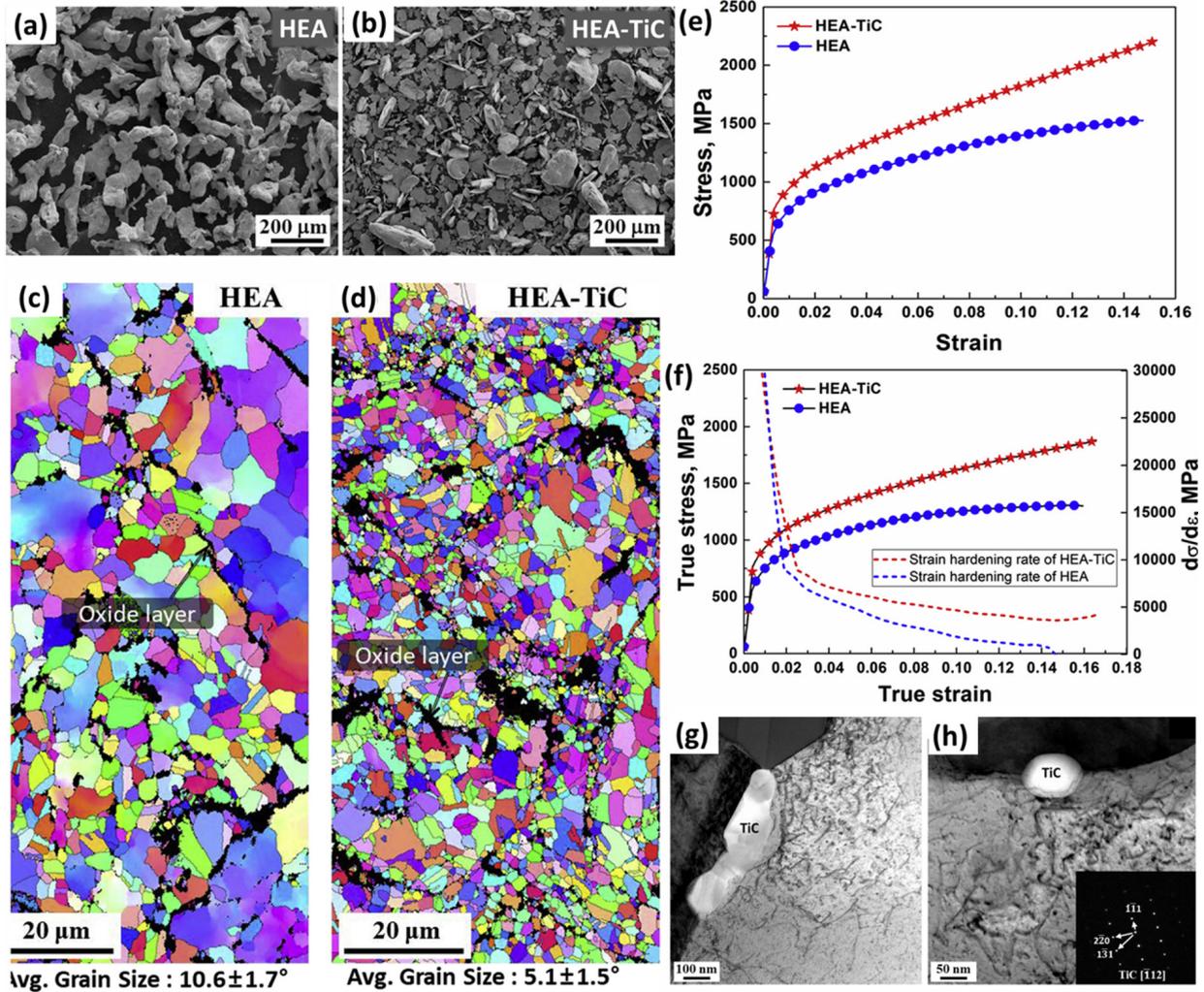


Fig. 4. (a) Scanning electron microscopy (SEM) images of milled high-entropy alloy (HEA) powders. (b) SEM of milled HEA-TiC powders. (c, d) EBSD inverse pole figure maps of sintered HEA and HEA-TiC. (e) Compressive stress-strain curves. (f) True stress-strain and strain-hardening curves. (g) Transmission electron microscopy of 2%-deformed HEA-TiC showing dislocations at the TiC/FCC interface. (h) Dislocation bowing at the TiC/FCC interface [57].

properties.

Thus, powder metallurgy is an effective method for producing composite structures. By incorporating fine, stable particles in HEAs, it impedes dislocation motion and promotes grain refinement, resulting in increased yield strength, hardness, thermal stability, and superior wear resistance.

3.3. Heterogeneous structures

In general perspective, enhancing strength without compromising ductility highlights the importance of microstructural engineering in alloys. Consequently, various methods are now available to optimize the microstructure of CoCrFeNiMn high-entropy alloys (HEAs) to meet the demands of a wide

range of industrial applications. Former studies reported that conventional ingot metallurgy associated with severe plastic deformation (SPD) and subsequent annealing methods exhibit uni-dimensional or partially bi-modal structures, which exhibits uncertainty between strength and ductility due to lack of controlling fraction of coarse- and fine-grained regions and their spatial distribution [58]. To overcome the strength and ductility trade-off synergy, developing heterogeneous microstructures such as harmonic structure, bimodal grain structures, lamellar structures have emerged as promising in designing advanced materials. In homogeneous materials, strength is typically enhanced through conventional mechanisms like solid solution strengthening, precipitation hardening, dislocation

hardening, and grain boundary strengthening. However, the outstanding strength and ductility observed in heterogeneous structure materials cannot be fully explained by these traditional methods alone. In heterogeneous materials, the deformation process unfolds in three stages. Initially, both soft and hard domains deform elastically. As plastic deformation starts in the soft domains while the hard domains remain elastic, strain gradients and geometrically necessary dislocations (GNDs) form at the interfaces, generating back-stress that strengthens the soft domains and enhances overall yield strength. In the final stage, both domains deform plastically, with the soft domains taking on higher strain and the hard domains experiencing increased flow stress. This results in strain partitioning and further strengthening due to back-stress, improving both strength and ductility in heterogeneous structure materials [59]. The deformation behavior of heterogeneous materials is graphically represented in Fig. 5.

3.3.1. Harmonic structures

The harmonic structure (HS), which includes coarse-grained areas within a three-dimensional ultra-fine-grained shell, is an effective design strategy for enhancing the strength and ductility of metallic materials. Conventional thermo-mechanical processes, such as cold rolling and annealing, often result in uni-dimensional or bi-dimensional structures with difficult control over hard and soft domains, leading to anisotropy and variability in mechanical properties. Thus, PM combined with mechanical milling is the most convenient method to produce HS via controlled milling parameters with low cost. Originally, atomized HEA exhibits poor strength with good elongation. To enhance the strength and ductility of HEAs, some of the recent studies developed harmonic structure using the atomized powders by controlling the milling time and speed. In a previous

study [60], HS was developed in CoCrFeMnNi HEA by adjusting milling time, starting with atomized HEA powder. To observe the morphological changes of powders, SEM analysis was carried out for the initial (Type A) and harmonic structured (Type B and C) HEA powders. The as-atomized HEA powders were spherical with an average size of 97 μm (Fig. 6a). After optimizing high-energy milling to develop a harmonic structure, the powders became coarser. After milling for 90 minutes, powder particles first refined through fracturing but later coarsened due to cold welding, forming a gradient structure with surface-to-interior deformation (Fig. 6b). Further increasing milling time to 120 minutes refined the surface layers, resulting in a finer microstructure at the powder boundaries, as shown in Fig. 6(c). After sintering by SPS, the microstructures of homogeneous and harmonic structured HEAs were examined. It was observed that Type A HEA showed closely packed powder boundaries with no porosity (Fig. 6d). Besides, Types B and C HEAs differ from the homogeneous Type A HEA by having soft coarse-grained cores with hard fine-grained shells (Fig. 6e and f). Additionally, Types B and C vary in the size and distribution of these regions. In Type C HEA, the fine-grained regions at the powder boundaries are more pronounced than in Type B HEA, due to a higher fraction of fine-grained regions resulting from increased milling time. This variation is influenced by the degree of plastic deformation during powder processing. Soft coarse grains enhance ductility by allowing dislocation motion, while hard fine grains improve strength by hindering dislocation movement. The original Type A HEA bulk displays a homogeneous microstructure with an average grain size of approximately 30 μm [46]. To investigate the gradient microstructure from the surface to the center of the powder, EBSD analysis was conducted (Fig. 6g). It has been observed that the grain size decreases from the center to the interface due to plastic deformation, with fine-grained regions outlined by white dotted lines. The magnified EBSD images from Fig. 6(g) show detailed microstructural changes at the center and interface, as seen in Fig. 6(h) and (i), respectively. The center region consists of coarse-grained structures with an average grain size of approximately 20 μm , while the surrounding regions contain fine-grained structures with an average grain size of around 4 μm . The interface thickness for the type C HEA is about 150 μm , which is larger than that of type B HEA (~90 μm). A thicker interface along with smaller grain sizes may contribute to enhanced strength in the HEA by promoting grain boundary strengthening. Moreover, the significant difference in grain size from center to interface develops mechanical incompatibility,

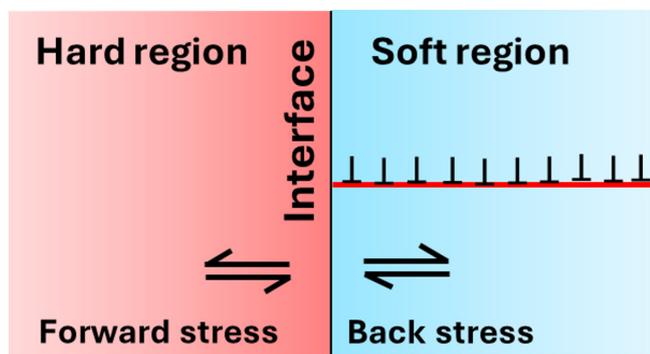


Fig. 5. Strengthening mechanism of a heterogeneous structure [59].

