

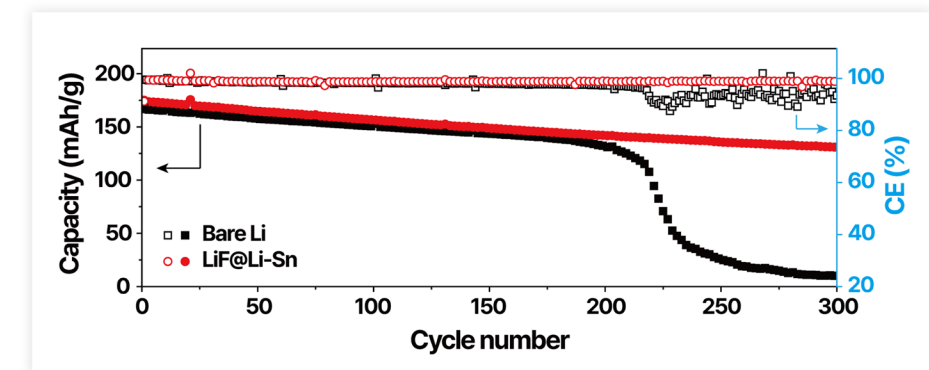
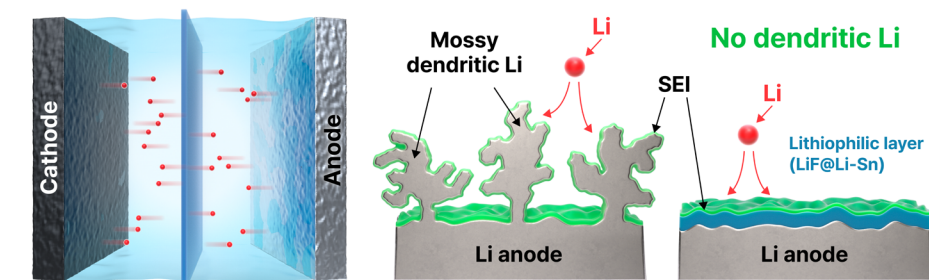
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Journal of Powder Materials

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Aims and Scope

The Journal of Powder Materials (JPM) is dedicated to sharing cutting-edge research and advanced technologies in the fields of powder metal-lurgy 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 mate-rial 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 consoli-dation, additive manufacturing, injection molding, and powder-based coating technologies. The journal also encompasses research on charac-terization, testing, quality assurance, and diverse industrial applications. Furthermore, *JPM* actively promotes research incorporating data-driv-en 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

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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.

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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>

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Self-Assembled Monolayers in Area-Selective Atomic Layer Deposition and Their Challenges

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Area-selective atomic layer deposition (AS-ALD) is a bottom-up process that selectively deposits thin films onto specific areas of a wafer surface. The surface reactions of AS-ALD are controlled by blocking the adsorption of precursors using inhibitors such as self-assembled monolayers (SAMs) or small molecule inhibitors. To increase selectivity during the AS-ALD process, the design of both the inhibitor and the precursor is crucial. Both inhibitors and precursors vary in reactivity and size, and surface reactions are blocked through interactions between precursor molecules and surface functional groups. However, challenges in the conventional SAM-based AS-ALD method include thermal instability and potential damage to substrates during the removal of residual SAMs after the process. To address these issues, recent studies have proposed alternative inhibitors and process design strategies.

Keywords: Area selective atomic layer deposition; Self-assembled monolayer; Inhibitors; Surface deactivation; Selectivity

Received: April 7, 2025

Revised: April 26, 2025

Accepted: April 28, 2025

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1. Introduction

Atomic layer deposition (ALD) is a well-established and widely used method to deposit a variety of thin film materials with excellent thickness control, uniformity, and conformality. ALD is extensively used in the production of today's electronic devices [1-4]. Therefore, ALD can produce highly uniform thin films with a high aspect ratio for a wide range of materials, including oxides, nitrides, sulfides, and pure metals, making it a widely used deposition method in the fabrication of today's electronic devices [1, 4, 5].

However, ALD lacks the ability to selectively deposit thin films on target areas. The approach of depositing materials only on desired areas can be achieved through area selective atomic layer deposition (AS-ALD). AS-ALD is a process that selectively deposits a film only on specific substrate areas [1, 2, 5-7]. In the deposition process, the "bottom-up" approach is utilized to reduce additional post-processing steps, such as photolithography and etching, thus significantly shortening the overall manufacturing time. In multilayer patterning, AS-ALD facilitates

the self-alignment of 3D structures and offers the potential for the bottom-up fabrication of 3D materials in various nano-fabrication applications [9-13]. Therefore, it can meet the increasing demands of semiconductor production, making it cost-effective [9, 13]. Nanopatterning using AS-ALD is expected to facilitate the fabrication of next-generation electronic and sensing devices, particularly for 2D or 3D metal/dielectric patterns in integrated circuits, transistor backends, interconnects, and FinFET structures. Additionally, it enables the production of higher transistor stacks [13-15].

AS-ALD includes both surface activation and surface deactivation methods [16]. This paper aims to introduce AS-ALD through surface deactivation. The surface deactivation method selectively blocks nucleation in the non-growth surface (NGS) of the substrate during the ALD process, allowing materials to be selectively deposited only in the growth surface (GS). In this case, deactivation can be achieved by chemically passivating the top surface of the NGS using inhibitors such as self-assembled monolayers (SAMs) [1, 4, 5, 17]. Achieving AS-ALD using SAMs to block ALD typically requires the starting substrates to have significantly different chemical properties [18]. A common reason for the loss of selectivity during deposition is the alteration of surface properties in areas where deposition should not

<https://doi.org/10.4150/jpm.2025.00094>

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occur upon exposure to ALD chemistry.

In recent years, active research has focused on AS-ALD processes utilizing SAMs as chemically selective masking layers to prevent deposition on undesired surfaces [4]. SAMs are used to deactivate the surface to ALD growth [19]. The use of SAMs is strongly related to the chemical and physical stability of thin films. SAM is a spontaneously formed, regularly well-aligned organic molecular thin film on the surface of a given substrate, with the structure of SAM shown in Fig. 1(a) [20]. SAMs are organic films composed of amphiphilic molecules, which consist of three essential components. The reactive headgroup, also referred to as the anchoring group, enables selective binding to the substrate surface. The tail group ensures that the film remains inert to ALD chemistry, while the backbone facilitates the formation of a densely packed monolayer through van der Waals dispersion forces [19]. SAM forms a strong molecular film through direct chemical bonds between the molecules and the substrate surface. Since it is not affected by the shape or size of the substrate, it can be fabricated on substrates with complex shapes and is also suitable for large-area applications [21].

More commonly, the substrate surface is chemically modified using SAMs [10]. Because of differences in the chemical affinity between SAM molecules and various substrates, selective SAM formation on one surface over another has been demonstrated and used to enable inhibition for AS-ALD [18]. ALD combined with SAMs passivation allows selective deposition on patterned substrates at the nanoscale, enabling bot-

tom-up material fabrication for various applications [3]. SAMs can be removed after the completion of the ALD process through laser irradiation [20], e-beam patterning [17], sonication in ethanol [5], treatment with alcohol or acetic acid etching [28], oxidative methods [29, 30], or by using acetone and deionized water. The appropriate method for removing residual SAMs varies depending on the type of SAM.

Fig. 1(b) is a schematic of the self-assembly mechanism of SAM. In process i), SAM monomers are applied to the substrate and physically adsorbed. Then, in process ii), chemical adsorption occurs due to covalent bonding between the lying SAM molecules and the substrate, and island-preferred nucleation takes place. In process iii), monomers adsorb around the nucleus and grow in the form of islands, gradually coating the substrate surface. As a result, in process iv), a monolayer with a densely packed, ordered structure is formed [31].

The previous paper by Jo et al. reviewed AS-ALD for single metal materials [16]. This paper focuses on SAMs and aims to present the conditions for effective AS-ALD using SAMs and precursors, as well as the issues and limitations related to the implementation of the process.

2. Surface deactivation using SAM

This section aims to discuss the functions and requirements of SAM structures for enhancing the selectivity of the AS-ALD process, as well as the conditions of the precursors.

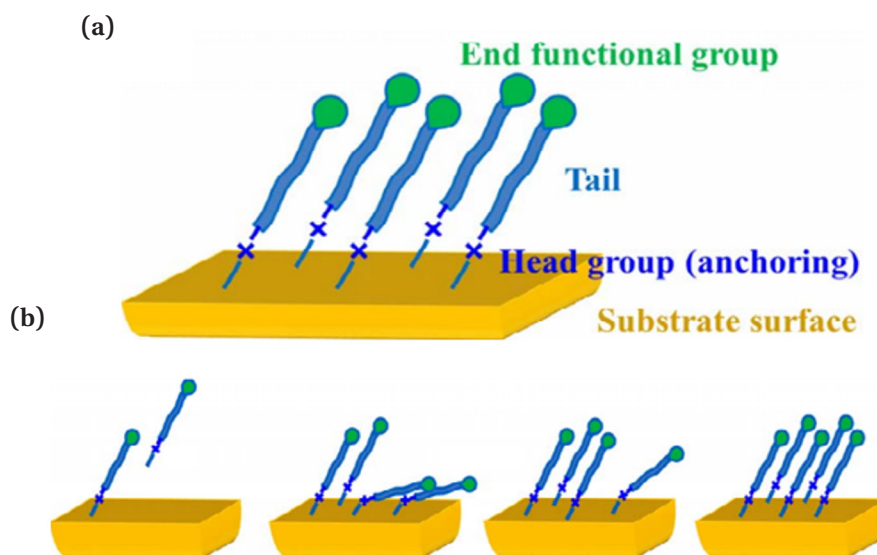


Fig. 1. (a) Structure of a self-assembled monolayer (SAM) (b) Mechanism of SAM formation. [8] (Reprinted from Mastrangelo F, Fioravanti G, Quaresima R, Vinci R, Gherlone E, Journal of Biomaterials and Nanobiotechnology, Vol. 2, No. 5, 2011, pp. 533–543, under CC BY 4.0 license).

2-1. Condition of head group

The head group of SAMs is the part that chemically adsorbs onto the surface, adhering to all areas of the substrate and ultimately forming a close-packed monolayer [32]. The head group must firmly adhere to the substrate surface for subsequent processes to proceed smoothly and for the formation of a uniform and stable layer. In this case, the head group selectively adsorbs onto specific areas of the GS [18]. Table 1 summarizes various studies and presents a compilation of SAM substrate applications based on the head group.

SAMs with thiol as the head group have been used to deactivate substrates such as Cu, CuO, Cu₂O, and Au. SAMs with phosphonic acid as the head group have been applied to deactivate substrates such as Al₂O₃, Cu, CuO, Co₃O₄, WO₃, and RuO₂. SAMs with alkyl silane as the head group have been used to deactivate substrates like TiN and SiO₂. Finally, SAMs with carboxyl as the head group have been used to deactivate substrates such as Cu and Co. SiO₂ is primarily used as the GS, and the deposition temperature of the precursors in these studies typically ranges from 100 to 200°C [18].

2-2. Condition of tail group

The blocking efficiency of ALD precursors is determined by the packing density of the SAM, with the tail group of the SAM

playing a key role in this function. Longer molecular chains of SAMs result in higher packing densities, while variations in chain length can influence their wetting performance [33, 34]. To enhance the selectivity of the process, the steric shape of the tail group plays a critical role, as highlighted by Bent et al [33].

The packing density of SAMs depends on intermolecular van der Waals (VDW) dispersion forces, which are proportional to the strength of the induced dipole. As shown in Fig. 2(a), the thickness of the SAM film increases linearly with the number of carbon atoms in the Alkylchlorosilane. Conversely, the water contact angle sharply increases upon the addition of the first one or two methyl units to the alkyl chain, followed by a gradual rise until it stabilizes at a plateau, with a static water contact angle (WCA) of approximately 110°. Furthermore, the Hf atom % of the ALD precursor in the experiment decreases inversely with the WCA, indicating that as the length of the tail group of the deposited SAM increases, the precursor's blocking efficiency improves. The strengthening of VDW interactions with increasing alkyl chain length explains this phenomenon. Longer alkyl chains exhibit stronger VDW interactions due to the greater number of electrons and the extended molecular structure, which allows for more extensive induced dipole interactions. In contrast, shorter-chain deactivating agents experience relatively weak interchain VDW attraction, as evidenced by

Table 1. Precursors, self-assembled monolayers (SAMs), deposition temperature, growth surface (GS), non-growth surface (NGS), and patterning method of area-selective atomic layer deposition by surface activation organized by head groups

Head Group	SAM	Precursor	Temperature (°C)	NGS	GS	Reference
Thiol	ODT, DDT (solution)	DEZ, TIP	120	CuO	SiO ₂	[1]
	UDT, ODT (solution)	TDMAHf	170	CuO	SiO ₂	[2]
	ODT	TDMAHf	130~200	Cu, CuO, Cu ₂ O	SiO ₂	[3]
	1-dodecanethiol	TMA, DEZ	115	Au	SiO ₂	[4]
	(DDT),1-octanethiol, and ethanethiol					
Phosphonic acid	DDT	DEZ	120	Cu	SiO ₂	[5]
	ODTS, ODPA, DDPA	TMA	50~200	Al ₂ O ₃	SiO ₂	[6]
	PA, ODPA, OPA, EPA, PPA (solution)	Ethylbenzyl (EBECHRu)c	250	SiO ₂ /Si, TiN/SiO ₂ /Si, W/TiN/SiO ₂ /Si, line patterend TiN on SiO ₂	SiO ₂	[22]
	ODPA	TMA, DEZ	120	CuO, Co ₃ O ₄ , WO ₃ , RuO ₂	SiO ₂	[7]
	ODPA	DEZ	150	Cu	SiO ₂	[23]
Alkyl silane	DETA, FAS, TMODS, PEDA (solution)	TiCl ₄	100, 140, 150	TiN	SiO ₂	[24]
	ODTS	Pb(tmhd) ₂	160	SiO ₂	Si	[25]
	ODTS	Co(MeCp) ₂	300, 350	SiO ₂	SiO ₂	[8]
	ODTS	Ti[OCH(CH ₃) ₂] ₄	150	SiO ₂	SiO ₂	[17]
	ODTMS	TMA, DEZ	200	SiO ₂	Cu	[9]
Carboxyl	SA (solution)	DEZ	100	SAM-treated Cu, Co	Cu, Co	[26]
	SA (solution)	DEZ	70	Cu	SiO ₂	[27]

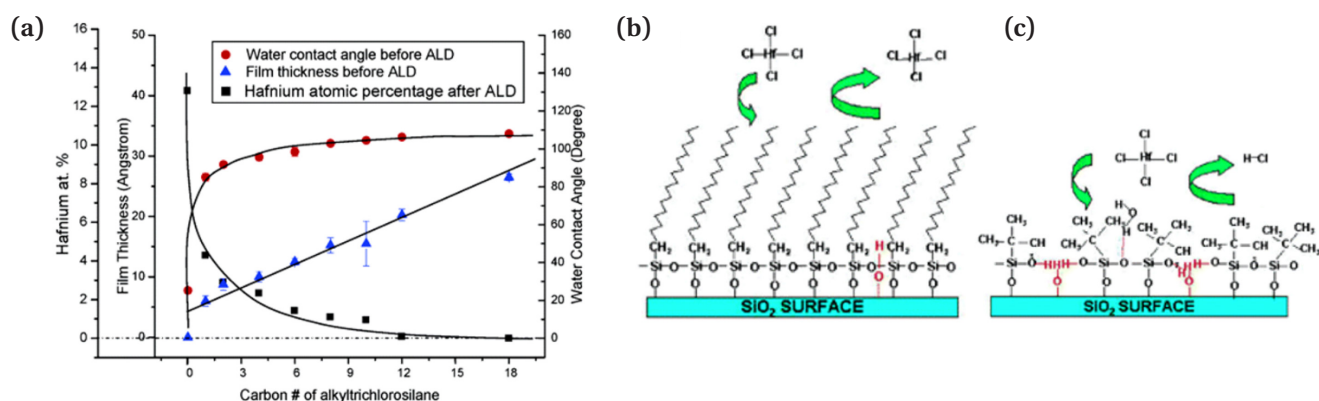


Fig. 2. (a) Chain length dependence of alkylchlorosilane blocking efficiency. The figure shows the film thickness of the contact angle before ALD, and the percentage of hafnium atoms by X-ray photoelectron spectroscopy (XPS) analysis after the ALD process. (b) Densely packed, chain, self-assembled monolayer. (c) self-assembled monolayer with bulky tail groups (adapted with permission from [33]. Copyright 2005 American Chemical Society).

their lower packing density and reduced hydrophobicity, as indicated by WCA measurements. As a result, for molecules with the same tail group structures, longer alkyl chains enhance deactivation efficiency.

Moreover, since molecular structure also affects the strength of intermolecular VDW interactions, the shape of the tail group in SAMs is a key factor in selecting effective deactivating agents. In the case of Fig. 2(b), using a long linear chain as the tail group effectively blocks the precursor from penetrating the monolayer. On the other hand, in Fig. 2(c), the large volume of the tail group leads to a lower packing density, resulting in surface defects and pinholes. As a result, the precursor penetrates the SAM, binds with the substrate surface, and decreases the selectivity of the process [33]. To use SAM as an ALD monolayer resist, a thin film with high packing density is required. Therefore, to obtain the most closely packed film, simple, linear alkyl chain groups are necessary.

Therefore, the longer the chain length and the simpler the linear shape of the SAM's tail group, the higher the packing density and the better the blocking efficiency. For this reason, linear alkyl chain groups like C₁₈ (octadecyl group) have been widely used in many studies.

2-3. Condition of functional group

To enhance the deactivation effect through SAMs, the design of the functional group, also known as the end group, is crucial. Selective deposition can be realized by manipulating, prior to deposition, surface functional groups according to a chosen pattern to either block or allow film growth as desired [5]. This functional group is located on the opposite side of the part of

Table 2. Comparison of proton affinity, activation barrier, and total energy for self-assembled materials SAMs with different termination [35] (Reprinted with permission from [35]. Copyright 2002 American Chemical Society)

	-OH	-NH ₂	-CH ₃
H+ affinity	13.90	14.89	17.85
Barrier	0.65	1.22	1.82
Total energy	-1.44	-0.94	0.09

the SAM that interacts with the substrate, and in AS-ALD, it plays a role in controlling the reactivity with the ALD precursor. In other words, due to the well-ordered structural characteristics of the SAM, when the terminal functional groups are exposed to the surface, the surface properties can be controlled at the molecular level using these groups [32]. Inhibiting surface reactions with the precursor to enhance deactivation efficiency leads to improved selectivity. The conditions for the functional groups to increase deactivation efficiency are as follows.

Firstly, a SAM should be used that has no thermodynamic driving force for the reaction and a large reaction barrier. Table 2 presents the reactivity of OTS-based SAMs with different terminal groups (-OH, -NH₂, -CH₃) with TMA precursors [14]. A lower proton affinity indicates that less energy is required for the TMA reaction. The barrier energy shown in the table is the energy barrier for the reaction between TMA and the terminal group, and it is directly proportional to the proton affinity. The total energy at the end reflects the calculated trend for activation energy. A negative value indicates that the state where TMA and the terminal group are bound is stable, while a posi-

tive value suggests that the dissociated state is more stable.

OH-terminated SAM has a very low energy barrier, so when heat is applied, it reacts easily with TMA and becomes adsorbed. The reaction path of NH_2 -terminated SAM with TMA is similar to that of OH-terminated SAM with TMA; however, for $-\text{NH}_2$, the reaction barrier energy is higher, necessitating elevated temperatures for the reaction to occur. CH_3 -terminated SAM has not only a very high reaction barrier energy but also no thermodynamic driving force for adsorption. In conclusion, within the comparison groups of this study, CH_3 -terminated SAM can be considered the most efficient SAM. Therefore, to enhance deactivation efficiency through SAMs, it is important to design the terminal groups by considering the reaction kinetics with the precursor.

Additionally, this study found that the rate constant for the reaction between the terminal groups and TMA varied with temperature. Subsequently, TMA can be selectively adsorbed onto the SAM or the exposed substrate, depending on the functional group's affinity for TMA. Finally, ALD can be performed on the adsorbed state to grow uniform, thin Al_2O_3 films.

The second condition is that for SAM to be completely well-ordered, the compatibility reaction between the chemical functional group of the substrate surface and the terminal group of the SAM is crucial. Fig. 3 describes the deposition of an APDMES SAM with an NH_2 terminal group on a silica surface [35]. Fig. 3(a) shows a schematic in which the amino-terminal group forms a hydrogen bond with the silanol groups on the SiO_2 surface, preventing the formation of a well-ordered SAM. This suggests that, to achieve a well-ordered SAM, it is important to design terminal groups that are unreactive with the substrate.

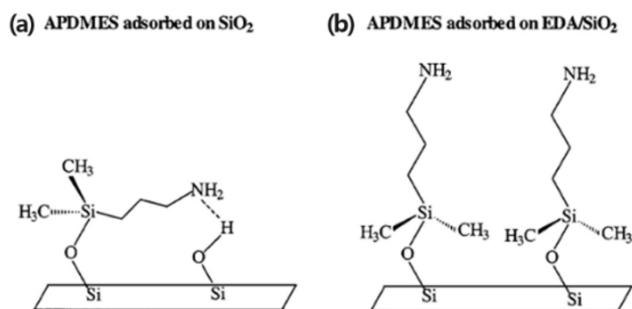


Fig. 3. The surface bonds of EDA absorbed on silica and APDMES adsorbed on (a) silica and (b) silica pretreated with EDA [35] (Reprinted with permission from [35]. Copyright 2002 American Chemical Society).

However, Fig. 3(b) shows an example where a well-ordered monolayer is formed even with a terminal group that is reactive with the substrate. Before applying the SAM, a catalytic substance, ethylenediamine (EDA), is first attached to the surface. This EDA modifies the silanol group at the Si surface to an amino-propyl group, preventing the amino-terminal group of APDMES from adsorbing onto the substrate. Additionally, the monoethoxy head group catalyzes reactions, facilitating the formation of a well-ordered SAM. Therefore, to achieve a well-ordered SAM, it is crucial to design an end group that is non-reactive with the substrate. However, if a reactive terminal group is employed, surface treatment of the substrate can enable the formation of a well-ordered SAM [35].

2-4. Condition of ALD precursor in AS-ALD

The conditions of the ALD precursor during AS-ALD are outlined below. If the precursor molecule is small, it can more easily penetrate the SAM during the deposition process, potentially affecting passivation. Additionally, both ALD and AS-ALD processes are highly dependent on ALD chemistry. For instance, nucleation and growth behavior vary depending on the precursor type and process temperature during material deposition.

The study shown in Table 3 discusses the influence of precursor design on AS-ALD [36]. Al_2O_3 was deposited on a SiO_2/Si substrate using five types of SAMs: $\text{Al}(\text{CH}_3)_x\text{Cl}_{3-x}$ ($x = 0, 2$, and 3) and $\text{Al}(\text{C}_y\text{H}_{2y+1})_3$ ($y = 1$ and 2). The selectivity was evaluated using an ODTS SAM. The five precursors used in this experiment are all aluminum-based but contain different ligands. As a result, their reactivity and molecular size vary. This study aims to examine how the reactivity and molecular size of aluminum precursors influence the SAM during AS-ALD.

First, the role of Lewis acidity in the physical adsorption of chloride precursors on SAM-passivated surfaces is investigated. The Lewis acidity of aluminum precursors varies for each precursor. Due to the high electronegativity of the Cl ligand, the Lewis acidity of $\text{Al}(\text{CH}_3)_x\text{Cl}_{3-x}$ decreases as the number of chlorine ligands decreases. Consequently, an increase in chloride ligands leads to greater precursor adsorption on the surface, reducing the effectiveness of precursor blocking. Among the aluminum precursors examined in this study, AlCl_3 , which exhibits the highest Lewis acidity, may lead to unintended Al_2O_3 nucleation if not sufficiently purged.

Additionally, the strong Lewis acidity of chlorine ligands facilitates precursor dimerization, resulting in a larger effective volume (V_{eff}). The increase in V_{eff} of such chlorine-based pre-

Table 3. Summary of ΔH , $-T\Delta S$, ΔG , dissociated dimer fraction, and effective average size of the precursors at 200°C (Reprinted with permission from [36]. Copyright 2021 American Chemical Society)

	AlCl_3	AlCH_3Cl_2	$\text{Al}(\text{CH}_3)_2\text{Cl}$	$\text{Al}(\text{CH}_3)_3$	$\text{Al}(\text{C}_2\text{H}_5)_3$
ΔH (kJ/mol)	113.4	111.8	111.7	66.6	73.4
$-T\Delta S$ (kJ/mol)	-87.9	-93.6	-88.9	-97.5	-103.1
ΔG (kJ/mol)	25.6	18.3	22.9	-31.0	-29.7
Dissociated dimer fraction (x)	0.010	0.035	0.012	0.998	0.998
Effective average size (V_{eff} , Å ³)	143.7	147.6	151.6	87.2	140.2

cursors enhances the blocking effect; however, due to their strong Lewis acidity, they adsorb more readily on the surface and require longer purge times. Therefore, precursors with chlorine ligands cannot be considered highly effective.

Next, the study aims to investigate how precursor size and dimerization, in addition to Lewis acidity, influence precursor blocking during AS-ALD. To understand the thermodynamic equilibrium of dissociation, the Gibbs free energy for the dissociation of dimers to monomers of the five precursors was calculated at 200°C (Table 3). According to the calculation results, the dissociation ΔG of $\text{Al}(\text{CH}_3)_3$ and $\text{Al}(\text{C}_2\text{H}_5)_3$ precursors is negative. Therefore, the dissociation reaction to a monomeric structure occurs spontaneously, and these two precursors predominantly remain in their monomeric form. In contrast, for the other three precursors, the dissociation ΔG for the decomposition of Al dimers is positive, indicating that the dissociation reaction to monomer is not spontaneous. As a result, they predominantly remain in their dimeric form. At the process temperature of 200°C, 99% of the dimers of $\text{Al}(\text{CH}_3)_3$ SAM and $\text{Al}(\text{C}_2\text{H}_5)_3$ SAM dissociate into monomers, while only 1% of the dimers of the remaining three SAMs dissociate into monomers.

As shown in Fig. 4(a), the VDW volume of the monomer and dimer for the five aluminum precursors is presented. In this case, for all precursors except $\text{Al}(\text{C}_2\text{H}_5)_3$, the sizes of the dimer and monomer are similar. $\text{Al}(\text{C}_2\text{H}_5)_3$, while predominantly remaining in the monomeric form, has a relatively large monomer size. This large volume effect prevents the precursor from penetrating effectively during the ALD process, thereby enhancing selectivity.

(1)

$$V_{\text{eff}} = \frac{C_{\text{monomer}} V_{\text{monomer}} + C_{\text{dimer}} V_{\text{dimer}}}{C_{\text{monomer}} + C_{\text{dimer}}}$$

Through this equation (1), considering the relative sizes of C_{monomer} , C_{dimer} , and the precursor, the effective average size of the precursor molecule, V_{eff} , can be calculated. This V_{eff} value represents the average size of the precursor molecule that can

exist at 200°C and serves as an indicator of how efficiently the AS-ALD process can be conducted through the SAM. When the precursor size is small at the ALD process temperature, the precursor can easily penetrate the SAM during the process, potentially affecting passivation. Therefore, precursors that maintain a larger volume during the AS-ALD process lead to higher selectivity.

In Table 3, the effective volumes of $\text{Al}(\text{CH}_3)_3$ and $\text{Al}(\text{C}_2\text{H}_5)_3$ are 87.2 and 140.2, respectively. These represent the precursors with the smallest and largest molecular sizes. By comparing selectivity between these two precursors, the blocking effect related to precursor size is examined. The experimental results show that, even with a higher number of cycles and thicker alumina layers, $\text{Al}(\text{C}_2\text{H}_5)_3$ exhibits the highest selectivity, while $\text{Al}(\text{CH}_3)_3$ shows the lowest selectivity (Fig. 4(b)). This indicates that when a larger molecular size SAM is deposited, better selectivity is achieved. Additionally, during the ALD process, longer purge time and higher pressure of the Ar gas used during purging allow for more effective blocking of the precursor. Therefore, $\text{Al}(\text{C}_2\text{H}_5)_3$, with a larger molecular size compared to $\text{Al}(\text{CH}_3)_3$, more effectively prevents diffusion into the SAM.

Il-Kwon Oh et al. explains the influence of precursor design, including reactivity and molecular size, on the blocking effect during AS-ALD [36]. While the size of the precursor molecule is the most dominant factor influencing selectivity in terms of adsorption by the SAM, the reactivity of the precursor, such as its Lewis acidity, also plays a crucial role in determining the blocking ability. Among the five aluminum precursors, $\text{Al}(\text{C}_2\text{H}_5)_3$, which has a low Lewis acidity and relatively large molecular size, exhibited the best blocking effect. In other words, the blocking effect is improved when the precursor has low Lewis acidity, large effective volume, high purge pressure, and long purge time during the process. Therefore, when performing the AS-ALD process using SAM, the design of the precursor, including its reactivity and molecular size, must be carefully considered.

ALD precursor choice can also negatively affect SAM stabi-

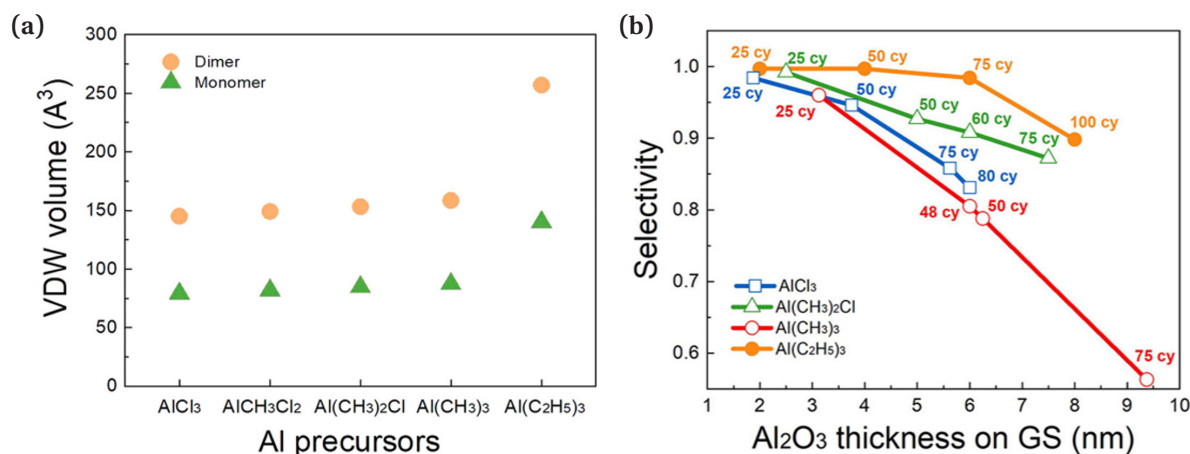


Fig. 4. (a) Molecular size and quantum chemical calculations. VDW volumes of the monomeric and dimeric structures of $\text{Al}(\text{CH}_3)_x\text{Cl}_{3-x}$ ($x = 0, 1, 2$, and 3) and $\text{Al}(\text{C}_y\text{H}_{2y+1})_3$ ($y = 1$ and 2). (b) Selectivity of Al_2O_3 ALD replotted as a function of equivalent thickness on a Si surface (growth surface, GS) (Reprinted with permission from [36]. Copyright 2021 American Chemical Society).

ty depending on the SAM molecule being used. For example, ALD precursors containing chloride ligands may reduce the stability of SAMs adsorbed on metal oxides. This instability arises from the generation of HCl gas as a primary by-product when water is used as a coreactant with chloride-based precursors, potentially leading to surface etching. To ensure the stability of SAMs under ALD conditions, it is crucial that they form strong, high-density surface bonds with the underlying substrate, thereby minimizing the formation of surface defects. Extensive research on SAMs as inhibitors for AS-ALD has contributed to identifying two important factors in the interaction between precursors and inhibitors that enhance selectivity.