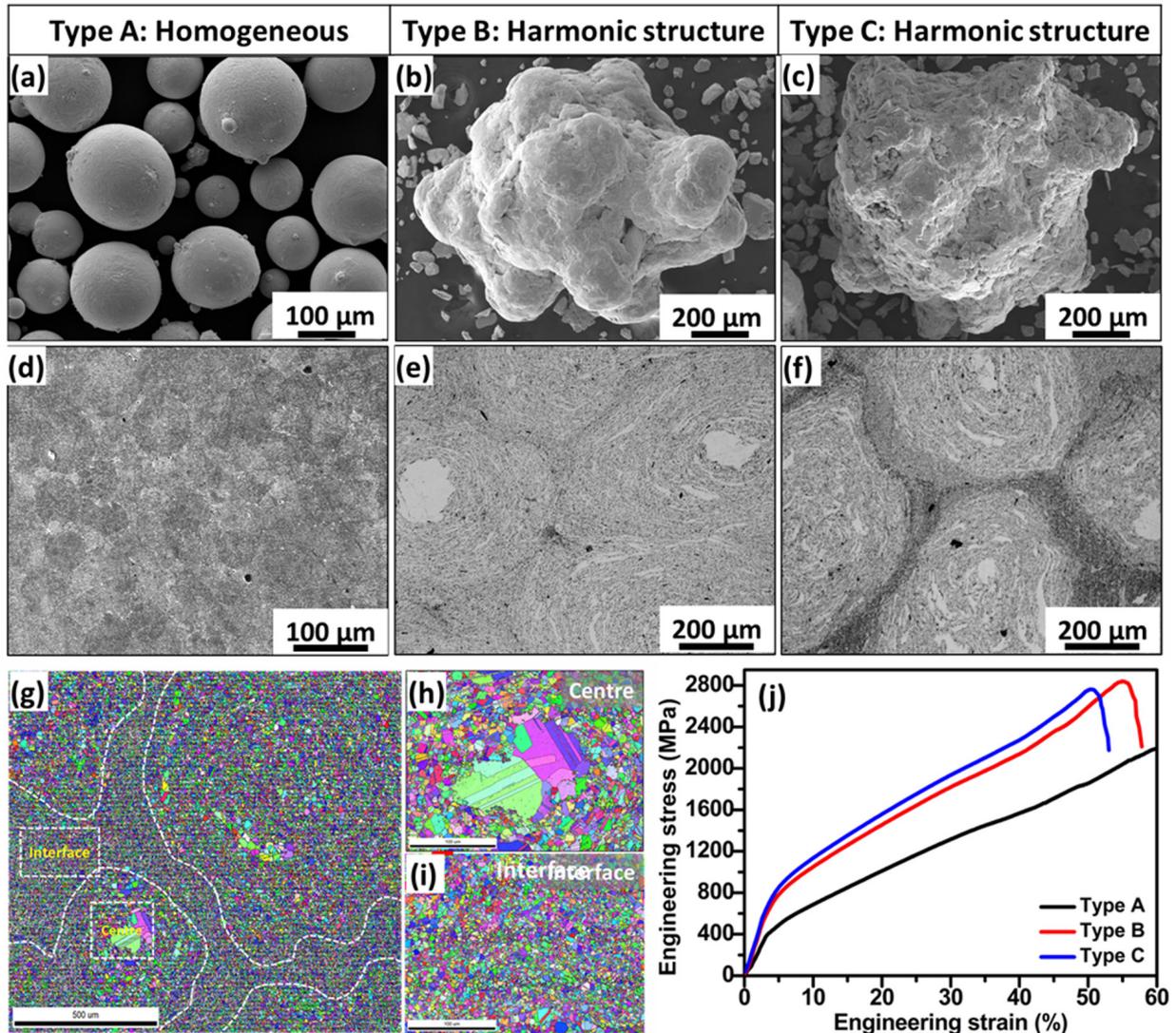


Fig. 6. (a) Scanning electron microscopy (SEM) images of as-atomized CoCrFeMnNi high-entropy alloy (HEA) powder (type A). (b, c) SEM of bimodal powders from 90 min (type B) and 120 min (type C) milling. (d-f) Corresponding SPS-fabricated bulks. (g) EBSD inverse pole figure (IPF) image showing harmonic structure in type C HEA, (h, i) Magnified IPF images from center and interface of type C, (j) Compressive stress–strain curves for homogeneous vs. harmonic structures [60].

resulting in back stress during deformation. Consequently, Fig. 6(j) shows the HS HEAs with higher compressive yield strength (CYS) than homogeneous structures. Type A HEA has a CYS of 370 MPa and a strain > 60%. Type B and C HEAs have CYS values of ~730 MPa and ~760 MPa, with fracture strains of ~56% and ~51%, respectively. Type C HEA offers slightly better CYS and lower fracture strain than Type B, due to its higher proportion of fine grains at the interface. Similarly, harmonic structure was developed in various alloys such as SUS304L steel [61], Co-Cr-Mo [62], pure Ni [63], and copper [64] and FeMn-CoCr [65] by controlling the milling parameters. On the other

hand, Banik et al. [66] investigated how harmonic structures affect the wear behavior of CoCrFeMnNi HEA processed by powder surface deformation and subsequent SPS. They found that this HEA offers better wear resistance compared to 304 L stainless steel and maraging steel under low applied loads. However, its wear resistance decreases at higher loads due to the removal of fine grains. Wang et al. [67] found that the core-shell network structure of CoCrFeMnNi HEA improves corrosion resistance over traditional coarse-grained or ultrafine-grained structures. They found that a shell fraction of around 30% provides the best corrosion resistance. From the

literature survey, it is noteworthy that developing HS in HEAs is advantageous for enhancing strength and ductility.

3.3.2. Bimodal structure

Grain refinement is an efficient method to enhance strength of HEAs but typically reduces ductility. To address this, developing bimodal microstructures with both fine and coarse grains can improve both strength and ductility [68]. Thus, PM is a useful method for achieving these optimal microstructures in HEAs. It is known that PM involves severe plastic deformation through mechanical milling to produce ultrafine or nano-sized powders, which are then combined with coarse powders in specific ratios before consolidation. For example, Lee et al. [69] developed a bimodal grain structure by using gas-atomized CoCrFeMnNi HEA powders by mixing coarse and fine powder. The powders were mixed in a low-energy mixer using mass ratios of coarse to fine powders such as 1:9, 2:8, 4:6, 6:4, and 8:2. The mixing process of coarse and fine powders was

schematically represented in Fig. 7(a and b). The mixed powders were then sintered using SPS, corresponding microstructures with coarse to fine powders as 1:9, 2:8, 4:6, 6:4, and 8:2 mass ratios, as shown in Fig. 7(c-g), respectively. The grain size was affected by the initial powder size, with a higher proportion of coarse powder resulting in larger grain size. By mixing fine powders with coarse powders improved interfacial bonding, resulting in a pore-free microstructure. To demonstrate the effect of the bimodal microstructure with varying mass ratios of coarse to fine particles, the tensile strength and ductility results are shown in Fig. 7(h). The results showed that adding coarse-to-fine particles with a mass ratio of 2:8 showed the highest yield strength of 491.95 MPa and an elongation of 19.64%. Further increasing the proportion of coarse particles beyond this ratio led to a decrease in strength. However, the strength remained higher (~41%) than that of fine grained CoCrFeMnNi HEA. The significant strength enhancement in the bimodal structure is mainly due to the optimized balance between dislo-

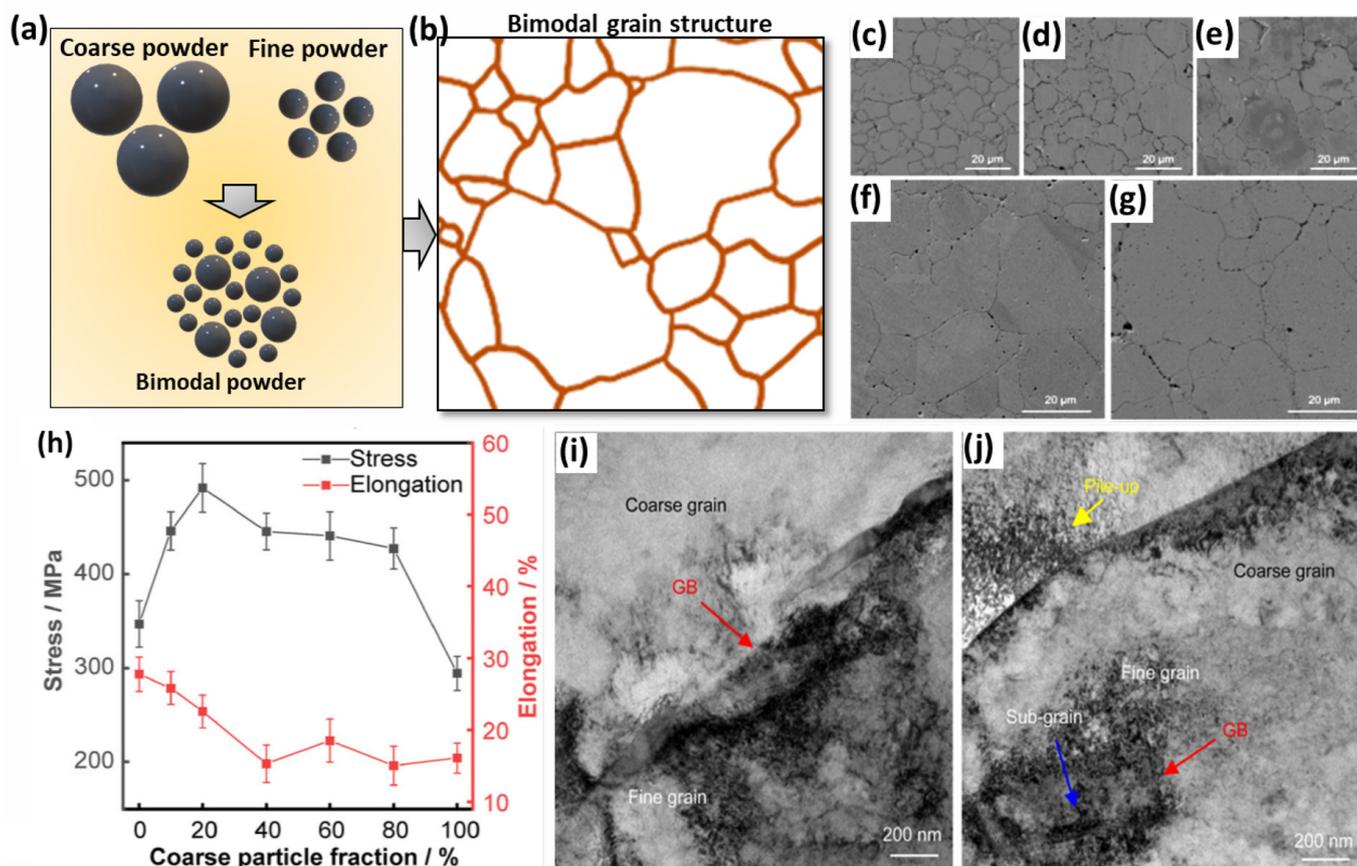


Fig. 7. (a) Fabrication of bimodal grain structure in CoCrFeMnNi high-entropy alloy (HEA) via powder mixing. (b) Schematic of bimodal structure. (c-g) Scanning electron microscopy images of microstructures with coarse powder ratios: (c) 1:9, (d) 2:8, (e) 4:6, (f) 6:4, (g) 8:2. (h) Tensile strength and elongation with different ratio of coarse particles, (i) Transmission electron microscopy images at 3% and (j) 5% deformation of bimodal CoCrFeMnNi HEA [69].

cation movement and grain boundary strengthening. In the bimodal microstructure, fine grains make it more difficult to introduce new dislocations, contributing to higher yield strength. Thus, the 2:8 coarse-to-fine particle ratio proves to be the optimal configuration. This ratio not only promotes dislocation introduction but also maintains a favorable balance between the strengthening effect of fine grains and the ductility offered by coarse grains. However, the bimodal HEA exhibited an unexpected trend: strength increased noticeably, while elongation decreased with the introduction of coarse grains. In particular, the elongation slightly increased with the addition of coarse to fine particles at ratio of 6:4 even though strength reduced. This differs from typical bimodal structure produced by conventional melting methods with homogeneous microstructure that usually exhibits highest elongation. In contrast, PM involves sintering, which can result in porosity and weaker intergranular bonding due to the limited driving force for sintering in coarse particles, restricting particle migration and reducing the contact area between particles. The decrease in elongation in PM HEAs with the addition of coarse particles is therefore attributed to these microstructural differences and residual stresses. To assess the strengthening effect of the bimodal structure, electron channeling contrast imaging and TEM analyses were performed on the 2:8 sample after 3% and 5% deformation. After tensile deformation under 3% strain, coarse particles had low dislocation density, while fine particles had significantly higher density (Fig. 7i). Under 5% strain, dislocation densities increase in both coarse and fine particles, with fine particles showing a marked increase and the formation of dislocation cells (Fig. 7j). It has been observed that dislocations accumulated at the grain boundaries with an increasing tensile strain. The formation of dislocation cells, which hindered dislocation movement, acted like grain boundary strengthening. Dislocations accumulated mainly at the boundaries of coarse grains, enhancing strength by effectively suppressing plastic deformation, especially in fine grains. The dislocation density in bimodal HEAs with a 2:8 ratio was five times higher compared to that in sintered HEAs with fine powders. In another study, a bimodal grain structure was developed by Xiang et al. [70] achieved by incorporating nanoscale grains from the TiZrNbTa HEA into pure Ti with a coarse grain size. The homogeneous mixing of fine and coarse powders offers high strength from fine particles due to their blocking of dislocation mobility, while the coarse particles contribute to ductility and toughness by passing through the dislocation mobility. By carefully controlling the PM process, materials with bimodal microstructures can be engineered to pro-

vide superior performance for a wide range of applications. As a result, yield strength of 1426 ± 30 MPa, a fracture strength of 2133 ± 88 MPa, and an acceptable compressive strain of $22.3\% \pm 1.8\%$. It has been demonstrated that heterogeneous structures enhance strength and ductility through HDI strengthening, which results from mechanical incompatibility between hard and soft regions. This HDI stress comes from the combined effects of back stresses and forward stresses caused by dislocation pile-up and accumulation [71]. Moreover, similar behavior was observed in various heterogeneous structures, such as FeMnCoCr HEA processed by cold deformation and annealing [72] multigradient heterostructured CoCrFeMnNi HEAs using laser deposition on highly deformation [73] and lamellar heterogeneous $\text{Fe}_{34.95}\text{Ni}_{27.5}\text{Co}_{17.5}\text{Al}_{11.5}\text{Cr}_{8.5}\text{B}_{0.05}$ HEA through thermomechanical process. From these results, it has been observed that bimodal grain structure tunes mechanical properties by combining the advantages of fine and coarse grains. Fine grains enhance strength through grain boundary strengthening, while coarse grains improve ductility and toughness by providing more room for plastic deformation. This structure optimizes overall toughness, fatigue resistance, and controlled deformation behavior, resulting in a material with a balanced combination of strength and ductility suitable for various applications.

3.3.3. Multi-metal lamellar composite structures

Recently, multi-metal composites have gained significant attention in materials engineering to address the long-standing strength-ductility trade-off. The conventional methods including grain refinement and work hardening enhance the strength but often reduce ductility. To address this, the development of multi-metal lamellar composites consisting of soft and hard layers with mechanical incompatibility $> 100\%$ have drawn great attention. These materials exhibit superior mechanical properties that surpass those predicted by the rule of mixtures, which typically estimates composite properties based on the average of its constituents. The strengthening of heterogeneous lamellar structures comes from the interaction between soft and hard regions during deformation. As the soft regions plastically deform, constrained by the still-elastic hard regions, strain gradients form, generating geometrically necessary dislocations (GNDs) at the interfaces. This constraint and increased dislocation activity lead to enhanced strength and toughness, giving HLS superior mechanical properties over homogeneous materials. For example, Karthik et al. [74] prepared a multi-metal lamellar composite using HPT. The multi-metal

composite consists of CoCrFeMnNi and Inconel 718 reinforcement, indicating a well-bonded interface and ultra-fine grains, which was confirmed by STEM image (Fig. 8a). TEM micrographs of CoCrFeMnNi HEA annealed at 700 °C show a partially recrystallized structure, with some grains displaying annealing twins and others retaining high dislocation densities. Additionally, the brittle σ -phase was observed at grain boundary triple junctions (Fig. 8b). In CoCrFeMnNi HEA, the formation of the σ -phase may be due to local chemical fluctuations or segregation, suggesting that phase stability in HEA can be influenced under certain conditions. Further Fig. 8(c) shows the TEM micrographs of the IN718 showed ultra-fine grains with high dislocation densities in the 700 °C samples. Further, EBSD IPF maps (Fig. 8d) show a uniform equiaxed grain structure at the CoCrFeMnNi/IN718 interface after annealing, indicating a stable interface with no new phases up to 700 °C. Fig. 8(e) shows the tensile stress-strain curves of multi-metal composites processed by HPT and post heat treatment at 700 and 800 °C

for 1 h. The as-HPT samples had very high strength (~1800 MPa) but no ductility due to high dislocation density. Annealing improved ductility, with samples treated at 800 °C achieving a yield strength of ~900 MPa, an ultimate tensile strength of ~920 MPa, and an elongation of ~40%, effectively overcoming the traditional strength-ductility trade-off. The CoCrFeMnNi-IN718 multi-metal lamellar composite outperformed the monolithic CoCrFeMnNi alloy and most other multi-metal composites (Fig. 8f), showing an excellent balance of strength and ductility.

It has been demonstrated that developing multi-metal lamellar composites through HPT followed by annealing results in a uniform grain size distribution and enhanced interfacial bonding. This approach ensures consistent material properties and improvement in structural integrity.

3.3.4. Thermal Mechanical Processing.

It has already been mentioned that HPT can be used to refine

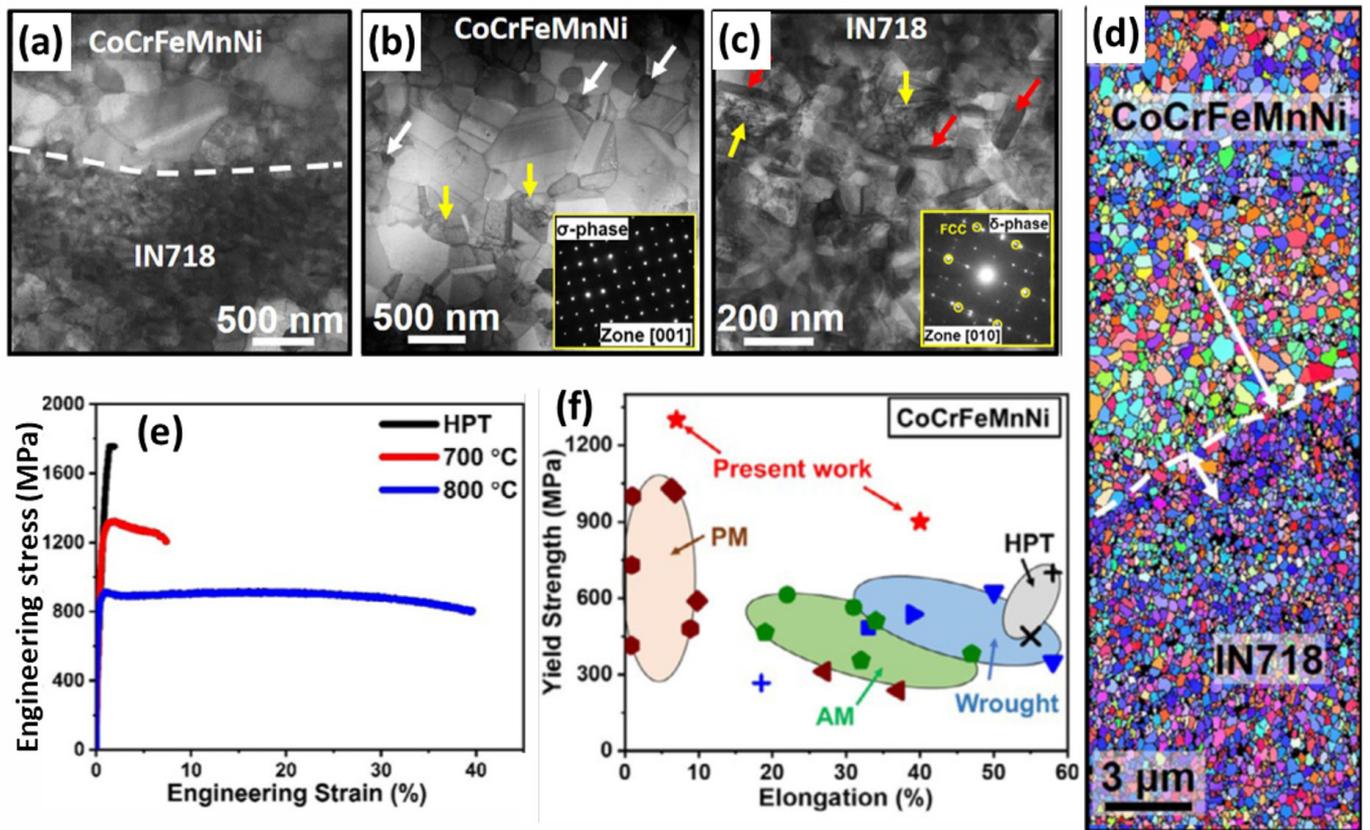


Fig. 8. (a) Scanning transmission electron microscopy (STEM) micrographs of CoCrFeMnNi-IN718 multi-metal composite after high-pressure torsion annealed at 700 °C for 1 h (b) CoCrFeMnNi high-entropy alloy (HEA) bulk showing σ -phase, (c) IN718 and (d) EBSD map of the CoCrFeMnNi/IN718 interface; (f) IN718 bulk showing δ -phase. Insets in (e) and (f) show electron diffraction patterns. (e) Tensile stress-strain plots of the composite. (f) Yield strength vs. elongation compared to monolithic CoCrFeMnNi HEA [74].

the microstructure by applying large strains, which enhances the strength of HEAs [75]. Conducting HPT at ambient temperature helps prevent grain growth and oxidation issues associated with high-temperature sintering. This method effectively densifies materials and overcomes traditional milling and sintering limitations. Recently, Asghari-Rad et al. [76] and his team showed that room-temperature densification and nano-structuring of CoCrFeMnNi HEA powder can be achieved with HPT followed by annealing. Firstly, atomized HEA powder was pre-compacted into disks by HPT at 5 GPa for four turns, and then annealed at 700 °C and 800 °C, which can be schematically presented in Fig. 9(a). Fig. 9(b) shows the XRD patterns of atomized HEA powder, indicating a single-phase FCC structure. After one turn of HPT, the FCC peaks broad-

ened due to strain and grain refinement, and after four turns, a BCC peaks appeared, indicating a martensitic transformation. In Fig. 9(c), TEM image of four turns HPT HEA showed a nanocrystalline structure with an average grain size of about 40 nm. The inset of selected area electron diffraction (SAED) pattern confirms the presence of FCC and BCC-martensite phases. Fig. 9(d) shows the dark-field TEM image obtained from the BCC spot shows the distribution of BCC-martensite in the structure. Fig. 9(e) provides a high-resolution (HR)-TEM image of a grain, while Fig. 9(f) shows that the FFT patterns reveal FCC structure in the grain interiors and a mix of FCC and BCC phases at the grain boundaries. The HPT-processed samples were annealed under various conditions to refine their microstructure and enhance tensile properties. The EBSD IPF