First, preventing the formation of access points that could lead to defects within the inhibitor layer is essential for maintaining its blocking performance. Second, this defect prevention is most easily achieved by maximizing the areal density of inert blocking groups at the interface between the inhibitor and the precursor [17, 37]. Finally, the precursor should be designed such that its effective volume is larger than the gap between the inhibitors at the temperature where ALD is performed. Kim et al. investigated ALD using TMA and dimethylaluminum isopropoxide (DMAI) precursors on substrates inhibited by ethanethiol (ET) [38]. They found that ET was much more effective at inhibiting deposition when using DMAI compared to TMA. This is because, at the ALD temperature, most of DMAI exist as dimers and is easily blocked by ET, while the majority of TMA exists as monomers, which can enter the gaps between the ET molecules, adsorb, and initiate nucleation.

3. Issues and Improvements in the Implementation of SAM

Several issues must be addressed to implement the deactivation AS-ALD process using SAM. This section discusses various process challenges encountered in AS-ALD through SAM and the research aimed at improving these challenges.

3-1. Thermal Instability of SAM

Thermal stability is desirable for future molecular electronics applications [15]. The low thermal stability of SAMs severely limits their applicability for achieving area-selective ALD, as most ALD processes have temperature windows in the range of 100–400 °C [12]. As each SAM has a different stable temperature, its passivation properties degrade, leading to precursor penetration and adsorption, which can cause film growth even in NGS.

Choi et al. reveals the mechanism of structural changes in SAMs caused by heat [13]. Fig. 5(a) illustrates a schematic showing the loss of passivation functionality in ODT SAMs on an Au substrate during AS-ALD at 80 °C and 200 °C. When ALD is performed on the ODT SAM at 80 °C, the terminal groups ($\text{C}_{16}\text{--}\text{C}_{17}$ and $\text{C}_{17}\text{--}\text{C}_{18}$) of the SAM, which have relatively weak VDW forces, begin to undergo internal rotation due to heat. At this point, since the terminal methyl groups undergo reversible rotation, cooling back to room temperature, as shown in Fig. 5(b), allows for the recovery of the structure. However, after about 50 ALD cycles, stress and heat cause the methyl groups to undergo irreversible rotation, causing gauche

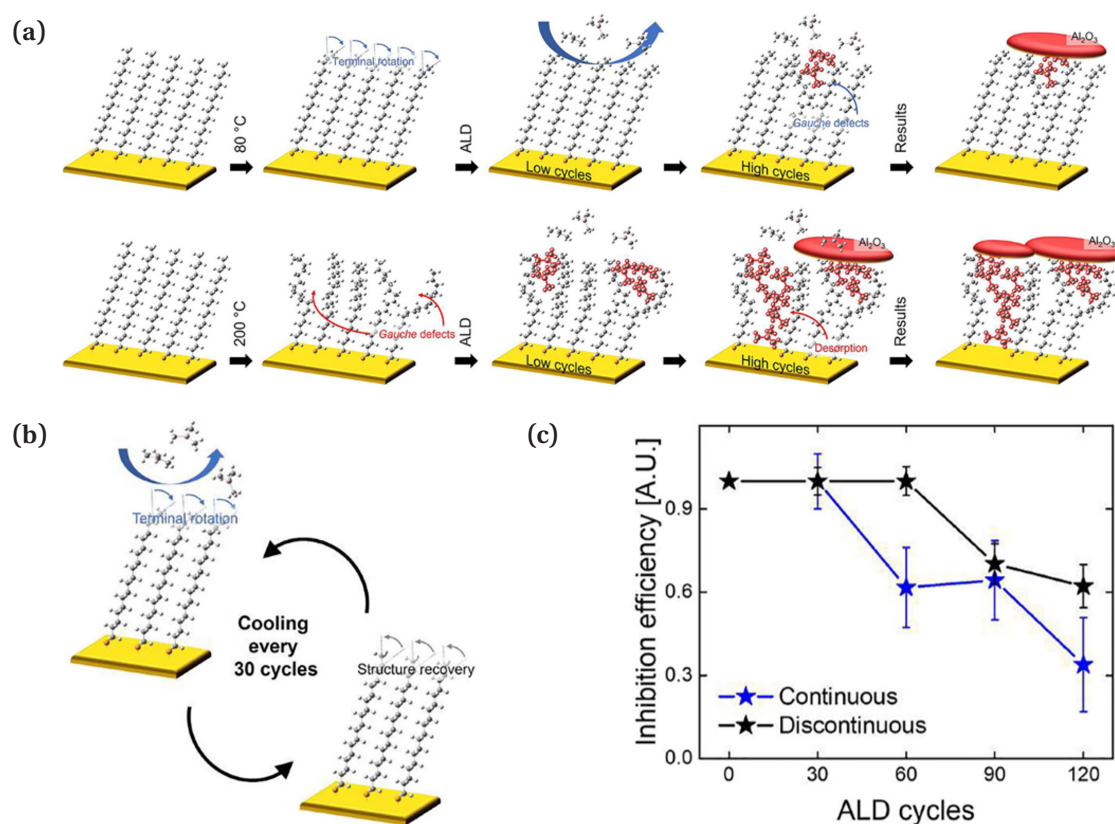


Fig. 5. (a) Schematic illustration of the temperature-dependent deposition mechanism of Al_2O_3 on 18 C-SAM. (b) Schematic illustration for temperature-controlled discontinuous ALD. (c) The inhibition efficiency of SAM for ALD is plotted with respect to the number of ALD cycles when either the continuous (blue star) or discontinuous (black star) ALD scheme was used (Reprinted with permission from [13]. Copyright 2023 American Chemical Society).

defects. While the process heat alone does not provide enough energy to overcome the energy barrier for irreversible rotation of the tail group, the additional stress from ALD exceeds the threshold, resulting in gauche defects. When ALD is performed at 200°C on the ODT SAM substrate, gauche defects due to irreversible rotation occur after just five cycles, and as the process continues, not only does the rotation of the tail group increase, but the SAM monomer can also decompose and detach.

Choi et al. proposes the discontinuous ALD process as a solution, in which the mechanism of SAM passivation loss due to thermal effects is utilized to restore the molecular structure of SAM by periodically cooling the substrate after a certain number of ALD cycles [13]. The molecular structure of the ODT SAM on an Au substrate undergoes reversible internal rotation, which is recoverable by thermal effects, at temperatures below 80°C for up to 50 ALD cycles. In this experiment, the substrate was cooled to room temperature every 30 ALD cycle to restore the SAM structure before resuming the ALD process. As shown in Fig. 5(c), the inhibition efficiency of the

SAM in typical ALD decreases to a low value after 60 cycles, while in the discontinuous ALD process, the inhibition efficiency remains close to 1 up to 60 cycles. Here, they showed that the discontinuous ALD scheme is a simple and easy way to increase the inhibition efficiency. However, this method is limited to materials that can undergo ALD at temperatures below 80°C [13].

Another effective solution to address the thermal instability of SAMs is the correction steps. According to Mackus et al., when the loss of function in the ALD NG region due to heat is inevitable, it can be restored through correction steps [12]. The Correction Steps are divided into two methods. This leads to the development of advanced ALD cycles by combining conventional two-step ALD cycles with correction steps in multi-step cycle and/or supercycle recipes.

The first method is repetitive functionalization. In this method, when the SAM monomer detaches to some extent due to heat during the ALD process, SAM is replenished every certain number of cycles to restore the detached SAM. This approach

helps maintain the deactivation functionality even at high ALD cycle counts. Hashemi et al. conducted AS-ALD of ZnO on a Si substrate covered with Cu/SiO₂ precursors on substrates inhibited by using repetitive functionalization using octadecylthiol (ODT) and dodecylthiol (DDT) SAMs [1]. The ZnO ALD was deposited for more than 600 cycles, with the DDT SAM undergoing a re-dosing process every 150 cycles, for a total of 4 times, while the ODT SAM underwent a re-dosing strategy every 100 cycles, for a total of 6 times.

According to the XPS analysis results shown in Fig. 6, the general DDT and ODT SAMs, without re-dosing, lose their blocking effect after approximately 200 and 350 cycles, respectively [1]. However, the DDT and ODT SAMs that underwent re-dosing processes can suppress the growth of ZnO on Cu up to 600 cycles [1].

The second method is selective etching. This approach is applicable to metal/dielectric patterning substrates. It is a method in which the SAM regions damaged by process heat and stress are removed through selective etching during the process, followed by re-patterning the SAM to enable continuous AS-ALD. The process is inherently self-correcting, because undesired deposition can be cleanly removed in the second step, allowing for high quality patterning. Hashemi et al. proposed a method in which, as shown in Fig. 7(a), when the patterned SAM on

Cu over Si substrate is damaged through repeated process cycles, a mild etchant such as acetic acid is used to selectively etch only the copper oxide layer, thereby restoring selectivity [28]. They propose and test a combined selective deposition-selective etch approach and show that it improves the film thickness for which selective deposition can be performed at least 10 times. This is a lift-off method in which the natural oxide of Cu is removed, along with the SAM and precursor, simultaneously. The lift-off process exposes the metal surface, and thereafter, the SAM is re-adsorbed, enabling high-selectivity AS-ALD to proceed.

As shown in Fig. 7(b, e), when ALD was performed on a Cu/SiO₂ substrate for 60 and 250 cycles, selectivity was lost as seen in Fig. 7(c) and (f). However, in both cases, when acetic acid was added, Fig. 7(d, g) demonstrates that only the Cu region was selectively etched [39]. This suggests that even if selectivity significantly decreases due to SAM damage, selectively etching the damaged part during the process can restore the well-ordered SAM structure, allowing for high-cycle AS-ALD with maintained high selectivity.

Moreover, the required formation time of the SAM resist can be significantly reduced from 48 h to at most 1 h, making the process much more efficient [28]. The selectivity between GS and NGS ultimately diminishes for all known combinations due to defects, the formation of new defects, and the Boltzmann distribution of molecular reactivities on the surfaces. This selectivity can be regained by implementing etch-back correction steps [40, 41].

3-2. Residual SAM removal issues

The elimination of residual monolayers typically requires strong treatments such as plasma [42], UV light [43, 44], ozone [21], or acid etching [28, 30], which can cause substrate damage and present issues in various applications [27-28, 40]. López et al. proposed the use of stearic acid (SA) SAM with a carboxyl group as a headgroup, which can be removed using an appropriate polar solvent, as a solution to this issue, rather than employing surface treatment methods such as UV light or acids [27].

The study concludes that SA SAM serves as an effective and removable copper passivation agent for AS-ALD without requiring exposure to harsh conditions such as etching or acid treatments [27]. Its chemical structure exhibits the typical characteristics of SAM molecules utilized in AS-ALD, featuring a saturated 18-carbon chain terminating in a carboxylic acid group (CH₃(CH₂)₁₆COOH). ODT and ODT SAMs, which

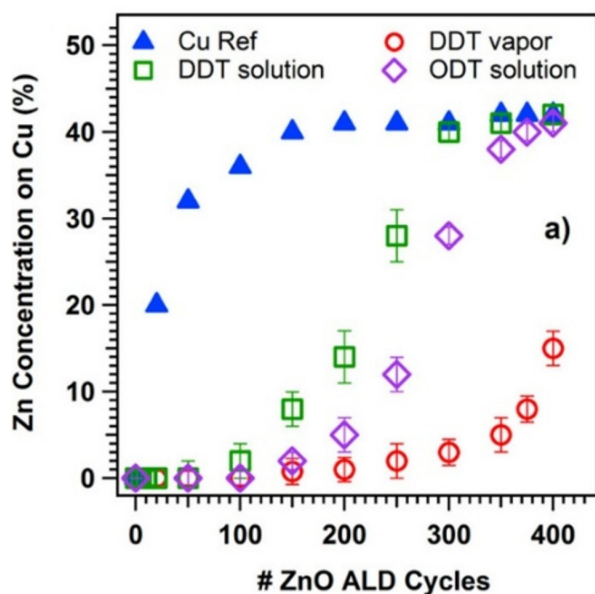


Fig. 6. Zn concentration on Cu substrates measured by X-ray photoelectron spectroscopy after various numbers of ZnO ALD cycle (Reprinted with permission from [1]. Copyright 2016 American Chemical Society).