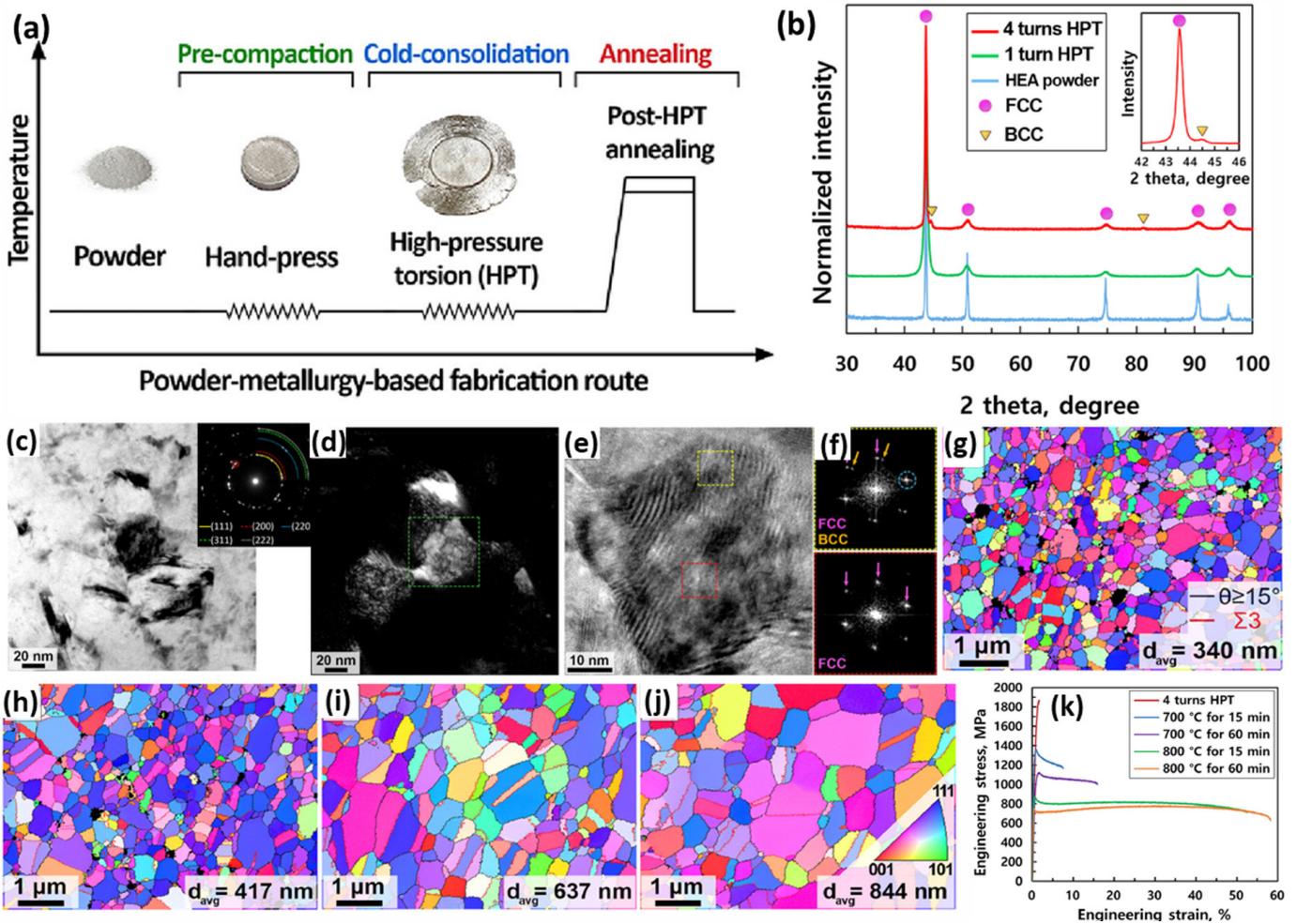


Fig. 9. (a) Fabrication of CoCrFeMnNi HEA by high-pressure torsion (HPT) and post annealing. (b) X-ray diffraction patterns of the HEA powder and HPT-processed HEAs. (c) Bright-field transmission electron microscopy (TEM) image of the four-turns HPT-processed HEA with selected area electron diffraction patterns, (d) Dark-field TEM image, (e) HR-TEM image, and (f) FFT patterns of the marked areas in (e). EBSD-inverse pole figure maps of the post-HPT annealed samples; Annealed at (g) 700 °C for 15 min, (h) 700 °C for 60 min, (i) 800 °C for 15 min, (j) 800 °C for 60 min and (k) Tensile stress-strain curves of the HPT and post-HPT annealed HEAs [76].

maps in Fig. 9(g-j) reveal that annealing at 700 °C for 15 minutes results in an equiaxed microstructure with an average grain size of 340 nm. As the annealing temperature and duration increase, the grain size grows; it reaches 844 nm after annealing at 800 °C for 60 minutes. Moreover, Fig. 9(k) shows the tensile stress-strain curves of HPT and post-HPT annealed HEAs, suggesting four-turn HPT HEA exhibits a high tensile strength of about 1867 MPa, with limited elongation. Post-annealed HEAs showed an increase in ductility but yield strength decreases with temperature due to reduction in dislocation density and grain growth. The formation of sigma phase at 700 °C caused to reduce elongation. The best performance is achieved with annealing at 800 °C for 60 minutes, resulting in a yield strength of 754 MPa and an elongation of 58%, due to its ultra-fine grain structure and high dislocation density.

It is worth mentioning that HPT followed by annealing offers significant advantages for tuning mechanical properties. HPT refines grain size and increases dislocation density, enhancing strength and hardness. Subsequent heat treatment further optimizes the microstructure by relieving internal stresses, controlling grain growth, and managing phase transformations. This combination allows for precise adjustments to properties such as ductility, toughness, and overall workability, making the material suitable for specific engineering applications.

3.3.5 Developing hierarchical microstructure via additive manufacturing

In recent years, powder metallurgy-based additive manufacturing (AM) technology has emerged as a transformative process with numerous industrial advantages, such as reduced processing times, high dimensional accuracy, and minimal material wastage [77]. These benefits make it an ideal method for producing complex metallic parts. Since the physical, chemical, and mechanical properties of AM products are influenced by the feedstock powders, the fabrication of high-quality powders has drawn great attention in materials engineering. Among various powder fabrication routes, gas atomization is a well-established rapid solidification method for producing alloy powders with a spherical shape morphology, narrow size distribution, compositional uniformity, low oxidation risk, and the capability for mass production. These characteristics make gas-atomized powders highly suitable for AM applications, ensuring improved flowability, better packing density, and consistent properties in the final product. Among various AM techniques, binder jetting and powder bed fusion have emerged as promising methods for producing high quality HEAs.

1. Binder Jet Printing: Recently, binder jet printing technique has gained attention in metal additive manufacturing due to its simplicity and high productivity. The method uses binder and metal/ceramic powders as feedstock, with the binder applied to adhere the powder particles at room temperature. The parts are then densified through processes such as curing, sintering, or hot isostatic pressing (HIP). Although BJP is suitable for certain applications, its non-fusion nature limits its use for HEAs, with successful implementations in Al-CoCrFeNi and CoCrFeMnNi alloys [78].
2. Powder Bed Fusion: Powder bed fusion methods like selective laser melting (SLM) and electron beam melting (EBM) utilize focused energy sources to melt powder layer by layer, resulting in dense structures without post-processing. The higher solidification rate in these techniques promotes the formation of finer grain structures and increases dislocation density compared to other methods. By applying focused energy, laser powder bed fusion (LPBF) enables precise control over the microstructure, density, and mechanical properties of HEAs [79].

Thus far, various HEAs have successfully utilized AM technology to produce HEAs with high quality parts and investigated the microstructure and mechanical properties. For example, Zhu et al. [80] successfully developed hierarchical microstructure in CoCrFeMnNi HEA via SLM technique by adjusting the laser power (P : 160–290 W) and scanning speed (V : 1500–2500 mm/s). For this, high quality CoCrFeNiMn HEA powder was fabricated by gas atomization. The morphology of CoCrFeMnNi HEA powder examined by SEM analysis, showing a spherical-shaped powder with an average particle size of 36 μm (Fig. 10(a)). The EBSD inverse pole figure map of the HEA powder in Fig. 10(b) shows a polycrystalline microstructure. The as-built HEA by SLM technique showed a hierarchical structure, including melt pools, columnar grains, sub-micron cellular structures, and dislocations with an average size of $0.34 \pm 0.04 \mu\text{m}$, where the cell walls are decorated with a high density of dislocations and the interiors are clean (Fig. 10(c)). Furthermore, the mechanical properties of the as-built HEA were assessed through stress-strain curves, which demonstrated an excellent balance of strength and ductility, as shown in Fig. 10(d). For instance, the as-built V2000 HEA exhibits a significantly higher yield strength (σ_y) of 510 MPa, nearly twice that of the as-recrystallized counterparts. Post-heat treatment, although σ_y decreases due to the recovery of the cell structures but the ductility improves. The post-mortem bright-field STEM image in Fig. 10(e) reveals an effective dislocation trap-

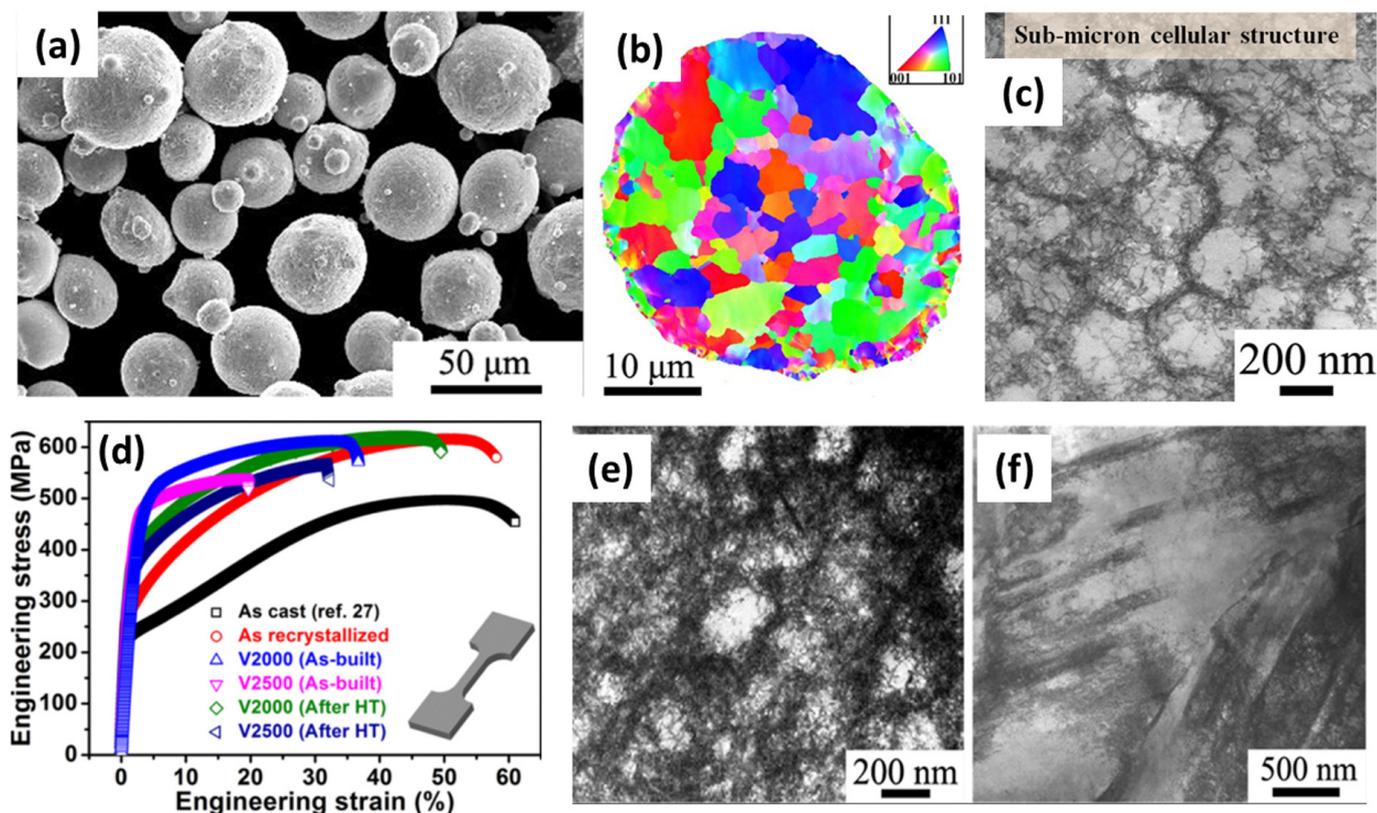


Fig. 10. (a) Morphology of gas atomized CoCrFeMnNi HEA powder (b) EBSD inverse pole figure (IPF) map of the powder, (c) Bright-field scanning transmission electron microscopy (STEM) image showing the cellular structure, (d) Engineering stress–strain curves of the samples under different conditions, and (e and f) show the bright-field STEM images of an as-built sample strained to fracture [80].

ping and retention mechanism within the cells, leading to an increased dislocation density inside the cell walls. Additionally, planar slip bands shown in Fig. 10(f), interact with cellular structures to form a three-dimensional dislocation network. The deformation behavior of the as-built HEA was primarily governed by hierarchical dislocation activities, with deformation twinning also contributing to plastic flow. It has been observed that the fabrication of hierarchical structured CoCrFeMnNi HEA by SLM technique with superior strength and ductility, offering a promising alternative to conventional manufacturing techniques.