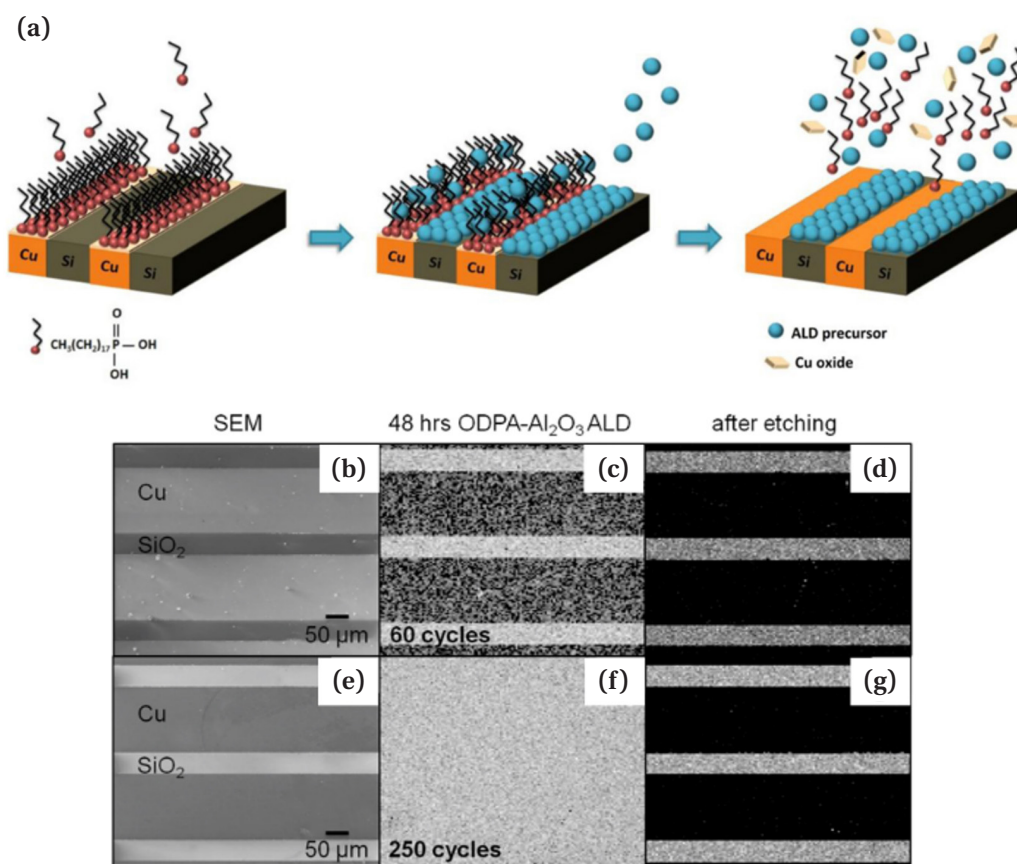


Fig. 7. (a) Schematic demonstrating self-aligned patterning through a combination of selective deposition (using ODPA SAM blocking layer on Cu oxide) and selective removal (using acid) of dielectric material, (b, e) Scanning electron microscopy images on the patterned Cu/Si substrates, (c, f) Al Auger maps of the patterned Cu/Si substrates treated with ODPA for 48 h followed by (c) 60 and (f) 250 cycles, (d, g) Al Auger maps after sonication of the corresponding substrates in acetic acid for 10 min (adapted with permission from [28]. Copyright 2015 American Chemical Society).

have been frequently studied in AS-ALD, strongly adsorb and are challenging to remove even when immersed in polar solvents such as water, ethanol, or acetone, requiring immersion times of over 1 hour for ODPA and 25 hours for ODT. In contrast, stearic acid SAM can be efficiently removed with a much shorter immersion time of just 25 minutes. This makes stearic acid a promising candidate for AS-ALD, especially when efficient removal of residual SAM is required. Through the experiments conducted, SA SAMs were successfully removed after 40 minutes in deionized water and 30 minutes in ethanol. These results demonstrate that no strong etching treatment is necessary for monolayer removal, offering a new approach for AS-ALD that involves mild monolayer removal.

4. Conclusion

This paper examines the key factors for achieving high effi-

ciency and selectivity in deactivation-based AS-ALD using SAMs as inhibitors, with a focus on SAM structure and precursor design. The blocking efficiency of SAMs improves when the tail group is a simple linear chain, while the functional group should neither be thermodynamically reactive with the substrate nor strongly interact with the precursor. Furthermore, the precursor's reactivity with SAMs and its molecular size within the ALD environment significantly influence selectivity.

Despite their promising precursor-blocking performance, SAM-based deactivation in AS-ALD faces several implementation challenges. SAMs can develop gauche defects or detach due to ALD heat, necessitating correction steps. Additionally, the removal of SAMs after deposition often requires strong treatments that may damage the substrate; however, SA SAMs, which can be dissolved in polar solvents, present a potential solution.

A promising alternative is small molecule inhibitors (SMIs),

which consist of a chemisorptive reactive moiety and an inert functional group, preventing precursor adsorption through chemical passivation and steric shielding [45]. SMIs' higher volatility allows vapor-phase delivery, improving selectivity in sub-10 nm, high-aspect-ratio structures. For effective AS-ALD using SMIs, it is crucial to design SMI-precursor pairs that exhibit strong reactivity with the substrate without reacting with the precursor. Although SAMs offer strong selectivity, their inherent limitations restrict their broader applicability, while SMIs are emerging as a promising alternative for future AS-ALD research.

Funding

This work has supported by the National Research Foundation of Korea (NRF) grant funded by the Korea government (MSIT) (NRF-2023R1A2C1006831).

Conflict of Interest

Byung Joon Choi serves as an editor of the Science editing, but has no role in the decision to publish this article. Except for that, no potential conflict of interest relevant to this article was reported.

Data Availability Statement

Data will be made available on request.

Author Information and Contribution

Si Eun Jung: Student; conceptualization, investigation, visualization, writing—original draft

Ji Woong Shin: Student; visualization, writing—original draft

Ye Jin Han: Student; visualization, writing—original draft

Byung Joon Choi: Professor; supervision, writing—review & editing

Acknowledgments

None.

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Thermodynamic and Electronic Descriptor-Driven Machine Learning for Phase Prediction in High-Entropy Alloys: Experimental Validation

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High-entropy alloys (HEAs) exhibit complex phase formation behavior, challenging conventional predictive methods. This study presents a machine learning (ML) framework for phase prediction in HEAs, using a curated dataset of 648 experimentally characterized compositions and features derived from thermodynamic and electronic descriptors. Three classifiers—random forest, gradient boosting, and CatBoost—were trained and validated through cross-validation and testing. Gradient boosting achieved the highest accuracy, and valence electron concentration (VEC), atomic size mismatch (δ), and enthalpy of mixing (ΔH_{mix}) were identified as the most influential features. The model predictions were experimentally verified using a non-equiatomic $\text{Al}_{30}\text{Cu}_{17.5}\text{Fe}_{17.5}\text{Cr}_{17.5}\text{Mn}_{17.5}$ alloy and the equiatomic Cantor alloy (CoCrFeMnNi), both of which showed strong agreement with predicted phase structures. The results demonstrate that combining physically informed feature engineering with ML enables accurate and generalizable phase prediction, supporting accelerated HEA design.

Keywords: High-Entropy Alloys (HEAs); Phase Prediction; Machine Learning (ML); Thermodynamic Descriptors; Experimental Validation

Received: May 1, 2025

Revised: June 11, 2025

Accepted: June 12, 2025

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1. Introduction

High-entropy alloys (HEAs), also known as multi-principal element alloys, are a transformative class of metallic materials characterized by the presence of five or more principal elements in near-equiatomic or significant proportions (typically 5 to 35 at.%) [1-16]. Their definition has evolved significantly in recent years. While the original definition emphasizes element count, contemporary research increasingly recognizes configurational entropy ($\Delta S_{\text{mix}} \geq 1.5R$) as a more robust criterion, accommodating both non-equiatomic and quaternary systems [17]. Unlike conventional alloys, which are generally centered around a single principal element, HEAs derive their distinctive structural and functional characteristics from the synergistic interactions among multiple principal elements [18-20]. As a

result, this compositional complexity gives rise to outstanding properties, including superior mechanical strength, excellent thermal stability, and enhanced corrosion resistance [19].

The theoretical foundation of HEAs relies on four “core effects” [18]: the high-entropy effect, which stabilizes simple solid-solution phases (like FCC, BCC) over complex intermetallic compounds; the sluggish diffusion effect, which retards phase transformation kinetics [21]; the severe lattice-distortion effect, arising from atomic size differences, which causes lattice strain and enhances strength; and the cocktail effect, describing synergistic properties that are not merely the arithmetic averages of the constituent elements, but rather emergent properties arising from their interactions [22, 23].

However, recent works have revisited these core effects, particularly questioning the universality of the sluggish diffusion and high-entropy stabilization mechanisms. For example, Hsu et al. [18] demonstrated that sluggish diffusion is not always observed, with differences noted between Mn-containing and

<https://doi.org/10.4150/jpm.2025.00143>

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Mn-free systems. Similarly, studies have pointed out that multi-phase HEAs can often exhibit multifunctional properties comparable to or even superior to those of single-phase systems [3, 19, 20], challenging the presumption that high configurational entropy alone guarantees solid-solution stability.

Although HEAs hold great promise, accurately predicting and controlling their phase formation remain significant challenges, hindering the accelerated discovery and optimization of advanced materials. Phase formation in HEAs is governed by a delicate interplay of thermodynamic and kinetic factors, including the entropy and enthalpy of mixing (ΔS_{mix} , ΔH_{mix}) [24, 25], atomic size mismatch (δ), valence electron concentration (VEC), and electronegativity difference ($\Delta\chi$) [26]. Several empirical and semi-empirical criteria have been proposed to guide phase prediction (e.g., extensions of Hume-Rothery rules, the Ω parameter, and VEC thresholds); however, accurate and generalizable prediction across the vast compositional space of HEAs remains difficult. Experimental exploration alone is often prohibitively costly and time-consuming, highlighting the need for data-driven predictive frameworks.

In this context, previous studies such as Singh et al. [27] have applied machine learning to predict phases and design new HEA compositions. However, these efforts often rely on datasets with mixed-quality entries and less consistent processing histories, which may limit predictive robustness. In contrast, the present study introduces a machine learning framework trained on a rigorously curated experimental dataset and emphasizes physically meaningful descriptors tied directly to practical synthesis conditions. Furthermore, this study provides dual validation—computational and experimental—on both equiatomic and non-equiatomic systems, highlighting both predictive accuracy and practical feasibility.

Recently, alloy design strategies have expanded beyond the strict equiatomic constraint towards non-equiatomic HEAs. This approach acknowledges that the stable solid solutions do not necessarily require equiatomic ratios, as the configurational entropy curve can be relatively flat near the equiatomic point, allowing a range of other compositions to possess similar entropy values and phase stability. This offers greater flexibility in alloy design for achieving desired properties and overcomes limitations encountered in some early equiatomic systems [28].

Advances in machine learning (ML) have opened new avenues for modelling the complex, non-linear relationships between composition and phase stability in multi-component systems [29–31]. ML holds the potential to significantly accelerate the materials design and discovery process [32]. However,

the predictive success of ML approaches critically depends on the quality of the input dataset, the physical relevance of the engineered features, and the ability to generalize beyond the training data. Moreover, explicitly validating ML predictions against experimentally synthesized and characterized HEA systems is crucial for building confidence in their practical applicability [33].

In this study, we address these challenges by developing a machine learning-based framework for phase prediction in HEAs, grounded in a curated dataset of 648 experimentally characterized alloys. The input features were meticulously engineered based on thermodynamic and electronic descriptors and, importantly, were calculated from actual material preparation conditions using 10-gram powder batches precisely weighed according to target atomic fractions. Three state-of-the-art ML classifiers—Random Forest (RF), Gradient Boosting (GB), and CatBoost—were trained, hyperparameter-optimized, and evaluated for phase prediction. The model predictions were further validated through the experimental synthesis and characterization of two distinct systems: a novel non-equiatomic alloy ($\text{Al}_{30}\text{Cu}_{17.5}\text{Fe}_{17.5}\text{Cr}_{17.5}\text{Mn}_{17.5}$) and the canonical equiatomic Cantor alloy (CoCrFeMnNi). This study demonstrates the predictive accuracy and robustness of the machine learning framework, providing a practical tool for accelerating the design of next-generation HEAs. Furthermore, this work highlights the critical role of physically meaningful feature engineering and experimental validation in enhancing the reliability of data-driven materials discovery.

2. Methodology

This study employs a comprehensive methodology encompassing dataset construction, feature engineering grounded in physical metallurgy principles, machine learning model development and evaluation, and ultimately, experimental synthesis and validation. Detailed descriptions of each step are provided below to ensure reproducibility.

2.1. Dataset Compilation and Preprocessing

The foundation of this work is a dataset comprising 648 distinct high-entropy alloy (HEA) compositions, curated by Professor Juliusz Dąbrowa (2019) from peer-reviewed experimental literature and further expanded with our own experiments. To promote consistency and minimize variability arising from different processing histories, the alloys included were predominantly synthesized via arc melting and evaluated in the as-cast

condition. Any documented minor surface treatments were considered negligible for the primary purpose of phase classification. Each alloy entry was classified into one of several primary phase types commonly observed in HEA research: single-phase Body-Centered Cubic (BCC) or Face-Centered Cubic (FCC) solid solutions (SS), single-phase intermetallic compounds (IM), amorphous (AM) structures, or multi-phase (MP) mixtures such as BCC+FCC, BCC+IM, FCC+IM, or BCC+FCC+IM. Compositions resulting in complex, highly metastable, or poorly characterized phases were excluded from the dataset to enhance homogeneity and to focus on practically significant phase outcomes.

2.2. Feature Engineering and Descriptor Calculation

To enable machine learning-based prediction of phase formation, compositional information was converted into quantitative descriptors reflecting fundamental thermodynamic, atomic, and electronic factors. Seven key features were engineered for each alloy:

- Entropy of mixing (ΔS_{mix}):

Calculated by the formula [34]:

$$\Delta S_{\text{mix}} = -R \sum_i C_i \ln c_i$$

where c_i is the atomic fraction of element i and R is the universal gas constant ($8.314 \text{ J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$).

- Enthalpy of mixing (ΔH_{mix}):

Determined using Miedema's semi-empirical model [35], adapted for multi-component systems [24, 25, 35]:

$$\Delta H_{\text{mix}} = \sum_i \sum_{j>i} \Omega_{ij} c_i c_j$$

where Ω_{ij} is the binary mixing enthalpy between elements i and j .

- Atomic size mismatch (δ):

This parameter quantifies the degree of atomic packing disorder and is computed as follows [36]:

$$\delta = 100 \times \sqrt{\sum_i c_i \left(1 - \frac{r_i}{\bar{r}}\right)^2}$$

where r_i is the atomic radius of element i and \bar{r} is the average atomic radius.

- Valence electron concentration (VEC):

Weighted-average of the valence electrons per atom, guiding phase stability towards FCC or BCC structures [36].

- Electronegativity difference ($\Delta\chi$):

Calculated by the formula [34]:

$$\Delta\chi = \sqrt{\sum_i c_i (\chi_i - \bar{\chi})^2}$$

where χ_i is the electronegativity of element i and $\bar{\chi}$ is the mean electronegativity.

- Mean melting temperature (T_m): Averaged over all constituent elements using their atomic fractions.

- Ω parameter:

A combined stability indicator is defined as [36]:

$$\Omega = \frac{T_m \Delta S_{\text{mix}}}{|\Delta H_{\text{mix}}|}$$

which integrates thermodynamic stability and chemical disorder.

All features were normalized either to a [0,1] range or standard-scaled to prevent variables with large numeric magnitudes from dominating the learning process.

2.3. Machine Learning Model Development

Three distinct machine learning algorithms were selected and implemented for HEA phase prediction: Random Forest (RF), Gradient Boosting (GB), and CatBoost [37, 38]. RF utilizes bootstrap aggregation (bagging) to build an ensemble of de-correlated decision trees, enhancing robustness and generalization. GB and CatBoost employ sequential boosting techniques, where each tree learns from the errors of the preceding ones; CatBoost incorporates specific enhancements for handling categorical features (though not heavily utilized here) and regularization. These models were chosen for their demonstrated strong performance in materials science classification tasks. They were implemented using the Python-based scikit-learn and CatBoost libraries within a Google Colab environment.

A systematic hyperparameter optimization was performed using grid search coupled with 5-fold cross-validation executed exclusively on the training set (88% of the total dataset, leaving 12% as a hold-out test set). Key hyperparameters tuned included the number of estimators (trees/iterations), maximum tree depth, minimum samples per leaf/split, learning rate, and regularization terms (e.g., `l2_leaf_reg` for CatBoost), specific to each algorithm's requirements.

2.4. Model Training, Validation, and Feature Importance Analysis

After hyperparameter optimization, the models achieving the highest cross-validation scores were trained on the full

training dataset (88%) and subsequently evaluated on a hold-out test set (12%). Model performance was assessed using standard classification metrics: accuracy, precision, recall, and F1-score.