4. Conclusions and future directions

In conclusion, PM emerges as a highly effective method for fabricating HEAs with customized microstructure and enhanced mechanical properties. By adapting PM techniques in developing HEAs, overcomes the limitations of traditional melting methods, such as segregation and coarse-grained den-

dritic microstructures. PM offers precise control over microstructural features, including grain size and uniform chemical composition. The review highlights several such as grain refinement through the Hall-Petch effect, dispersion strengthening with fine particles to impede dislocation movement, and the development of heterogeneous microstructures such as harmonic, bimodal, multi-metal lamellar structure and hierarchical structures, significantly enhance the strength and ductility of HEAs, making them more suitable for a wide range of demanding engineering applications. Additionally, thermomechanical treatments, such as HPT followed by annealing is the most effective PM route for further refining grain sizes and tailor microstructural features to enhance mechanical properties. Therefore, PM offers advantages for producing HEAs with optimized properties for demanding engineering applications.

However, the fabrication of novel HEAs remains challenging due to issues like elemental segregation and incomplete alloying, which can lead to the formation of metastable phases. To address these problems, precise control of powder mixing and

sintering parameters is essential for uniform element distribution, effective diffusion, and defect reduction. The mechanical properties of HEAs depend on their phase stability. Controlling phase transformations and avoiding brittle phases during PM processing are key to maintaining high strength and toughness, especially at room temperature. Identifying cost-effective and sustainable alloying elements is crucial for making HEAs more commercially viable for widespread structural applications. Incorporating reinforcement phases can improve HEAs strength at room temperature. To ensure superior mechanical performance, especially at elevated temperatures, it is crucial to optimize particle size, concentration, and bonding between HEAs and nanoparticles. Further investigation into heterogeneous microstructures is essential to balance strength, ductility, and toughness in HEAs. Future research should focus on understanding the mechanisms behind their strengthening and deformation. Utilizing machine learning and computational modeling to predict optimal alloy compositions and microstructures that can improve mechanical properties while reducing trial-and-error experimental methods.

Funding

This work was supported by the National Research Foundation of Korea (NRF) grant funded by the Korea government (MSIT) (No. 2021R1A2C1005478).

Conflict of Interest

The authors declare no competing financial interests or personal relationships.

Data Availability Statement

All data generated or analyzed during this study are included in this published article

Author Information and Contribution

Cheenepalli Nagarjuna, Postdoctoral researcher, conceptualization, formal analysis, investigation, writing - original draft, writing - review & editing. Sheetal Kumar Dewangan: Postdoctoral researcher, formal analysis, investigation. Hansung Lee: Postdoctoral researcher, formal analysis, investigation. Eunhyo Song: Graduate student, formal analysis, investigation. K. Raja Rao: Postdoctoral researcher, formal analysis, investigation.

Byungmin Ahn: Professor, conceptualization, funding acquisition, supervision, writing - review & editing.

Acknowledgments

None.

References

- [1] Q. He, Z. Ding, Y. F. Ye and Y. Yang: *JOM*, **69** (2017) 2092.
- [2] J. Williams and E. Starke Jr: *Acta Mater.*, **51** (2003) 5775.
- [3] M. Lee, J. Lee, D. Bae, W. T. Kim, D. J. Sordelet and D. H. Kim: *Intermetallics*, **12** (2004) 1133.
- [4] A. Inoue: *Acta Mater.*, **48** (2000) 279.
- [5] J. W. Yeh, S. K. Chen, S. J. Lin, J. Y. Gan, T. S. Chin, T. T. Shun, C. H. Tsau and S. Y. Chang: *Adv. Eng. Mater.*, **6** (2004) 299.
- [6] S. Y. Liu, S. Zhang, S. Liu, D. J. Li, Z. Niu, Y. Li and S. Wang: *J. Eur. Ceram.*, **42** (2022) 3089.
- [7] A. Sharma, H. Lee and B. Ahn: *Met. Mater. Int.*, **28** (2022) 2216.
- [8] C. Nagarjuna, S. K. Dewangan, H. Lee and B. Ahn: *Mater. Sci. Eng. A*, **886** (2023) 145680.
- [9] Y. Lv, R. Hu, Z. Yao, J. Chen, D. Xu, Y. Liu and X. Fan: *Mater. Des.*, **132** (2017) 392.
- [10] T. Gu, L. M. Wang, Q. Hu, X. B. Liang, D. X. Fu, Y. X. Chen, X. M. Zhao and Y. W. Sheng: *Met. Mater. Int.*, **28** (2022) 2571.
- [11] E. P. George, W. A. Curtin and C. C. Tسان: *Acta Mater.*, **188** (2020) 435.
- [12] Z. Han, W. Ren, J. Yang, Y. Du, R. Wei, C. Zhang, Y. Chen and G. Zhang: *J. Alloys Compd.*, **791** (2019) 962.
- [13] D. B. Miracle and O. N. Senkov: *Acta Mater.*, **122** (2017) 448.
- [14] N. Ali, L. Zhang, D. Liu, H. Zhou, K. Sanaullah, C. Zhang, J. Chu, Y. Nian and J. Cheng: *Mater. Today Commun.*, **33** (2022) 104686.
- [15] M. Chuang, M. Tsai, W. R. Wang, S. J. Lin and J. W. Yeh: *Acta Mater.*, **59** (2011) 6308.
- [16] Y. Zhang, T. T. Zuo, Z. Tang, M. C. Gao, K. A. Dahmen, P. K. Liaw and Z. P. Lu: *Prog. Mater. Sci.*, **61** (2014) 1.
- [17] J. Yeh: *JOM*, **65** (2013) 1759.
- [18] H. S. Oh, S. J. Kim, K. Odbadrakh, W. H. Ryu, K. N. Yoon, S. Mu, F. Kormann, Y. Ikeda, C. C. Tسان, D. Raabe, T. Egami and E. S. Park: *Nat. Commun.*, **10** (2019) 2090.
- [19] M. Moschetti, P. A. Burr, E. Obbard, J. J. Kruzic, P. Hosemann and B. Gludovatz: *J. Nucl. Mater.*, **567** (2022) 153814.

- [20] M. Zamani, H. Mirzadeh, M. Malekan, S. Cao and J. Yeh: *High Entropy Alloys Mater.*, **1** (2022) 25.
- [21] K. Y. Tsai, M. H. Tsai and J. W. Yeh: *Acta Mater.*, **61** (2013) 4887.
- [22] J. Dabrowa, W. Kucza, G. Cieslak, T. Kulik, M. Danielewski and J. W. Yeh: *J. Alloys Compd.*, **674** (2016) 455.
- [23] Y. Y. Tan, Z. J. Chen, M. Y. Su, G. Ding, M. Q. Jiang, Z. C. Xie, Y. Gong, T. Wu, Z. H. Wu, H. Y. Wang and L. H. Dai: *J. Mater. Sci. Technol.*, **104** (2022) 236.
- [24] A. Mehta and Y. Sohn: *J. Phase Equilib. Diffus.*, **43** (2022) 803.
- [25] C. C. Chang, Y. T. Hsiao, C. Y. Tsai, Y. J. Lee, P. H. Ko and S. Y. Chang: *Appl. Surf. Sci.*, **577** (2022) 151894.
- [26] Y. Wu, F. Zhang, X. Yuan, H. Huang, X. Wen, Y. Wang, M. Zhang, H. Wu, X. Liu, H. Wang, S. Jiang and Z. Lu: *J. Mater. Sci. Technol.*, **62** (2021) 214.
- [27] Y. A. Alshataif, S. Sivasankaran, F. Mufadi, A. S. Alaboodi and H. Ammar: *Met. Mater. Int.*, **26** (2019) 3.
- [28] C. Nagarjuna, S. K. Dewangan, A. Sharma, K. Lee, S. J. Hong and B. Ahn: *Met. Mater. Int.*, **29** (2023) 1968.
- [29] M. Vaidya, G. M. Muralikrishna and B. S. Murty: *J. Mater. Res.*, **34** (2019) 664.
- [30] C. Nagarjuna, S. K. Dewangan, H. Lee, K. Lee and B. Ahn: *Vacuum*, **218** (2023) 112611.
- [31] B. S. Murty, J. W. Yeh, S. Ranganathan and P. P. Bhattacharjee: *High-Entropy Alloys*, (2019).
- [32] Y. Lee, C. Nagarjuna, J. W. Song, K. Y. Jeong, G. Song, J. K. Lee, J. H. Lee and S. J. Hong: *Powder Metall.*, **64** (2021) 219.
- [33] C. Han, Q. Fang, Y. Shi, S. B. Tor, C. K. Chua and K. Zhou: *Adv. Mater.*, **32** (2020) 1903855.
- [34] C. Nagarjuna, S. K. Dewangan, K. Lee and B. Ahn: *Powder Metall.*, **66** (2023) 613.
- [35] S. H. Joo, H. Kato, M. J. Jang, J. Moon, E. B. Kim, S.-J. Hong and H. S. Kim: *J. Alloys Compd.*, **698** (2017) 591.
- [36] W. Ji, W. Wang, H. Wang, J. Zhang, Y. Wang, F. Zhang and Z. Fu: *Intermetallics*, **56** (2015) 24.
- [37] P. Dai, A. Li, T. Tu, L. Yang, X. Luo, C. Wang and X. Lv: *J. Mater. Res. Technol.*, **26** (2023) 4871.
- [38] M. Kang, M. S. Rizi, S. J. Jo, M. Ebrahimian, H. Nersisyan, J. H. Lee, J. Moon, H. S. Kim and S. J. Hong: *J. Alloys Compd.*, **1010** (2025) 177494.
- [39] Y. Liu, Y. He and S. Cai: *Mater. Sci. Eng. A*, **801** (2021) 140429.
- [40] H. Shahmir, P. Asghari-Rad, M. S. Mehranpour, F. Forghani, H. S. Kim and M. N. Ahmadabadi: *Mater. Sci. Eng. A*, **807** (2021) 140875.
- [41] J. Moon, Y. Qi, E. Tabachnikova, Y. Estrin, W. M. Choi, S. H. Joo, B. J. Lee, A. Podolskiy, M. Tikhonovsky and H. S. Kim: *Sci. Rep.*, **8** (2018) 11074.
- [42] Y. Liu, J. Wang, Q. Fang, B. Liu, Y. Wu and S. Chen: *Intermetallics*, **68** (2016) 16.
- [43] F. Otto, A. Dlouhý, C. Somsen, H. Bei, G. Eggeler and E. P. George: *Acta Mater.*, **61** (2013) 5743.
- [44] B. Schuh, R. Pippan and A. Hohenwarter: *Mater. Sci. Eng. A*, **748** (2019) 379.
- [45] H. Shahmir, T. Mousavi, J. He, Z. Lu, M. Kawasaki and T. G. Langdon: *Mater. Sci. Eng. A*, **705** (2017) 411.
- [46] C. Nagarjuna, K. J. Jeong, Y. Lee, S. M. Woo, S. I. Hong, H. S. Kim and S. J. Hong: *Adv. Powder Technol.*, **33** (2022) 103519.
- [47] W. Ji, W. Wang, H. Wang, J. Zhang, Y. Wang, F. Zhang and Z. Fu: *Intermetallics*, **56** (2015) 24.
- [48] M. L. Brocq, P. A. Goujon, J. Monnier, B. Villeroy, L. Perrière, R. Pirès and G. Garcin: *J. Alloys Compd.*, **780** (2019) 856.
- [49] G. Tang, J. Yang, Z. Huang, J. Li, M. Yang, H. Hu and Z. Liang: *J. Alloys Compd.*, **1014** (2025) 178853.
- [50] X. D. Xu, P. Liu, A. Hirata, S. X. Song, T. G. Nieh and M. W. Chen: *Materialia*, **4** (2018) 395.
- [51] M. Nagini, R. Vijay, K. V. Rajulapati, A. V. Reddy and G. Sundararajan: *Mater. Sci. Eng. A*, **708** (2017) 451.
- [52] K. R. Rao, S. K. Dewangan, A. H. Seikh, S. K. Sinha and B. Ahn: *Met. Mater. Int.*, **30** (2024) 726.
- [53] H. Hadraba, Z. Chlup, A. Dlouhy, F. Dobes, P. Roupčova, M. Vilemova and J. Matejicek: *Mater. Sci. Eng. A*, **689** (2017) 252.
- [54] L. Rogal, D. Kalita and L. Lityńska: *Intermetallics*, **86** (2017) 104.
- [55] J. Xiao, H. Tan, J. Chen, A. Martini and C. Zhang: *J Alloy Compd.*, **847** (2020) 156553.
- [56] R. Ravi and S. R. Bakshi: *J Alloy Compd.*, **883** (2021) 160879.
- [57] D. Yim, P. Sathiyamoorthi, S. J. Hong and H. S. Kim: *J. Alloys Compd.*, **781** (2019) 389.
- [58] B. Srinivasarao, K. Oh-ishi, T. Ohkubo, T. Mukai and K. Hono: *Scr. Mater.*, **58** (2008) 7599.
- [59] Y. Zhu and X. Wu: *Mater. Res. Lett.*, **7** (2019) 393.
- [60] C. Nagarjuna, J. W. Song, K. Y. Jeong, M. W. Pin, G. Song, J. K. Lee, Y. S. Na, H. S. Kim, K. B. Kim and S. J. Hong: *J. Mater. Res. Technol.*, **17** (2022) 1686.
- [61] Z. Zhang, S. K. Vajpai and D. Orlov: *Mater. Sci. Eng. A*, **598** (2014) 106.