To interpret the models and understand the driving factors behind phase prediction, a feature importance analysis was conducted. Model-specific techniques were used: mean decrease in Gini impurity for Random Forest, and permutation importance for Gradient Boosting and CatBoost. This analysis aimed to rank the input features based on their contribution to the models' predictive decisions [39].

2.5. Experimental Synthesis and Validation

To rigorously validate the predictive capability of the developed ML framework, two distinct HEA compositions were selected for experimental synthesis and characterization: the novel non-equiatomic $\text{Al}_{30}\text{Cu}_{17.5}\text{Fe}_{17.5}\text{Cr}_{17.5}\text{Mn}_{17.5}$ alloy and the canonical equiatomic CoCrFeMnNi (Cantor) alloy. Our samples were synthesized via mechanical alloying using a planetary ball mill (AGO-2 type), employing tungsten carbide (WC) milling media at a ball-to-powder ratio of 20:1, a rotation speed of 500 rpm, with stearic acid as the process control agent, all conducted under an argon atmosphere. Elemental powders (purity > 99.9%, particle size 45–75 μm) were accurately weighed in 10-gram batches to achieve the target atomic ratios, following process parameters consistent with established protocols in previous studies [40–43]. Phase identification was performed using X-ray diffraction (XRD) with Cu-K α radiation ($\lambda = 1.5406 \text{ \AA}$), a 2θ range of 20° – 100° , and a step size of 0.02° . The resulting diffraction patterns were analysed using a Python-based tool, as described in [44].

3. Results and Discussion

This section presents the outcomes derived from the analysis of the curated dataset, the performance evaluation of the developed machine learning models, and the subsequent experimental validation, both designed to assess the framework's predictive capabilities. The findings are interpreted within the context of established physical metallurgy principles governing phase formation in high-entropy alloys.

3.1. Exploratory Data Analysis and Feature Relevance

Initial analysis of the curated dataset of 648 HEAs provided valuable insights into the relationships between the engineered features. Examination of the correlation heatmap (Fig. 1) re-

vealed expected several physical trends. A strong positive correlation (0.92) was observed between the entropy of mixing (ΔS_{mix}) and the number of constituent elements, reflecting the fundamental definition of ideal configurational entropy. Furthermore, moderate negative correlations were identified between the valence electron concentration (VEC) and atomic size mismatch (δ) (-0.45), as well as between the enthalpy of mixing (ΔH_{mix}) and δ (-0.68). These correlations suggest a complex interplay in which electronic structure, atomic packing efficiency, and chemical bonding affinity collectively influence phase stability within these multi-component systems.

Analysis of the feature distributions (Fig. 2 and Table 1) further reinforced the physical relevance of the selected descriptors. VEC values were found to predominantly cluster between 6 and 8, aligning with established ranges governing FCC and BCC phase stability in HEAs. Similarly, the distribution of ΔH_{mix} values centered near zero (mean = -8.335 kJ/mol), consistent with the thermodynamic competition between the formation of energetically favorable ordered intermetallic phases and entropically favored disordered solid solutions. These preliminary analyses confirmed the sound physical basis of the engineered features chosen for subsequent machine learning model development.

3.2. Machine Learning Model Performance and Feature Importance

After conducting systematic hyperparameter optimization, we assessed the predictive performance of three models — Random Forest (RF), Gradient Boosting (GB), and CatBoost models — on the unseen hold-out test set (Table 2). All three models demonstrated high predictive accuracy, indicating their effectiveness in capturing the composition–phase relationships within the dataset (Fig. 3) [45]. The Gradient Boosting model exhibited slightly superior performance, achieving the highest cross-validation accuracy (88.5%, Table 2), and demonstrated strong generalization capabilities on the test set. These performance levels are competitive with those reported in other machine learning studies focused on HEA phase prediction. Consistent with observations in the literature, predicting phases involving intermetallic compounds was more challenging than predicting single-phase solid solutions.

To explain the differences in hyperparameters, RandomForest employs hyperparameters like `n_estimators`, `max_depth`, `min_samples_split`, and `min_samples_leaf` to control the number of trees, tree depth, and minimum samples for splits or leaves, aligning with its bagging approach (independent tree

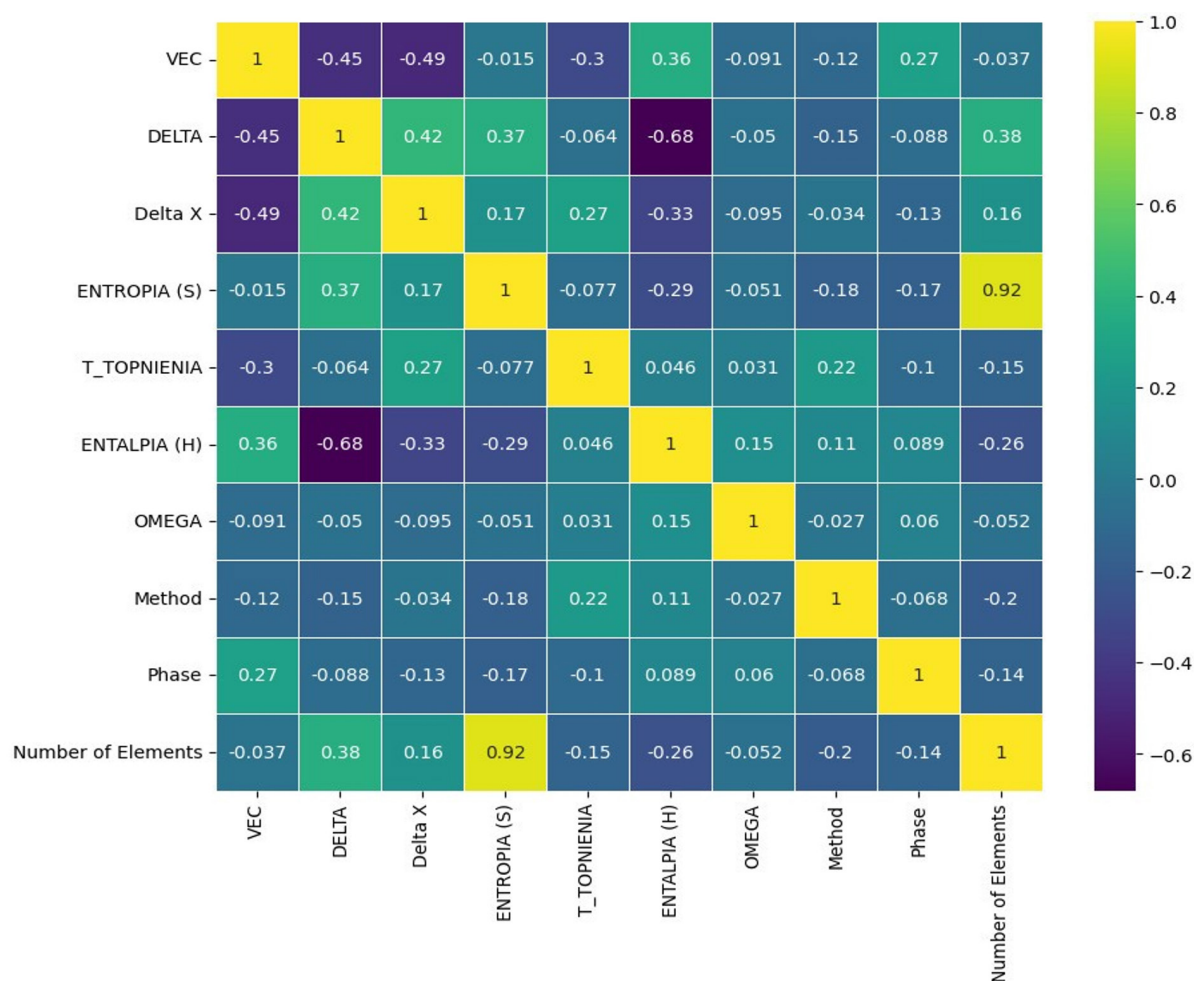


Fig. 1. Correlation heatmap of the engineered input features for the dataset of 648 high-entropy alloys.

training). In contrast, CatBoost and GradientBoosting, both based on gradient boosting, use similar parameters such as iterations/n_estimators and depth/max_depth, but include learning_rate to control the contribution of each tree during the boosting process. CatBoost also uses l2_leaf_reg for explicit regularization, while GradientBoosting relies on min_samples_leaf (like RandomForest) for implicit regularization. Additionally, RandomForest and GradientBoosting use min_samples_split to control node splitting, a parameter that CatBoost manages internally. These differences stem from their algorithms: RandomForest averages independent trees, whereas CatBoost and GradientBoosting train sequentially to correct errors, requiring additional parameters like learning_rate to balance performance and accuracy on the material dataset (predicting phases from features like ΔH_{mix} , VEC).

Feature importance analysis was conducted to elucidate the key factors driving the models' predictions (Fig. 4). Across all

three distinct algorithms, VEC consistently emerged as the most influential feature (~38–40% importance), underscoring its critical role in differentiating between FCC and BCC crystal structures. Atomic size mismatch (δ) (~14–21%) and enthalpy of mixing (ΔH_{mix}) (~9–11%) were identified as the next most significant factors, primarily governing the propensity for forming disordered solid solutions versus ordered intermetallic or amorphous phases. The remaining features showed moderate importance, contributing to the overall phase stability landscape but playing secondary roles compared to VEC, δ , and ΔH_{mix} in determining the primary phase structures within this dataset [36].

3.3. Model Application and Experimental Validation

The predictive capability of the developed machine learning framework was assessed through its application to two distinct high-entropy alloy (HEA) systems: a novel non-equiatomic

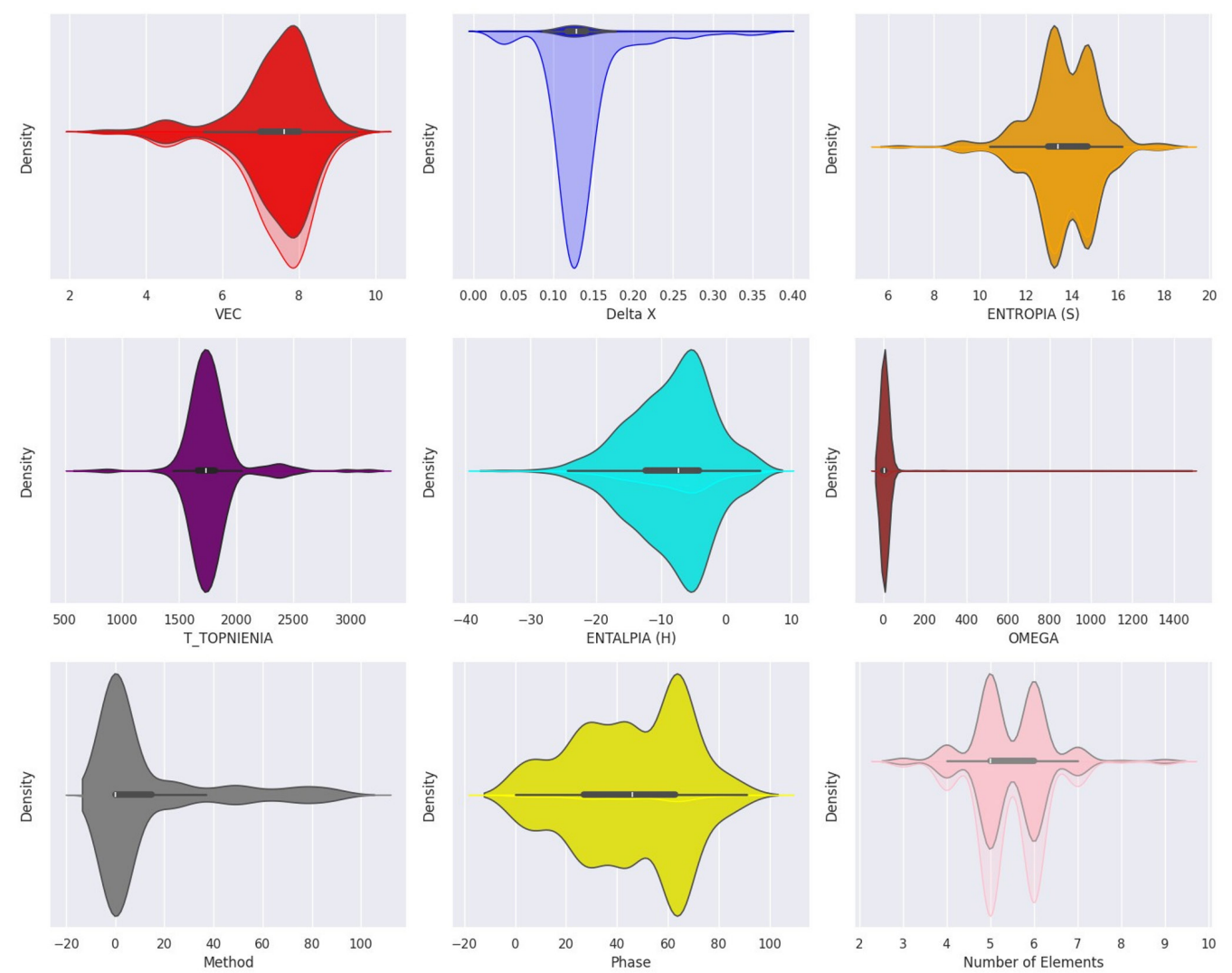


Fig. 2. Data density distribution of each thermodynamic parameter for the dataset including 648 high-entropy alloys

Table 1. Descriptive statistics for the key engineered features across the dataset of 648 high-entropy alloys

	Mean	Std. Dev	Min	Max
VEC	7.363	1.072	2.800	9.500
δ	4.770	2.477	0.376	19.110
$\Delta\chi$	0.136	0.045	0.031	0.364
ΔS_{mix}	13.654	1.462	6.466	18.215
ΔH_{mix}	-8.335	6.316	-34.348	5.125
T_m	1768.783	237.338	701.456	3155.500
Ω	8.589	46.134	0.836	1002.369

system, $\text{Al}_{30}\text{Cu}_{17.5}\text{Fe}_{17.5}\text{Cr}_{17.5}\text{Mn}_{17.5}$, and the well-established equiatomic Cantor alloy, CoCrFeMnNi . For both alloys, thermodynamic and electronic descriptors including the entropy of mixing (ΔS_{mix}), enthalpy of mixing (ΔH_{mix}), valence electron

concentration (VEC), atomic size mismatch (δ), electronegativity difference ($\Delta\chi$), mean melting temperature (T_m), and the Ω parameter were calculated based on their compositions, and normalized prior to input into the trained models.