- [62] S. K. Vajpai, C. Sawangrat and O. Yamaguchi: *Mater. Sci. Eng. C*, **58** (2016) 1008.
- [63] M. Nagata, N. Horikawa, M. Kawabata and K. Ameyama: *Mater. Trans.*, **60** (2019) 1914.
- [64] C. Sawangrat, S. Kato, D. Orlov and K. Ameyama: *J. Mater. Sci.*, **49** (2014) 6579.
- [65] G. Li, M. Liu, S. Lyu, M. Nakatani, R. Zheng, C. Ma, Q. Li and K. Ameyama: *Scr. Mater.*, **191** (2021) 196.
- [66] D. Banik, S. Mukherjee, H. Fujiwara, K. Ameyama and K. Mondal: *Wear*, **534–535** (2023) 205125.
- [67] J. Wang, Z. Zhang, H. Dai, H. Fujiwara, X. Chen and K. Ameyama: *Corros. Sci.*, **209** (2022) 110761.
- [68] B. Schuh, F. Mendez-Martin, B. Völker, E. P. George, H. Clemens, R. Pippan and A. Hohenwarter: *Acta Mater.*, **96** (2015) 258.
- [69] J. Lee, S. Kim, T. Kwon, Y.I. Kim, S. Kim, S. H. Song, B. Lee and D. Lee: *Rare Met.*, **43** (2024) 3893.
- [70] T. Xiang, P. Du, W. Bao, Z. Cai, K. Li and G. Xie: *Mater. Sci. Eng. A*, **849** (2022) 143488.
- [71] S.W. Wu, G. Wang, Q. Wang, Y.D. Jia, J. Yi, Q.J. Zhai, J.B. Liu, B.A. Sun, H.J. Chu, J. Shen, P.K. Liaw, C.T. Liu and T.Y. Zhang: *Acta Mater*, **165** (2019) 444.
- [72] M. S. Rizi, H. Minouei, B. J. Lee, H. Pouraliakbar, M. R. Toroghinejad and S. I. Hong: *Mater. Sci. Eng. A*, **824** (2021) 141803.
- [73] G. H. Gu, E. S. Kim, H. Kwon, S. Son, R. E. Kim, T. G. Oh and H. S. Kim: *Mater. Sci. Eng. A*, **836** (2022) 142718.
- [74] G. M. Karthik, A. R. Peyman, S. Praveen, A. Zargaran, E. S. Kim, T. S. Kim and H. S. Kim: *Scr. Mater.*, **195** (2021) 113722.
- [75] S. Praveen, J. Moon, J. W. Bae, P. Asghari-Rad and H. S. Kim: *Scr. Mater.*, **163** (2019) 152.
- [76] P. Asghari-Rad, S. Praveen, N. T. C, Z. Alireza, T. S. Kim and H. S. Kim: *Scr. Mater.*, **190** (2021) 69.
- [77] Z. Xu, Z. Zhu, P. Wang, G. K. Meenashisundaram, S. M. L. Nai and J. Wei: *Addit. Manuf.*, **35** (2020) 101441.
- [78] D. Karlsson, G. Lindwall, A. Lundbäck, M. Amnebrink, M. Boström, L. Riekehr, M. Schuisky, M. Sahlberg and U. Jansson: *Addit. Manuf.*, **27** (2019) 72.
- [79] L. He, S. Wu, A. Dong, H. Tang, D. Du, G. Zhu, B. Sun and W. Yan: *J. Mater. Sci. Technol.*, **117** (2022) 133.
- [80] Z. G. Zhu, Q. B. Nguyen, F. L. Ng, X. H. An, X. Z. Liao, P. K. Liaw, S. M. L. Nai and J. Wei: *Scr. Mater.*, **154** (2018) 20.

Code of Ethics for the Journal of Powder

Established: 2007. 10. 23

Full Text

First published in April 1994, with the purpose for the revitalization of technical exchange between Academics & Industry in Powder Metallurgy related advanced studies. Journal of Powder Materials is currently published on a bi-monthly basis.

The Korean Powder Metallurgy & Materials Institute has prepared a code of ethics for a qualitative improvement to its journal. We can therefore secure the ethics required for scientific research through this code of ethics; and we intend to raise the value of our journal through the addition of originality and integrity to our journal. Therefore, all authors of theses, review committee members and editorial committee members shall observe this code of ethics in order to reject any dishonesty in the publication of theses and secure the integrity of any research.

Chapter 1. Matters to be observed by the author of thesis

1. The criteria of the authorship

The Author of academic paper means a person who meets all of the following criteria for authorship (based on the criteria of International Committee of Medical Journal Editors). Those who are not satisfied with any of the following criteria shall be divided into "contributor".

- A. Substantial contributions to the conception or design of the work; or the acquisition, analysis, or interpretation of data for the work.
- B. Drafting the work or revising it critically for important intellectual content.
- C. Final approval of the version to be published.
- D. Agreement to be accountable for all aspects of the work in ensuring that questions related to the accuracy or integrity of any part of the work are appropriately investigated and resolved.

2. The duty of the author

The author of thesis shall explain the results and discussions of the research which the author has performed in a concise and

accurate manner. When submitting the research results to the Journal of Powder Materials, an author of a thesis shall observe the code of ethics of this institute and conform to the honesty, accuracy and integrity of the research result submitted as such.

- A. When submitting a thesis to the Journal of Powder Materials, the author of a thesis shall abide to the code of ethics as outlined by the Journal of Powder Materials
- B. The author of a thesis shall reject any fabrication or falsification of the results for conducting all activities including the proposal, planning and execution of the research activities.
- C. Submittal or publishing the same result to more than one journal simultaneously shall be regarded as an act of cheating and as such shall be eradicated.
- D. The author of a thesis shall not submit and publish research results which were already published to this Journal.
- E. An act of submitting another researcher's results under his/her own name shall be deemed as unethical and unacceptable.
- F. An author who has submitted a thesis shall obtain proper consent from all existing co-authors and shall not include any inappropriate authors to the thesis. Co-authors shall contribute to the research academically and share the responsibility and achievements for the results altogether, and in the case of administrative and financial support for research, such shall be advised to state details through an "Acknowledgement".
- G. An author of thesis shall obtain approval from the person concerned in advance with regards to submission if required, and confirm that there will be no future disputes of agreements and ownership.
- H. The author of the thesis shall observe the regulations as provided in relevant laws, norms and as stated in the code of ethics; and to internationally accepted principles of the entire process of research and submission. Also, the author of such thesis shall also secure universality including the respect of human rights, the observation of bioethics, and the preservation of biological diversity and protection

for environments.

- I. In the case of an error discovered in a submitted thesis during the publication process, the author of such thesis shall be obligated to correct any mistakes or withdraw the thesis altogether.

Chapter 2. Matters to be observed by the reviewer

The journal reviewer shall review a submitted thesis in compliance with this code of ethics and provide advice in regards to the publication of such thesis to the editorial committee members.

- A. The journal reviewer shall review a submitted thesis fairly and objectively under consistent standards regardless of ethnicity, gender, religion, educational environment or acquaintance of the author of thesis.
- B. The journal reviewer shall be obligated to review a thesis requested for review faithfully within the set period as determined in the review regulations.
- C. The journal reviewer shall not disclose the information of the research results acquired through the review process to any third party or misuse such information.
- D. The journal reviewer shall respect the personality of the author of the thesis and value the independence of intellectual ability. The journal reviewer shall prepare an amicable and supplementary written opinion without making subjective evaluations and shall avoid hostile expressions.
- E. The journal reviewer shall request the author of the thesis to modify any inappropriate quoted contents and lead the author to quote references correctly. Also, the journal reviewer shall strictly review the thesis to determine if such has any similarity with previous published manuscripts that were presented in other publications.
- F. The journal reviewer shall be obligated to reject review in the case of having any connection with the submitted thesis. The journal reviewer shall promptly notify such fact to the editorial committee members to appoint another journal reviewer.

Chapter 3. Matters to be observed by the editorial committee member

The editorial committee member shall retain full responsibility and authority to carry out the procedures to approve or reject a

submitted thesis for publication in the journal. Each editorial committee member shall cooperate with the journal reviewer and other editorial committee members shall observe and carry out the following items.

- A. The editorial committee member shall fairly evaluate the intellectual level of a thesis as submitted by the author regardless of ethnicity, gender, religion, educational environment or acquaintance of the author of a thesis.
- B. The editorial committee member shall not delay the screening of a submitted thesis intentionally and shall perform prompt measures accordingly.
- C. The editorial committee member shall screen the submitted thesis objective based on consistent standards, and the editorial committee member shall assume full responsibility and obligation for the required procedures.
- D. The editorial committee member shall not release information regarding the submitted thesis to the public and shall not use such information for his/her own research purposes.
- E. The editorial committee member shall be obligated to supervise any unethical behavior in a thesis submitted to the journal, and take any necessary measures for any wrongful acts. In the case of an appeal for wrongful acts, the editorial committee member and the review committee shall be obligated to investigate such matters.
- F. The editorial committee member shall be obligated to reject screening in the case where editorial committee has written the thesis, or such has any connection with the submitted thesis. Another editing committee member shall be appointed for the screening process.

Chapter 4. Activities of the review committee

- A. Clarifying integrity and responsibility of the research results – In the case where cheating has occurred, including plagiarism, duplicated submission or inappropriate citation is suspected, an investigation shall be carried out based on the editorial committee members recommendation. The author of such thesis shall be responsible for any cheating including plagiarism, fabrication and falsification and duplicated presentation of the result.
- B. In the case where any cheating is suspected in the process of a thesis submission and review, the editorial committee member shall submit such to the review committee and

request the review committee to investigate such in private. The review committee shall then carry out an inspection in compliance with the following guidelines to ensure that no victim shall suffer in good faith.

1. The review committee shall observe "the principle of presumption of innocence" until such is proven to be a wrongful act.
 2. The review committee shall begin and perform such inspection fairly and without discrimination in private circumstances.
 3. The review committee shall prepare, arrange and store documents in regards to the investigation.
 4. The review committee shall suspend all process in regards to the thesis publication.
 5. The review committee shall carry out an investigation promptly to reduce any damages due to delay.
- C. The review committee shall carry out an investigation promptly and fairly at the editorial committee member's request. The investigation shall notify, carry out and finish based on the following guidelines.
1. The review committee shall notify any beginning of an investigation to the person or organization concerned that is questionable for cheating and also inform such as to any postponing of the publication of such thesis until the investigation is complete.
 2. The review committee shall provide an opportunity for explanation to the person or organization subject to investigation within 30 days of written notice.

3. The review committee shall acquire and investigate any internal records or other publications related with cheating.
4. In the case of unintended mistakes or errors, the review committee shall finish the investigation promptly.
5. In the case where cheating is discovered, the review committee shall supervise measures for such cheating. The review committee shall return the submitted thesis to the author, notify the Institute's guideline to the author, remove or publish the withdrawal of the thesis in the case where such was already published, and restrict the author's thesis publication for 3 years afterwards.
6. In the case of a duplicated submission and publication with a joint publisher, such actions shall be notified to the relevant publisher and handled in conjunction with the relevant publisher.
7. All cases and investigations carried out by the review committee shall be documented and stored. In cases where cheating is not apparent, the relevant document shall be sealed.

Supplementary Provision

1. This code of ethics shall be in effect from October 23, 2007.
2. This Revised code of ethics shall be in effect from March 6, 2020.
3. This Revised code of ethics shall be in effect from February 10, 2022.

Enacted: June 17, 2016

Chapter 1 General Provisions

1. Purpose

The purpose of this guide is to strengthen research ethics by setting the standards, operation, and discipline of research

2. Ethics Committee

- ① The ethics committee of The Korean Powder Metallurgy & Materials Institute will be formed to deliberate and decide on the regulations.
- ② The chair of the Research Ethics Committee shall be the Editor-in-chief of The Korean Powder Metallurgy & Materials Institute Committee. The chair convenes and presides over the Research Ethics Committee when the Editorial Committee proposes an issue as regards research misconduct.
- ③ The Research Ethics Committee shall consist of no more than five members. The committee members are appointed by the president of the society after the recommendation of the Editorial Committee.

Chapter 2 Research Misconduct

3. Subject of Research Misconduct

Research misconduct is directed to articles, documents, and data submitted or published to the Journal of Powder Materials.

4. Simultaneous Submission

Submitted papers may not be submitted to other domestic or foreign academic journals simultaneously, or as a duplicate, regardless of whether it is submitted beforehand or afterwards.

5. Duplicated Publication

- ① Dissertations published in other domestic or foreign academic journals may not be duplicated.
- ② When submitting a research report or a part of a doctoral or a master's thesis as it is, or if it is corrected or supplemented, the correct description must be clearly stated.

6. Plagiarism

- ① Plagiarism is the act of deliberate description of the content of academic ideas, opinions, expressions, and research results already published through all written media, including domestic or foreign journals, academic papers, research reports, master's or doctoral dissertations, books, magazines, and the internet without reference to the source.
- ② Plagiarism also applies when the researcher is the same as the author of the paper already published (self-plagiarism). However, it is not considered plagiarism if it describes widely used academic knowledge or research results without citation.

Forgery and Falsification Forgery or falsification involves the act of intentionally expressing, among others, numerical values and photographs of the data or results used in the research differently from the truth.

1. Forgery is the act of untruthful creation of false data or research results that do not exist.
2. Falsification refers to the act of artificial manipulation of research materials, equipment, processes, or distorting research contents or results by modifying or deleting data arbitrarily.

Chapter 3 Deliberation and Resolution Procedures

8. Judgment of Research Misconduct

- ① If there is a report on research misconduct within or outside the institute, the chair of the Editorial Committee must convene the committee to collect relevant data and confirm the credibility of the report.
- ② When the chair of the Editorial Committee confirms the authenticity of the report, he/she will submit the document of issue to the Research Ethics Committee.
- ③ The chair of the Research Ethics Committee gives the researcher an opportunity to document the proposed issues within two weeks in advance of the hearing.
- ④ The Research Ethics Committee shall make a unanimous

decision on whether there has been a case of research misconduct. If there is a disagreement between the two parties, it shall be decided by a vote of 3/5 of the attending committee members.

9. Discipline and Result Processing

- ① A person who violates research ethics shall be subject to and notified of a disciplinary action through the following measures:
 1. Member expulsion
 2. Prohibition of contributing to the Journal of Powder Metallurgy
 3. If the article is published, the article will be deleted. Papers that are scheduled to be published cannot be published.
 4. Relevant organizations will be notified of ethics violations.
 5. Other disciplinary actions that are deemed necessary
- ② The content of the violated research ethics shall be posted on the homepage after a two-week protest period.
- ③ The contents of the disciplinary action in Items 2, 3, and 5 of Clause 1 shall be notified in the name of the editor-in-chief after the decision of the Research Ethics Committee. The contents of disciplinary action in Items

10. Objection

- ① A researcher who is judged for a research misconduct may file an objection only once within one month from the date of notification, if the decision of the Research Ethics Committee or the reason for misconduct is unreasonable.
- ② The Research Ethics Committee can review or revise the contents of the resolution by deliberating the validity of the objection.

Supplement

1. Amendment, Opening, and Closing of Regulations

This regulation may be amended, opened, or closed through the resolution of the Board of Directors.

2. Effective Date

1. This regulation shall be effective beginning on the date of the Board of Directors' approval (June 17, 2016).
2. This Revised code of ethics shall be in effect from February 10, 2022.

Written Oath of Observance of Research Ethics

Article title: _____

Author name: _____

To Editor-in-chief of the Journal of Powder Materials

I, as a contributor to the Journal of Powder Materials, hereby declare that I have abided by the following Code of Research Ethics of The Korean Powder Metallurgy & Materials Institute while writing this article.

1. I swear that I shall observe The Korean Powder Metallurgy & Materials Institute's Research Ethics Code and regulations related to research misconduct, and have written this article through honest and rigorous research.
2. I swear that I have not published this article elsewhere and have no plan to submit this article in other journals until the deliberation is over.
3. I swear that I have not committed any research misconducts that can be defined as a violation of Research Ethics, such as forgery (falsification), alteration, plagiarism, duplicate publication, etc., that compromises academic integrity.
4. I swear that I acknowledge the legitimate efforts of participating researchers and did not make unreasonable authorship of those who have not contributed to the research.
5. I swear that I shall take full responsibility for all problems and disadvantages that may arise from noncompliance with the Research Ethics if found guilty of any of the above-mentioned research misconducts.

All authors must sign this Written Oath of Observance of Research Ethics, but in case of necessity, the correspondent author can obtain the consent of other authors and replace them.

All Authors:

_____ Signature	_____ Date	_____ Signature	_____ Date
_____ Signature	_____ Date	_____ Signature	_____ Date

One author on behalf of all co-authors:

"I warrant that I am authorized to execute this copyright on behalf of all the authors of the article referred to above."

Instructions for authors

The Korean Powder Metallurgy & Materials Institute, founded in 1994, is a research journal that primarily aims to publish original research papers on a bi-monthly basis.

1. Forms and contents of publication

- Original Papers: This form of publication represents original research articles on various aspects of powder metallurgy, namely fabrication, characterization, and forming of metal powders for advanced industrial applications.
- Letters or Rapid Communications: Short reports of original researches are accepted for publication.
- Critical Reviews or Reports : Invited or submitted review papers and technical reports are accepted.

The journal overall serves as a much-desired international platform for publications of wide researches in materials science. The emphasis, however, has been given on originality and quality of the paper rather than quantitative research. Short reports on material development, novel process or properties are also welcome. The following list of topics is of particular interest to the journal: (1) Powder fabrication techniques, (2) Characterization, (3) Compaction and sintering methods, (4) Heat treatment processes in powder metallurgy, (5) Industrial application of powders, (6) Powder process control, (7) Particle modification, (8) Particle motion and rheology, and (9) Particle growth.

2. Submission of papers

- 1) Manuscript should be submitted online at the KPMI homepage (<http://www.kpmi.or.kr>) or e-mail to the KPMI (journal@kpmi.or.kr)
- 2) File type: MS Word files according to instructions below. Pictures and photos should be submitted in JPG or TIFF format (300 dpi).
- 3) Prior to publications: Submitted manuscript must not previously been published in a journal and it is not being simultaneously considered for publication elsewhere.

3. Preparation of manuscripts

- 1) All papers should be written in English and SI units should

be used throughout. Abbreviations should be defined the first time they occur in manuscript. Manuscripts should be typed on a paper of A4 format with 2.5 cm margins (right, left, top, bottom), and double-spaced, using Times Roman 11 font.

2) Structure of the manuscript:

The Title : The title should be carefully chosen to indicate as clearly as possible the subject of the manuscript. The first letter of each word should begin with a capital letter except for articles, conjunctions, and preparations. The first word after a hyphen should also be capitalized such as "Variation of Magnetic Properties of Nd-Fe-B Sintered Magnets with Compaction Conditions".

Bylines should include all those who have made substantial contributions to the work. The first author should be the major contributor of the work. All authors' names should be written in full. At least one author should be designated with a sign as the corresponding author.

Affiliations should include the following information in the order of Institute, Department, City, Zip Code, and Country.

Abstract and Keywords : Each paper should include 120~200 words abstract and five key words for use in indexing.

3) Text: Description headings should be used to divide the paper into its component parts as below.

1. Introduction
2. Experimental
3. Results & Discussions
4. Conclusions

Acknowledgement (This is author's option.)

References

List of Table and Figure captions

Tables and Figures

4) References:

References should be indicated in the text by consecutive numbers in square parentheses, e.g. [1, 2, 5-7], as a part of the text, the full reference being cited at the end of the text. References should contain all the names of the authors together with their initials, the title of the journal, volume number (Bold type), year and the first page number as below. References to books should contain the names of the authors, the title (the names of

editors), the publisher name, location and year as below.

- [1] J. D. James, B. Wilshire and D. Cleaver: Powder Metall., 33 (1990) 247.
- [2] I. H. Moon: J. Korean Powder Metall. Inst., 1 (1991) 66.
- [3] H. E. Exner and G. Petzow: Sintering and Catalysis, G. C. Kuczynski (Ed.), Plenum Press, New York (1976) 279.
- [4] D. R. Dank and D. A. Koss: High Temperature Ordered Intermetallic Alloys, C. T. Liu (Ed.), MRS Symp. Proc. Vol. 133, Pittsburg, PA (1989) 561.
- [5] Daido Steel: USA, US 5,193,607 (1993).
- [6] M.G.Kim and J.H.Kim: Korea, KR 0041070 (2010).
- [7] Germany: DIN EN ISO 11876N, Hardmetals.
- [8] ASTM B213:03, Standard Test Method for Flow Rate of Metal Powders.
- [9] J. C. Kim: M.S. Thesis, Title of Dissertation, Daehan University, Seoul (2011) 123.
- [10] J. C. Kim: Ph. D. Dissertation, Title of Dissertation, Hankook University, Seoul (2011) 123.

5) Tables and Figures

Tables: type each table on the separate page, number consecutively in Arabic numerals and supply a heading. Figures for best results submit illustrations in the actual size (300 dpi) at which they should be published. The line drawings and the photographs should be originals and sharp images, with somewhat more contrast than is required in the printed version. Each figure should be typed on a separate page. The figure captions must be included.

6) Equations

Equations are placed must be clearly printed and numbered sequentially with Arabic numbers enclosed with round parentheses at the right-hand margin.

$$\text{Ex)} f = f_{\infty} + (f_0 - f_{\infty}) \exp(-\gamma r / \gamma \sim r) \quad (1)$$

4. Peer-review

All manuscripts are treated as confidential. They are peer-reviewed by at least 3 anonymous reviewers selected by the editor. Letters to the editor are reviewed and published on the decision of the editor. The corresponding author is notified as soon as possible of the editor's decision to accept, reject, or request revision of manuscripts. When the final revised manuscript is com-

pletely acceptable according to the KPMI format and criteria, it is scheduled for publication in the next available issue. Rejected papers will not be peer-reviewed again.