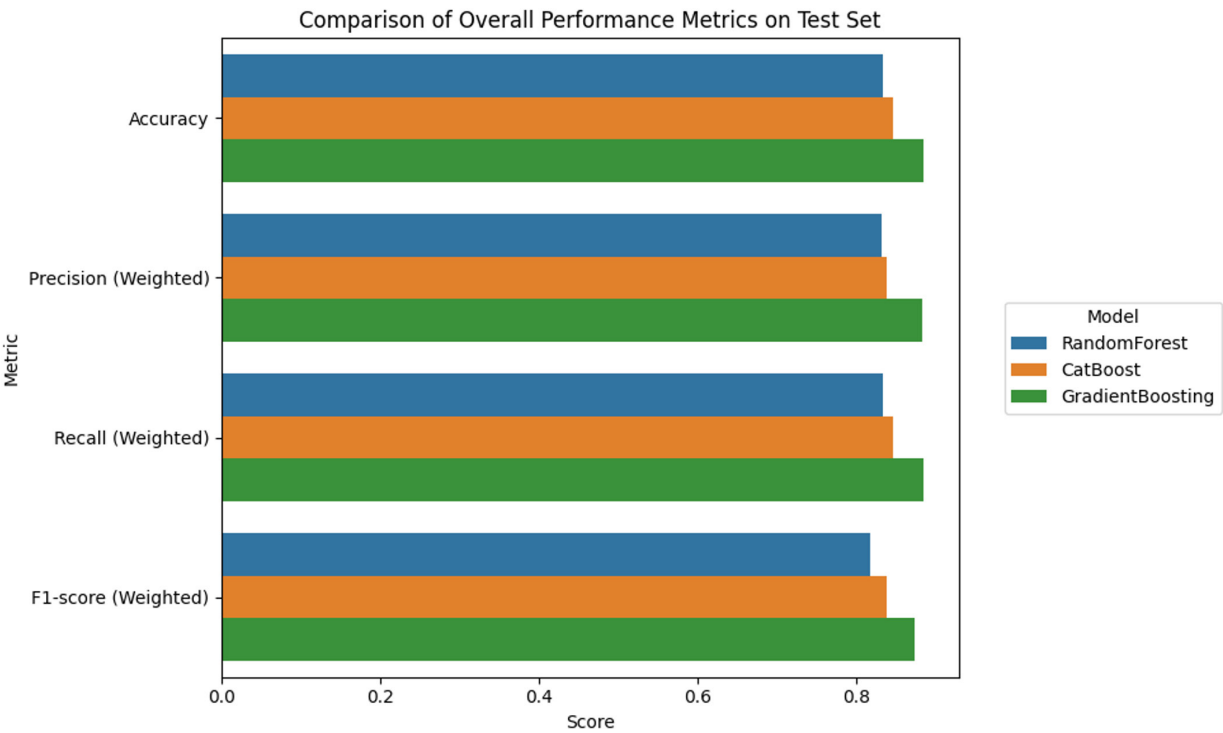


Fig. 3. Bar chart comparing key performance metrics (accuracy, precision, recall, F1-score) of the random forest, CatBoost, and gradient boosting models on the test set.

Table 2. Optimized hyperparameters identified via grid search and 5-fold CV for the Random Forest, Gradient Boosting and CatBoost models

	Preset Range	Random Forest	Gradient Boosting	CatBoost
max_depth (depth)	[1,9]	7	5	8
n_estimators (iterations)	[50,200]	50	100	100
min_samples_leaf	[1,5]	2	2	x
min_samples_split	[1,4]	2	2	x
l2_leaf_reg	[1,5]	x	x	1
learning_rate	[0.01, 0.1]	x	0.07	0.1
Best CV Score (Accuracy)	x	0.833	0.885	0.846

Note: x is “not applicable”.

In the case of $\text{Al}_{30}\text{Cu}_{17.5}\text{Fe}_{17.5}\text{Cr}_{17.5}\text{Mn}_{17.5}$, all three machine learning classifiers—Random Forest, CatBoost, and Gradient Boosting—converged on a consistent prediction: that the dominant phase under standard synthesis conditions would be a single-phase BCC solid solution [36]. This prediction was experimentally verified by synthesizing the alloy through high-energy mechanical alloying (MA) for 3.5 hours, followed by heat-treatment at temperatures at 700 °C, as seen in Fig. 5. X-ray diffraction (XRD) analysis of the as-milled powders prior to heat-treatment revealed the presence of a dual-phase mix-

ture comprising both FCC and BCC structures. The emergence of dual phases at this stage is attributed to competing thermodynamic forces—namely, a moderately negative ΔH_{mix} and relatively high atomic size mismatch δ , combined with suboptimal entropy levels due to the non-equiatomic nature and dominant Al content [26]. These parameters position the alloy near the FCC-BCC phase boundary, and thus a kinetic pathway favoring multi-phase formation during MA is expected [36]. Upon heat-treatment, however, the material transformed into a well-defined single BCC phase, as evidenced by sharp diffrac-

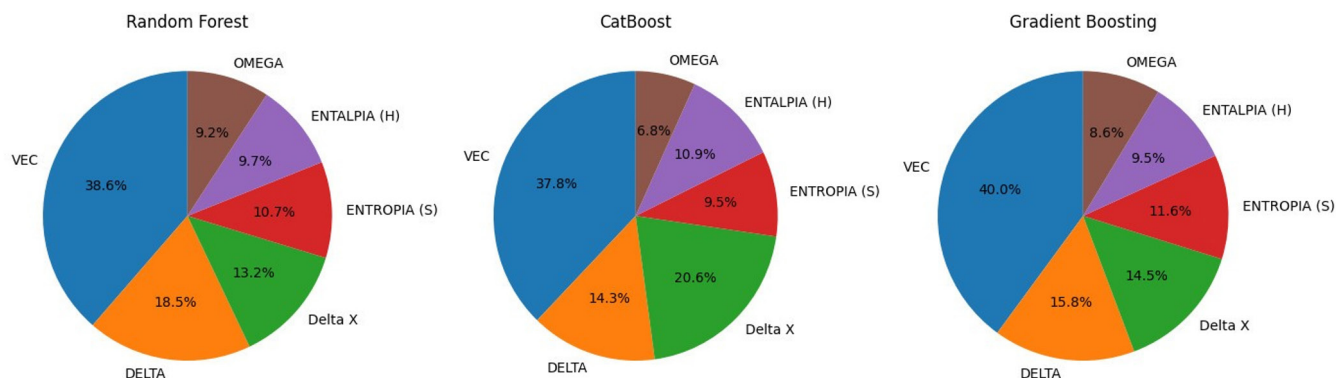


Fig. 4. Pie graph of feature importance.

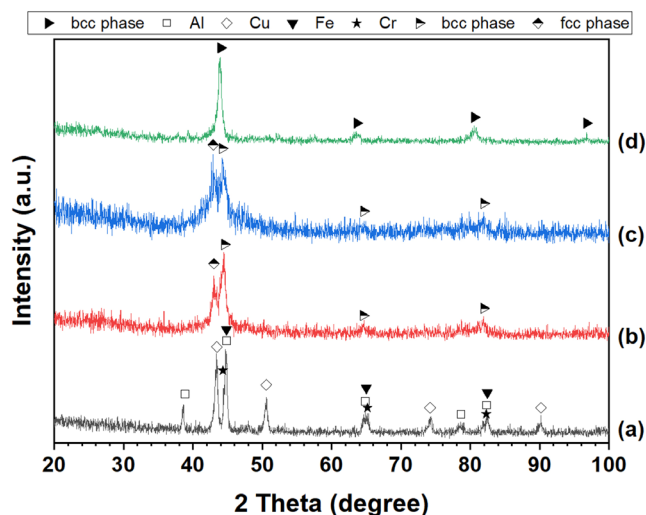


Fig. 5. X-ray diffraction patterns of the $\text{Al}_{30}\text{Cu}_{17.5}\text{Fe}_{17.5}\text{Cr}_{17.5}\text{Mn}_{17.5}$ samples: (a) MA 0.5h, (b) MA 2h, (c) MA 3.5h, and (d) MA 3.5h sintered at 700 °C.

tion peaks indicating improved crystallinity and phase purity at the temperature. This transformation from the initial dual-phase (FCC-BCC) mixture formed during MA is attributed to the high-temperature heat treatment effectively breaking down the metastable structure [28]. This strong agreement between predicted and experimentally observed stable phase supports the model's effectiveness in anticipating thermodynamically favored structures for complex alloy systems [46].

To further test the generality and robustness of the models, the equiatomic CoCrFeMnNi alloy was selected for validation. This composition is widely known for forming a stable single-phase FCC solid solution under a broad range of synthesis conditions, including non-equilibrium processing [16]. All

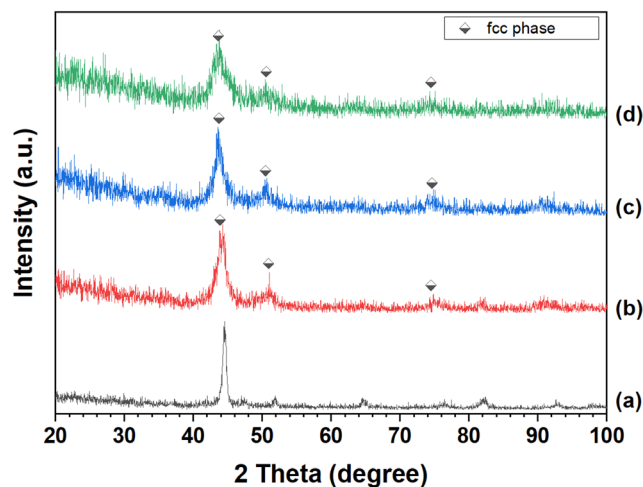


Fig. 6. X-ray diffractions patterns of CoCrFeMnNi powders (a) 1 h, (b) 5 h, (c) 10 h, and (d) 20 h after mechanical alloying.

models correctly predicted FCC as the primary phase, a result supported by computed descriptors: high configurational entropy ($\Delta S_{\text{mix}} \geq 1.5 R$), moderate negative enthalpy of mixing ($\sim -2 \text{ kJ/mol}$), $\text{VEC} \approx 8.0$ (strongly favoring FCC), atomic size mismatch $\delta < 5\%$, and an Ω value well within the stability regime of disordered FCC solid solutions.

Experimentally, CoCrFeMnNi powders were subjected to mechanical alloying for durations between 1 and 20 hours, as shown in Fig. 6. Remarkably, even at the early stages of milling, XRD patterns showed only FCC peaks, with no evidence of BCC or intermetallic phases, demonstrating the inherent thermodynamic preference for FCC formation in this system. The immediate emergence of a stable FCC phase, even in the ab-

Table 3. Summary comparison of alloy composition with the ML-predicted phase and experimental synthesis route,

	Gradient Boosting	Random Forest	CatBoost	Experimental
Al ₃₀ Cu _{17.5} Fe _{17.5} Cr _{17.5} Mn _{17.5}	BCC	BCC	BCC	BCC after MA and heat treatment
Cu ₂₀ Cr ₂₀ Fe ₂₀ Mn ₂₀ Ni ₂₀	FCC	FCC	FCC	FCC

BCC, body-centered cubic; FCC, face-centered cubic.

sence of any post-synthesis thermal treatment, underscores the role of high entropy and favorable elemental compatibility in suppressing phase competition during solid-state processing.

The stark difference in phase evolution between the two systems can be understood through comparative analysis of their thermodynamic and kinetic descriptors. In Al₃₀Cu_{17.5}Fe_{17.5}Cr_{17.5}Mn_{17.5}, the lower ΔS_{mix} (relative to equiatomic HEAs), combined with strong atomic radius mismatch and a VEC (~ 7.2) near the FCC-BCC transition zone, creates a compositional landscape prone to multiphase formation. The alloy requires thermal activation through sintering to homogenize the structure and enable the full transformation to the predicted BCC phase. In contrast, CoCrFeMnNi exhibits ideal HEA characteristics: equiatomic balance yields maximum configurational entropy, the VEC solidly resides in the FCC domain, and ΔH_{mix} and δ remain within the threshold ranges that suppress ordered compound or BCC formation. As a result, this system achieves its predicted single FCC phase immediately after milling without requiring subsequent processing steps [47-49].

These findings jointly validate the machine learning models not only in predicting the equilibrium phase of a complex non-equiatomic HEA after processing, but also in capturing phase behavior under non-equilibrium conditions for canonical HEA systems. The coherence between predicted and experimental phase outcomes across disparate compositions demonstrates the framework’s capacity to support accelerated HEA design and synthesis planning [50, 51].

4. Conclusion

In this study, a machine learning framework was developed and validated for predicting phase formation in high-entropy alloys (HEAs). Using a curated dataset of 648 experimentally characterized alloys with engineered thermodynamic and electronic descriptors, three machine learning models—Random Forest, Gradient Boosting, and CatBoost—were trained and optimized. The models achieved high predictive accuracies, consistently identifying valence electron concentration (VEC), enthalpy of mixing (ΔH_{mix}), and atomic size mismatch (δ) as the most critical factors governing phase stability.

Experimental validation on two distinct HEA systems, a non-equiatomic Al₃₀Cu_{17.5}Fe_{17.5}Cr_{17.5}Mn_{17.5} alloy and the canonical CoCrFeMnNi alloy, demonstrated strong agreement between predicted and observed phase structures under different processing conditions. These results underscore the reliability and practical applicability of the developed ML framework in supporting accelerated alloy design.

The successful integration of domain knowledge into feature engineering, along with systematic model training and experimental validation, emphasizes the potential of data-driven strategies for accelerating materials discovery. Future research will aim to broaden the dataset by incorporating diverse synthesis conditions and accounting for kinetic factors, thereby improving the robustness and generalizability of machine learning models for complex alloy systems.

Funding

This research is funded by the Ministry of Education and Training of Vietnam under grant number B2025-BKA-08.

Conflict of interest

The authors have no conflicts of interest to declare.

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

Nguyen Lam Khoa: MSc student; responsible for conceptualization, experimental design and execution, original draft preparation.

Nguyen Duy Khanh: Undergraduate student; contributed to experimental work and performed calculations related to the mechanical alloying and Midema’s model.

Nguyen Thi Hoang Oanh: Associate Professor; supervised the research activities, provided critical revisions, and contributed

to reviewing and editing the manuscript.

Le Hong Thang, Hoang Thi Ngoc Quyen: Ph.D Research members; contributed to conceptualization and conducted computational analyses supporting experimental findings.

Nguyen Hoa Khiem: MSc candidate; developed the Python code and user interface, and optimized the computational application for data analysis.

Nguyen Hoang Viet: Associate Professor; provided overall supervision, contributed to conceptual development, acquisition of funding, and participated in reviewing and editing the final manuscript.

Acknowledgments

None.

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기계학습을 활용한 3차원 적층제조용 알루미늄 합금 개발

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Development of Aluminum Alloys for Additive Manufacturing Using Machine Learning

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The present study introduces a machine learning approach for designing new aluminum alloys tailored for directed energy deposition additive manufacturing, achieving an optimal balance between hardness and conductivity. Utilizing a comprehensive database of powder compositions, process parameters, and material properties, predictive models—including an artificial neural network and a gradient boosting regression model, were developed. Additionally, a variational autoencoder was employed to model input data distributions and generate novel process data for aluminum-based powders. The similarity between the generated data and the experimental data was evaluated using K-nearest neighbor classification and t-distributed stochastic neighbor embedding, with accuracy and the F1-score as metrics. The results demonstrated a close alignment, with nearly 90% accuracy, in numerical metrics and data distribution patterns. This work highlights the potential of machine learning to extend beyond multi-property prediction, enabling the generation of innovative process data for material design.

Keywords: Directed Energy Deposition (DED) Additive Manufacturing; Machine Learning; Variational Auto Encoder(VAE); Process Design; Property Prediction

Received: May 13, 2025

Revised: June 9, 2025

Accepted: June 10, 2025

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1. Introduction

자동차 산업에서 경량화는 에너지 효율 향상과 이산화탄소 배출 저감을 위한 핵심 전략으로, 모터, 배터리, 엔진 하우징 등 주요 부품에 적용할 수 있는 경량 소재 기술 개발이 필수적이다. 이에 따라 기존 가공 방식보다 형상 자유도가 높고 재료 효율성이 우수한 적층 제조(Additive Manufacturing, AM) 기술이 주목받고 있으며, 그 중에서도 금속 소재에 적용 가능한 직접 용착 방식 적층 제조(Directed Energy Deposition, DED)가 효과적인 대안으로 부상하고 있다[1, 2].