5. The accepted manuscript

1) Copyright:

Upon acceptance of a paper, the author(s) will be asked to transfer the copyright of the paper to the publisher, The Korean Powder Metallurgy & Materials Institute. This transfer will ensure the widest possible dissemination of the information.

2) Proofs:

Proofs will be sent to the corresponding author for checking before publication and will not be returned to the author, unless requested otherwise. Only typographical errors may be corrected. Any substantial alterations other than these may be charged to the author. All joint communications must indicate the name and full address of the author to whom proofs should be sent.

3) Reprints:

The authors are entitled to 50 reprints or a PDF file of the article without additional charge, but are charged for additional reprints exceeding 50 in addition to the nominal publication charge.

4) Publication charge:

The publication fee is US\$200 up to 6 pages, and US\$30 per additional page regardless of a member or a non-member. Additional fee for acknowledgement is US \$100. For color printings, US\$100 per color page is charged to authors regardless of the membership.

6. Code of ethics

We can secure the ethics required for scientific research through this code of ethics; and we intend to raise the value of our journal through the addition of originality and integrity to our journal. Therefore, all authors of theses, review committee members and editorial committee members shall observe this code of ethics in order to reject any dishonesty in the publication of theses and secure the integrity of any research. For the policies on the research and publication ethics not stated in this instructions, International standards for editors and authors (<http://publicationethics.org/international-standards-editors-and-authors>) can be applied.

Copyright transfer agreement

Article No: _____

Article Title: _____

By: _____

It is hereby agreed that the copyright of the above article is transferred to The Korean Powder Metallurgy & Materials Institute. However, the author(s) reserves the following:

1. All proprietary rights other than copyright, such as patent rights.
2. The right to reuse all or part of this article in other works.
3. The right to use the article for the author's personal use provided the copies are not offered for sale.

All Authors:

Signature Date Signature Date

Signature Date Signature Date

One author on behalf of all co-authors:

"I warrant that I am authorized to execute this copyright on behalf of all the authors of the article referred to above."

signaturedate signaturedate

Signature Date Signature Date

This document must be signed by author(s) and be received by the production office before the article can be processed for publication. Please mail this document to the following address:

The Korean Powder Metallurgy & Materials Institute
Unit 706, (635-4, Yeoksam-Dong) 22, 7Gil, Teheran-Ro, Gangnam-Gu, 135-703 Seoul, Korea

Checklist

- 제목과 저자명, 저자 소속을 정확하게 확인하였습니다.
 - 교신저자를 기호로 구분되어 표기하였으며, E-mail 주소와 연락처를 정확하게 표기하였습니다.
 - Keyword는 학회지에 규정한 Keyword list에서 선정하여 정확하게 확인하였습니다.
 - 그림과 그림설명이 잘 매치 되었는지 정확하게 확인하였습니다.
 - 참고문헌은 한국분말재료학회지 작성 규정에 따라 정확하게 작성되었습니다.
-
- The paper title, authors' names, and authors' affiliations have been confirmed to be accurate.
 - The corresponding author has been distinguished using symbol(s), and e-mail address(es) and contact number(s) have been indicated accurately.
 - The keywords have been selected from the keyword list determined by the Journal and confirmed to be accurate.
 - The figures and their captions have been confirmed to be matched accurately.
 - The reference materials have been drawn up accurately according to the paper guidelines of the Journal of Powder Materials.

직 위	성 명	소 속
회장	김진천	울산대학교
수석부회장	이기안	인하대학교
대외협력부회장	이정구	한국재료연구원
학술부회장	홍순직	공주대학교
기술부회장	류성수	한국세라믹기술원
산업체부회장	이병윤	(주)창성
감사	김정근	인천대학교
	장시영	한국항공대학교
편집위원장	김경태	한국재료연구원
편집이사	김정환	한밭대학교
	박귀일	경북대학교
	양민호	단국대학교
	이석재	전북대학교
	최현주	국민대학교
편집간사	강정신	서울대학교
	김정준	고등기술연구원
	박정민	한국재료연구원
	박태주	한양대학교
	배재웅	국립부경대학교
	변종민	서울과학기술대학교
	손석수	고려대학교
	신세은	순천대학교
	안창의	한국세라믹기술원
	양승민	한국생산기술연구원
	이 빈	경희대학교
	이동주	충북대학교
	조승기	한국재료연구원
	최병준	서울과학기술대학교
학술이사	강석훈	한국원자력연구원
	공만식	고등기술연구원
	노기민	한국지질자원연구원
	임경목	한국생산기술연구원
	백연경	한국재료연구원
	이재범	충남대학교
	임효령	국립부경대학교
	채홍준	고등기술연구원
학술간사	김용주	국민대학교
	이지운	공주대학교
	정다운	한국생산기술연구원
	주수현	단국대학교
국제위원장	이창규	한국원자력연구원

직 위	성 명	소 속
국제이사	김범성	한국생산기술연구원
	류호진	KAIST
	안병민	아주대학교
	이근재	단국대학교
	이정구	울산대학교
국제간사	성효경	국민대학교
기술이사	김세훈	한국자동차연구원
	김영무	국방과학연구소
	박지환	엠티아이지
	윤중열	한국재료연구원
	이성희	목포대학교
	최한신	지아이텍
	황병철	서울과학기술대학교
기술간사	김연철	이화다이아몬드공업㈜
	김지원	고등기술연구원
	김충수	한국생산기술연구원
	정효연	한국생산기술연구원
	차희령	한국재료연구원
대외협력이사	강민철	3D프린팅연구조합
	박만호	㈜아스플로
	박진경	LG이노텍
	송인혁	한국재료연구원
	이찬기	고등기술연구원
	천영범	한국원자력연구원
	홍현선	성신여자대학교
대외협력간사	김영균	한국재료연구원
	이동근	순천대학교
	한준희	한국생산기술연구원
"지역이사 (지부장)"	권세훈	경상지부장 : 부산대학교
	김경훈	강원지부장 : 한국생산기술연구원
	오익현	호남지부장 : 전남테크노파크
	이진규	충청지부장 : 공주대학교
	현승균	경인지부장 : 인하대학교
지역간사	고원석	경인지부 : 인하대학교
	김태훈	호남지부 : 전남대학교
	양승민	강원지부 : 한국생산기술연구원
	엄두승	제주지부 : 제주대학교
총무이사	박경태	한국생산기술연구원
	이영인	서울과학기술대학교
총무간사	김태훈	한국재료연구원
	이 빈	경희대학교
	최상훈	고등기술연구원
	최현주	국민대학교
재무이사	변종민	서울과학기술대학교
	양상선	한국재료연구원
재무간사	송명석	한국생산기술연구원
	정재원	한국재료연구원

제16대 평의원

성명	소속	성명	소속	성명	소속
강철	한라스텍㈜	박귀일	경북대학교	이규수	MS가스
강두홍	(주)아스플로	박기봉	㈜엠케이	이근재	단국대학교
강민철	3D프린팅연구조합	박동규	경상대학교	이기안	인하대학교
강석중	KAIST	박만호	㈜아스플로	이동주	충북대학교
강석훈	한국원자력연구원	박성진	포스코홀딩스	이민하	한국생산기술연구원
고원석	인하대학교	박원욱	인제대학교	이민호	버추얼랩
공만식	고등기술연구원	박은수	서울대학교	이병윤	(주)창성
구용모	㈜창성	박은수	㈜이엠엘	이상관	한국재료연구원
권세훈	부산대학교	박정민	한국재료연구원	이석재	전북대학교
권영순	울산대학교	박정환	대광소결금속	이선영	한양대학교
권영태	한국재료연구원	박정효	국방과학연구소	이성모	HD현대중공업
김플	코오롱 미래기술원	박종관	㈜삼한	이성희	국립목포대학교
김경태	한국재료연구원	박지환	MTIG	이영인	서울과학기술대학교
김경훈	한국생산기술연구원	박진경	LG이노텍	이완재	한양대학교
김기범	세종대학교	박희동	이화다이아몬드공업㈜	이원식	한국생산기술연구원
김기한	용인전자(주)	백연경	한국재료연구원	이재범	충남대학교
김대현	(주)풍산홀딩스	백운형	한국전자재료	이재성	한양대학교
김덕주	하나테크	변종민	서울과학기술대학교	이정구	한국재료연구원
김동환	(주)성립첨단산업	석명진	강원대학교	이정구	울산대학교
김득중	성균관대학교	설재복	경상국립대학교	이지운	공주대학교
김범성	한국생산기술연구원	성효경	국민대학교	이진규	공주대학교
김병기	자화전자	손석수	고려대학교	이찬기	고등기술연구원
김상훈	산업연구원	손인진	전북대학교	이창규	한국원자력연구원
김세훈	한국자동차연구원	손현택	한국생산기술연구원	이학성	동아대학교
김신경	신한다이아몬드공업㈜	송광호	한국분말야금㈜	임경묵	한국생산기술연구원
김양도	부산대학교	송승철	한국회가내스㈜	임중경	대신강업주식회사
김영도	한양대학교	송용설	(주)아모그린텍	임효령	국립부경대학교
김영립	KAMI㈜	송인혁	한국재료연구원	장시영	한국항공대학교
김영무	국방과학연구소	신훈	㈜아이피티	장태석	선문대학교
김용진	한국재료연구원	신광섭	일진다이아몬드공업㈜	정영근	부산대학교
김우중	(주)대건테크	신세은	순천대학교	정임두	울산과학기술원
김정곤	인천대학교	안동길	대구텍㈜	정재원	한국재료연구원
김정기	경상국립대학교	안병민	아주대학교	정형식	아주대학교
김정한	한밭대학교	안상호	포항산업과학연구원	조권구	경상국립대학교
김종렬	한양대학교	안인섭	경상국립대학교	조승기	한국재료연구원
김주용	리프로텍	안중호	안동대학교	조영철	현대자동차
김지순	울산대학교	안창의	한국세라믹기술원	좌용호	한양대학교
김진천	울산대학교	양동열	한국재료연구원	채홍준	고등기술연구원
김충수	한국생산기술연구원	양민호	단국대학교	천병선	충남대학교
김태규	한국원자력연구원	양상선	한국재료연구원	천영범	한국원자력연구원
김태훈	한국재료연구원	양승민	한국생산기술연구원	최병준	서울과학기술대학교
김택수	한국생산기술연구원	오승탁	서울과학기술대학교	최준필	한국기계연구원
김형섭	포항공과대학교	오왕근	(주)양우메탈	최한신	지아이텍
김홍물	하나에이엠티	오익현	전남테크노파크	최현규	현대제철

성명	소속	성명	소속	성명	소속
김효섭	한국생산기술연구원	유봉영	한양대학교	최현주	국민대학교
김휘준	한국생산기술연구원	유지훈	한국재료연구원	한유동	한국재료연구원
김희수	월드인텍션	윤덕용	KAIST	현승균	인하대학교
노기민	한국지질자원연구원	윤준철	현대제철	홍순직	공주대학교
류성수	한국세라믹기술원	윤중열	한국재료연구원	홍순형	KAIST
류시완	(주)풍산홀딩스	윤태식	대신강업(주)	홍현선	성신여자대학교
류호진	KAIST	은광용	(주)기술과가치	황득규	현대모비스(주)
박준	제이피씨(주)	이빈	경희대학교	황병철	서울과학기술대학교
박경태	한국생산기술연구원	이성	국방과학연구소 민군협력진흥원		

본 학회지는 한국연구재단의 평가결과 등재학술지로 선정되었습니다.

“본 사업은 기획재정부의 복권기금 및 과학기술정보통신부의 과학기술진흥기금으로 추진되어 사회적 가치 실현과 국가 과학기술 발전에 기여합니다.”