DED는 금속 분말을 고출력 레이저로 용융·응고시켜 적층하는 방식으로, 자유로운 형상 제작, 높은 공정 속도, 다양한 소재 조성 적용 가능성 등의 장점을 갖는다[3]. 특히 분말 소결 방식(Powder Bed Fusion, PBF)에 비해 공정 유연성이 높고, 대형 부품의 제작이나 보수에도 적합하여 실용성이 크다[4]. 이러한 장점으로 인해, 알루미늄 합금과 DED 공정의 융합은 경량 부품 제조를 위한 유망한 기술 조합으로 주목받고 있다. 그러나 대표적인 상용 경량금속인 알루미늄 합금은 높은 레이저 반사율, 낮은 용접성, 공정 중 휘발성 원소의 증발로 인한 기공 형성 등으로 인해 DED 공정 적용 시 기술적인 어려움이 존재한다[5]. 동시에, 자동차 및 항공 분야에서 요구되는 고강도와 고방열 특성은 전도도와 기계적 강도 사이의 상반(trade-off) 관계로 인해 합금 설계에 큰 제약을 준다. 따라서 DED 공정에 적합하면서도 상반 특성을 동시에 만족할 수 있는 알

<https://doi.org/10.4150/jpm.2025.00150>

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루미늄계 신합금 개발이 필수적이다.

기존 적층제조용 합금 설계를 위해 실험적으로 조성과 공정 조건을 조정해가며 시행착오적으로 최적 조건을 도출하는 방식이 주로 사용되었으나, 이는 시간과 비용이 많이 소요되며 확장성이 떨어진다[6]. 이에 따라 최근에는 시뮬레이션과 기계학습 기반 데이터 분석을 활용하여 조성 설계와 공정 최적화를 동시에 수행하는 연구가 활발히 진행되고 있으며, 이러한 접근은 복잡한 물성 간 관계를 정량적으로 분석하고 새로운 소재를 효율적으로 설계하는 데 효과적인 대안으로 자리잡고 있다.

기계학습은 현재 적층 제조 분야에서 주목받고 있으며, 공정 및 소재 물성의 최적화를 위한 활용이 활발하게 이루어지고 있다[7]. Zouhri등은 SVM(Support Vector Machine)과 MLP (Multilayer perceptron) 분류 모델을 이용한 L-PBF공정으로 설계된 재료의 밀도 측정 및 두 모델에 대한 성능 비교를 진행하였고[8], Abdul 등은 GB(Gradient boosting)기법과 PSO(Particle Swarm Optimization)기법을 융합하여 L-PBF의 9가지 공정 변수에 따른 상대 밀도의 예측과 더불어 특성 중요도 분석과 SHAP(shapley Additive exPlanations)기법을 이용하여 모델의 예측 결과를 해석하였다[9]. Gu등은 L-PBF공정에서 상대 밀도와 표면 거칠기에 대한 예측과 특성 중요도 분석 그리고 학습 데이터의 비율에 따른 성능의 변화를 연구하였으며[10], Cao 등은 Ti-6Al-4V의 L-PBF공정 데이터를 K-means 알고리즘을 이용하여 3가지의 클러스터로 분류한 뒤, 가우시안 프로세스, 랜덤 포레스트, 서포트 벡터 회귀 기법을 이용하여 항복 강도, 인장 강도, 연신율의 예측을 실행한 후 각 클러스터와 예측하고자 하는 물성에 맞는 회귀 모델을 선정한 다음, SHAP 기법을 이용하여 각 물성 별 예측 결과에 따른 해석을 진행하였다[11]. DED 분야에서도 Israt 등은 L(Laser)-DED 공정으로 만들어진 SS316L의 항복강도, 인장강도, 연신율을 XGBoost(eXtreme Gradient Boosting)와 랜덤 포레스트 기법을 사용하여 예측한 다음 성능을 비교하였고[12], Choi는 SUS316L를 이용한 DED 공정의 물성을 예측하는 데 있어서, 하이퍼파라미터 튜닝이 진행된 5개의 기계학습 모델을 사용하여 어떤 모델이 가장 적합한지 다양한 성능 지표를 이용하여 연구하였다[13]. 그리고, Kim은 Random Forest, SVM 모델을 사용하여 티타늄 합금 DED 공정 최적화를 위해 표면 색깔과 재료 속성 간 연관성을 분석하였다[14].

이러한 선행연구에서는 연구자가 보유하고 있는 데이터셋을 기준으로 가장 성능이 좋은 모델과 최적의 하이퍼파라미터를 도출하였으나, 실험에 쓰이는 데이터셋의 종류, 개수 등의 특성에 따라 최적의 성능이 나올 수 있는 조합이 각기 달라지기에 모든 데이터셋에 일괄적으로 적용하기엔 한계가 있다. 이는, Abdul등[9]과 Cao 등[11]이 실시한 실험에서 사용한 SHAP 기법과 특성 중요도 분석 기법도 데이터셋의 특성에 따라 결과가 다르게 나올 수 있다는 것

을 의미한다. 위에 언급된 연구들 중 두 가지 이상의 물성에 대한 예측을 진행한 사례가 있었다. 하지만, Gu등[10]과 Israt등[12]이 실시한 실험에서는 모델 자체의 예측 성능이 좋지 않았으며, Cao 등[10]이 실시한 실험에서는 하나의 재료에 대하여 공정의 특성에 따라 분류한 클러스터마다 적절한 모델을 선정하였다. 이러한 접근 방식은 다양한 재료를 사용하거나 K-means 또는 기타 기법으로 뚜렷한 클러스터를 만들어내기 어려운 데이터에 적용하는 데 어려움이 있다는 한계가 있다. 또한, 데이터셋의 조성 또는 공정 변수 등의 독립변수와 그로부터 도출되는 종속변수인 물성간의 관계를 학습한 모델을 이용하여 물성을 예측하는 연구는 많이 진행되었으나, 특정 조건을 만족하는 두 가지 이상의 물성 값이 있는 조성과 공정 변수의 수치형 데이터셋을 만드는 연구사례는 적은 편이다.

본 연구에서 재료 설계 및 물성 예측을 목적으로 생성 모델과 기존 기계학습 기법을 융합하여 실험 데이터와 유사한 특성을 지닌 새로운 데이터를 생성하고 이를 검증하는 방안을 제시한다. 이를 위해 입력된 데이터의 분포를 학습할 수 있는 생성 모델인 변분 오토인코더(Variational AutoEncoder, VAE)와 복잡한 문제의 입출력 변수 관계 학습이 용이하여 소재 개발 및 물성 예측 연구에서 널리 쓰이는[15] 인공신경망(Artificial Neural Network, ANN), 그리고 그라디언트 부스팅 회귀 넷(Gradient Boosting Regression, GBR)을 사용하였다. 또한, 실험 데이터와 생성된 데이터 두 종류의 데이터 사이의 특성 유사도를 측정함으로써, 두 가지 이상의 상반특성을 모두 만족하는 재료의 DED 공정 설계 및 검증을 위한 새로운 접근법을 제시했다.

2. Experimental

직접 용착 적층 제조 공정에 쓰이는 구성 원소의 wt.%(Al, Mg, Si, Cu, Zn) 및 공정 조건(스캔 속도, 레이저 출력)을 포함하는 48개의 데이터를 수집했다. 그림 1은 수집한 데이터베이스에서 경도를 예측하는 방법을 나타내고 있다. 데이터 전처리 시 물성에 대한 조성 값 변화의 민감도가 큰 것을 고려하여, 조성 값과 공정 변수에 평균이 0이고 표준편차가 0.03인 작은 노이즈를 추가하거나, 0.97~1.03 범위의 작은 상수를 곱하여 증강하는 스케일링 과정을 거쳐 데이터를 증강하였다. 이후, 데이터 정규화 과정을 거쳐 기계 학습에 용이하도록 처리했다. 따라서 본 연구에서는 조성과 같은 민감 인자에 대해 증강 강도를 제한하고 분포 외삽을 방지하는 필터링을 적용함으로써, 물성 예측의 정밀도를 유지하면서도 데이터의 다양성을 확보하였다.

데이터의 최소값, 최대값, 중앙값 및 표준편차는 표 1에 정리되어 있다. 측정된 비커스 경도값의 평균은 87.14 HV이며, 표준편차는 15.68 HV이다. 중앙값은 87.12 HV로, 평균값과 거의 일치하는

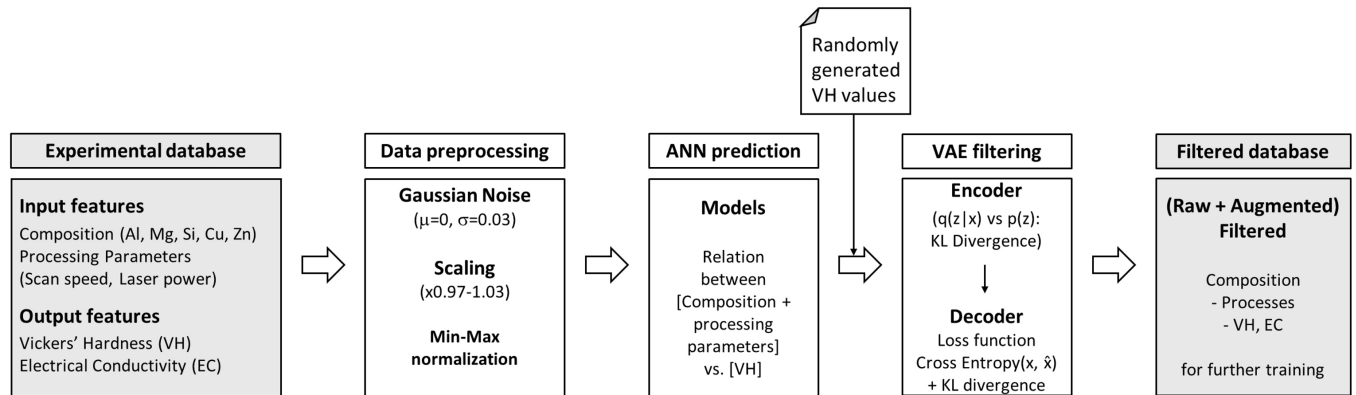


Fig. 1. Schematic illustration of the data augmentation and artificial neural network/variational autoencoder (ANN-VAE)-based composition/process-hardness prediction algorithm

Table 1. Ranges, median values, and standard deviations of elemental composition, process parameters, and property data

	Al (wt. %)	Si (wt. %)	Mg (wt. %)	Cu (wt. %)	Zn (wt. %)	Scan speed (mm/min)	Laser power (W)	Vickers hardness (HV)	Electrical conductivity (%IACS)
MAX	98.63	11.62	2.92	7.5	5.23	1000	800	118.9	46.2
MIN	88.31	0.08	0.01	0.03	0	500	400	50.1	25.5
Median	94.46	3.6	0.43	0.98	0	1000	550	87.12	33.02
Average	94.3	3.5	0.55	1.65	0.48	929.17	528.13	87.14	34.2
Standard deviation	2.29	2.96	0.68	1.63	1.26	152.7	74.24	15.68	5.34

것으로 나타나 전체 데이터가 특정 값에 편중되지 않고 비교적 균일하게 분포되어 있음을 확인하였다. 데이터 증강 기법을 통해 총 1920개의 데이터를 생성하였으며, 이는 원본 데이터 40개에 비해 약 40배에 해당하는 양이다. 증강 방법으로는 노이즈 추가와 스케일링 기법을 각각 수행하였으며, 이를 결합하여 각각 960개씩 총 1920개의 데이터를 확보하였다. 증강 데이터의 적정 규모를 검증하기 위해, 증강 배수를 30배, 40배, 50배로 조절하며 모델 성능을 평가하였다. 그 결과, 40배 증강 조건에서 모델의 학습 속도, 예측 정확도, 연산 효율성 간의 균형이 가장 우수하게 나타났으며, 테스트 데이터 기준 R^2 값도 약 0.85로 향상되었다. 반면, 30배 증강에서는 데이터 수 부족으로 인한 예측 정확도 낮아졌으며, 50배 증강에서는 연산 비용과 처리 시간이 과도하게 증가하는 비효율이 관찰되었다. 이처럼 40배 증강이 모델 학습과 일반화 성능 향상에 가장 적합한 조건임을 확인하였다. 또한, 데이터 증강은 적은 수의 원본 데이터로 인해 발생하는 과적합 문제를 완화하는 데 효과적임을 입증하였다. 원본 데이터의 한계로 인해 훈련, 검증, 시험 세트로의 분할이 어려워지고, 분할별 성능의 신뢰성과 안정성에 큰 변동이 발생하는 문제를 데이터 증강이 일정 수준 해결할 수 있음을 실험적으로 확인하였다.

이후 특정 범위의 비커스 경도 값을 가지는 데이터를 생성할 때,

데이터셋에서 데이터 학습에 적합한 분포인 70~110 HV를 생성 범위로 설정하였다. 초기에 기준을 70 HV으로 설정하고 +10 HV 범위까지 무작위로 20개 생성하였다. 그리고, 기준을 100 HV까지 설정하고 같은 과정을 반복하여 70~110 HV의 물성 값을 가지는 80개의 데이터를 생성하였다. ANN이 경도 값을 토대로 조성과 공정 변수를 예측한 데이터를 생성하고, VAE의 잠재 공간에서 ANN이 생성한 데이터와 실험 데이터 사이의 특성 차이가 비정상적으로 큰 데이터를 필터링함으로써, 데이터의 품질을 향상시켰다.

ANN을 설계할 때 학습 데이터에서는 성능이 좋고, 테스트 데이터에서는 성능이 떨어지는 과적합(Overfitting)을 막기 위하여 히든 레이어 개수를 2개로 설정했다. 출력 레이어를 제외한 나머지 레이어에 활성화 함수로 렐루(ReLU)를 적용하여 시그모이드(sigmoid) 함수의 문제인 기울기 소실 현상을 방지했다. 또한, 모델 학습 도중 검증 손실이 5번 이상 증가하면, 이를 과적합의 전조라 간주하여 학습을 조기 종료(Early Stopping)하도록 설정했다.

VAE는 오토인코더와 외형은 동일하나, 새로운 샘플 데이터를 학습 데이터 분포와 유사하게 생성하는 것이 목적인 생성 모델이다. 잠재 공간이 데이터 특징으로 일정한 분포를 나타내는 특수한 분포를 띈다. 또한, 데이터 분포를 학습할 때, 사후확률 분포를 다루기 쉬운 확률분포로 근사하는 변분 추론을 실시하는데, 분포가

잘 학습되면 자동으로 샘플링이 되며, 손실함수 평가 기준이 명확하기 때문에 학습이 안정적인 장점이 있다[16]. 손실함수는 학습한 잠재 공간과 표준정규분포와의 차이를 계산하는 Kullback-Leiber (KL) divergence와 디코더가 입력된 데이터를 잘 복원했는지 평가하는 cross-entropy함수로 구성된다. 손실함수는 등식 1과 같다.

$$\mathcal{L} = \text{CrossEntropy}(x, \hat{x} + D_{KL}(q(z|x)||p(z))) \quad (1)$$

등식1에서 x 는 인코더의 입력 값이고, \hat{x} 는 디코더의 출력 값이다. 또한, $q(z|x)$ 는 입력 데이터가 사상하는 잠재 공간이고, $p(z)$ 는 표준정규분포다. 계산된 손실함수를 기반으로 Adam(Adaptive Moment Estimation) 최적화 알고리즘을 이용하여 VAE의 가중치를 업데이트한다[17].

한편, 그림2는 경도가 예측된 데이터베이스에서 전기전도도까지 예측한 최종 데이터베이스를 구축하는 방법을 나타낸다. 전기 전도도의 예측은 GBR을 사용했는데, 이 모델의 성능을 최적화하기 위하여 하이퍼파라미터 튜닝을 실시했다. GBR의 경우 여러 개의 약한 학습기를 순차적으로 학습하고, 잘못 예측한 데이터에 가중치를 부여하며 오류를 개선해 나가면서 학습해 나가는 부스팅(Boosting) 기법을 사용한다. 이 모델의 성능은 학습 초기의 약한 학습기의 개수($n_{\text{estimators}}$), 학습을 진행할 때마다 적용되는 학습률(learning_rate), 학습기의 최대 깊이(max_depth)등의 하이퍼파라미터 조합에 따라 달라지며, 하이퍼파라미터 튜닝 대상으로 앞서 언급한 3개를 선정했다. 본 연구에서는 하이퍼파라미터 튜닝 방법으로 리스트에 입력한 하이퍼파라미터의 조합별 성능 확인을 용이하게 하기 위하여 GridSearchCV 기법을 활용하였는데, 학습기의 개수는 100, 200, 300, 400, 학습률은 0.05, 0.1, 0.15, 0.2, 최대 깊이는 2, 3, 4, 5로 정한 다음, 총 64개의 조합 별 학습기 성능 평가를 수행하였다. 이에 5겹 교차 검증(5-Fold cross validation) 방법을 적용하였다. 조합 한 개의 성능을 테스트할 때, 전체 데이터를 다섯 부분으로 나누고, 그중 한 부분을 테스트 폴드로 정의하였다. 나머

지 네 부분은 학습 폴드로 사용하였다. 모델은 학습 폴드로 학습시키고, 테스트 폴드로 예측하여 성능을 도출하였다. 이 과정을 총 5번 반복하여 수행하였다.

이러한 과정을 거쳐 성능이 향상된 GBR은 전기 전도도 실험 데이터를 학습한 다음 ANN과 VAE로 생성된 조성 및 공정 조건 데이터를 이용하여 새로운 데이터의 전기 전도도를 예측하는데 사용되었다.

물성 예측에 사용된 ANN과 GBR의 정확도를 나타내는 지표로 결정계수(R^2)를 사용하였으며, 식 (2)를 이용하였다. 이때, \hat{y} 는 모델이 예측한 값, y 는 실험값, \bar{y} 는 실험값의 산술 평균이다.

$$R^2 = 1 - \frac{\sum (y_i - \hat{y}_i)^2}{\sum (y_i - \bar{y})^2} \quad (2)$$

또한, 생성된 데이터의 품질을 효율적으로 검증하기 위하여, 본 연구에서는 분류를 목적으로 하는 기계 학습 모델인 K-NN(K-nearest neighbor) 모델과 시각화 모델인 t-SNE(t-distributed Stochastic Neighbor Embedding) 기법을 이용했다.

K-NN은 테스트 데이터와 학습 데이터 사이의 유클리드 거리를 기반으로 하는 기본적인 분류 모델로, 학습 데이터 중 가장 가까운 이웃의 클래스를 통하여 테스트의 클래스를 결정하는데, 본 연구에서는 $n_{\text{neighbors}}$ 의 값이 6으로 설정되었다. 이는 하나의 특징에 대한 테스트 데이터를 기준으로 주변의 가장 가까운 6개의 데이터를 사용하여 분류된다는 것을 의미한다. K-NN은 데이터를 가장 유사한 속성에 따라 데이터를 분류하는 거리 기반 모델로, 수치 기반 데이터 분류 작업에서 우수한 성능을 보인다[18].

t-SNE는 비선형 차원 축소 기법으로, 데이터 지점 간의 거리를 측정하고, t분포의 값을 선택하여 그 값을 친밀도로 정의한 다음, 친밀도가 유사한 데이터를 하나의 군집으로 할당한다. t-SNE 기법은 고차원 데이터를 저차원 데이터로 변환하는 차원 축소 기법이기 에, 군집들을 시각화해서 표현해주는 데 강점을 보인다[19].

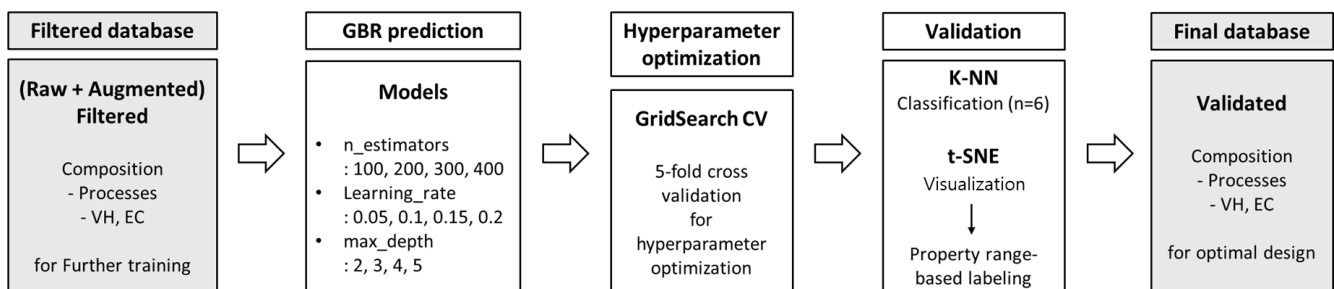


Fig. 2. Framework for conductivity prediction and validation using gradient boosting regression (GBR) modeling with K-nearest neighbor (K-NN) and t-distributed stochastic neighbor embedding (t-SNE)-based quality assessment.

K-NN모델에서 생성된 데이터를 학습 데이터로, 실험 데이터를 테스트 데이터로 설정했다. 이는 생성 데이터가 실제 실험값을 얼마나 잘 반영하는지 검증하고, 생성 데이터의 일반화 가능성과 신뢰도를 평가하기 위한 목적으로 수행된 것이다. 실제로, 생성 데이터와 실험 데이터 간의 분포 및 특성이 유사하다는 가정 하에, 두 데이터를 혼합하여 무작위로 분할한 경우에도 결정계수(R^2)에 유의미한 차이가 나타나지 않았다. 그러나 생성 데이터만을 이용하여 학습하고, 실험 데이터를 독립적인 테스트 셋으로 활용하는 방법은 데이터 간의 상관성에 따른 과적합을 방지하며, 모델의 실질적인 예측 성능을 보다 보수적으로 검증할 수 있다는 점에서 의미가 있다고 판단하였다. 품질을 검증하기 전에, 두 종류의 데이터에서 KNN에 이용할 범위 내에 있는 데이터를 추출한다. 이때의 범위는 비커스 경도는 70~110 HV, 전기 전도도는 25~47 %IACS로 정하고, 각각 두 물성을 70~90 HV, 90~110 HV, 25~32 %IACS, 32~47 %IACS 범위로 물성 값의 분포를 고려하여 범위를 나눈다. 레이블링하여 데이터 이산화를 진행하였다. 이후 정규화를 진행하고, 소수 클래스의 샘플을 합성하여 균형잡힌 데이터셋을 만드는 오버샘플링 기법 중 하나인 SMOTE(Synthetic Minority Over-sampling Technique)기법을 이용하여 학습 데이터를 보강하였다.

3. Results

그림3 (a)는 VAE의 학습 손실과 검증 손실의 변화를 나타낸 것이다. 이 그래프에서 손실은 에포크가 진행됨에 따라, 검증 손실이 큰 폭으로 증가하는 과적합의 징조 없이 입력 데이터의 중요한 특징을 포착하고, 데이터를 잘 복원한다는 것을 알 수 있다.

그림 3 (b)는 ANN모델의 학습 데이터와 테스트 데이터의 정확

도를 보여주는 그림이다. 학습 데이터에서의 성능은 0.89, 테스트 데이터에서는 0.91이 나왔는데, 대부분의 데이터 점은 빨간 점선의 $y = x$, 즉 모델이 예측 값과 실제 값이 동일한 범위 근처에 분포해 있었다. 이는 곧, 모델이 실제 값에 근접하게 예측한다는 것을 의미한다. 다만, 예측 값과 실제 값이 크게 차이나는 데이터가 존재하는데, 이는 스케일링과 노이즈 추가로 인한 데이터의 변형 및 증강으로 인하여 하나의 물성 값에 대응하는 데이터의 범위가 넓어져 물성 예측의 난이도가 전에 비하여 상승했기 때문이다. 다만, 학습 데이터보다 테스트 데이터의 결정계수가 높고, 분포 또한 작은 것으로 보아 학습 후의 모델 성능은 크게 나아졌다는 것을 알 수 있다.

그림4 (a)는 GBR의 하이퍼파라미터 조합별 성능을 색으로 표현한 3차원 좌표계로, 성능이 가장 좋은 조합의 좌표에 별도로 하이퍼파라미터 조합이 ($n_estimators$, $learning_rate$, max_depth) 형식으로 표시된다.

5점 교차 결과, 모든 조합에서 0.89 이상의 정확도를 보이고, 가장 높은 성능을 보인 조합은 (100, 0.15, 4)이며, 0.94의 정확도를 보인다. 가장 낮은 값은 모든 하이퍼파라미터 값이 낮은 (100, 0.05, 2)였으나, 3가지의 하이퍼파라미터 중에서 1개 이상의 가장 높은 값을 가지는 좌표 또한 상대적으로 성능이 좋지 않았다. 이는 트리의 개수와 깊이가 너무 크게 설정되었다면, 모델 자체가 너무 복잡해지기에 과적합으로 이어지기 쉽고, 학습률이 너무 높아진다면 오차가 최소점으로 수렴하기 어렵고 오히려 오차가 커지는 방향으로 최적화가 진행될 수 있기 때문이다.

그림 4 (b)는 GBR의 학습 데이터와 테스트 데이터의 정확도를 보여주는 그림이다. 학습 데이터에서의 성능은 1.00, 테스트 데이터에서는 0.94가 나왔는데, 대부분의 데이터 점은 빨간 점선의 $y = x$, 즉 모델이 예측 값과 실제 값이 같은 범위에 위치해 있었다. 이

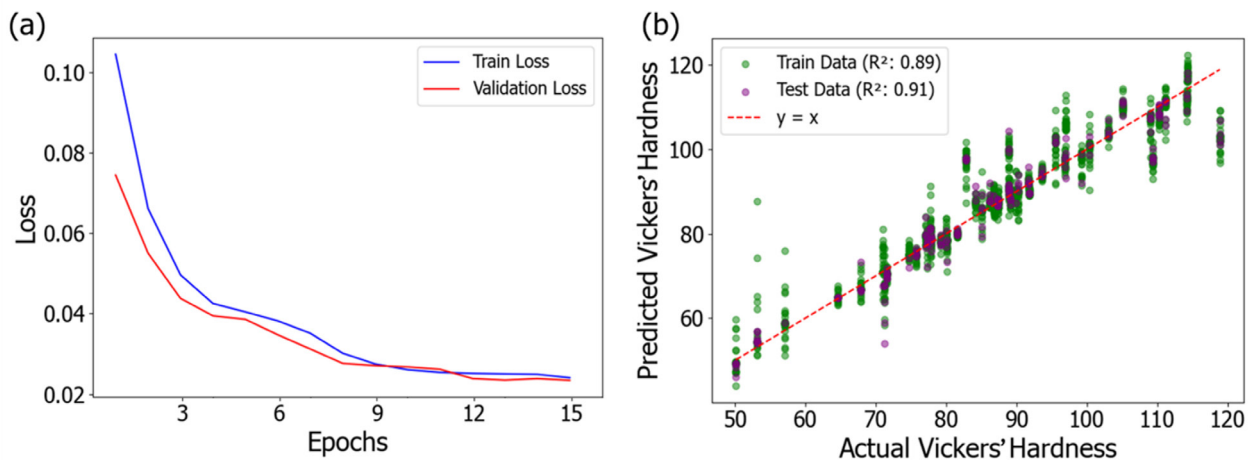


Fig. 3. (a) Training and validation loss progression during variational autoencoder (VAE) epochs and (b) comparison between predicted and measured Vickers hardness values

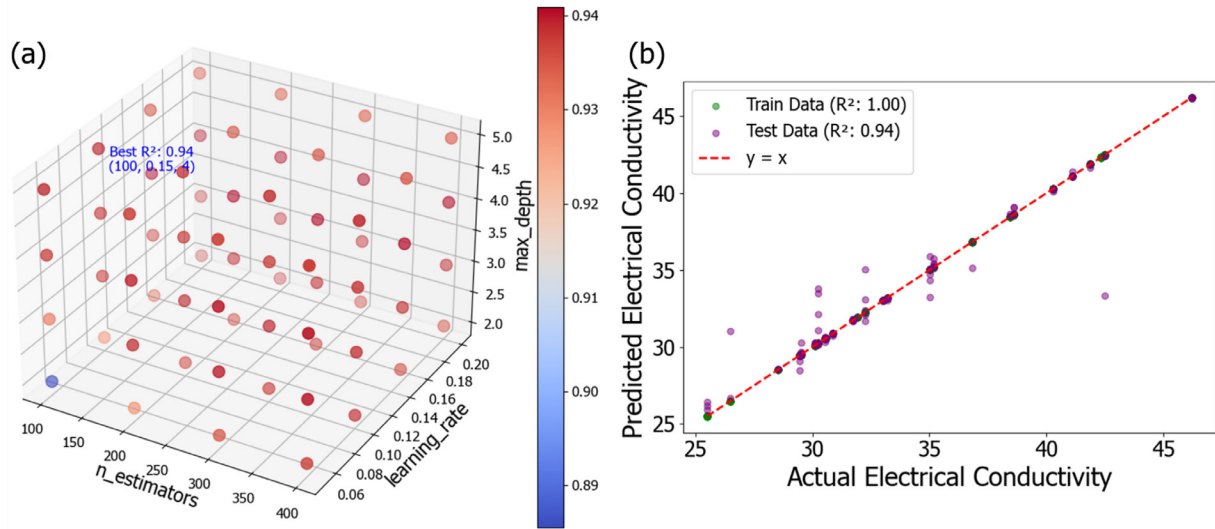


Fig. 4. (a) Model performance across different hyperparameter combinations and (b) comparison between predicted and measured electrical conductivity values.

는 곧, 두 값이 거의 동일하다는 것을 보여준다. 다만, 학습 데이터와 테스트 데이터 둘 다 일부의 데이터가 $y=x$ 위 아래로 분포한 것을 확인할 수 있는데, 이는 스케일링과 노이즈 추가로 인한 데이터의 변형 및 증강으로 인하여 하나의 물성 값에 대응하는 데이터의 범위가 넓어졌기 때문이다.

표 2는 K-NN의 정확도와, 각 물성의 구간별 F1-score를 나타낸 것이다. 두 물성에 관하여 K-NN의 정확도는 0.7 이상, 구간별 F1-score도 한 구간(90~110 HV)을 제외하면 0.75 이상으로 도출되어 실험 데이터 수 대비 유사성이 높은 데이터를 만들었다는 것을 확인할 수 있다. 90~110 HV 구간에서 F1-score가 낮게 나온 이유는, 70~90 HV 구간에 비하여 데이터의 연속성이 떨어져 데이터 학습에 다른 데이터에 비하여 상대적으로 불리했을 거라 추측된다. 본 연구에서 데이터 증강 기법을 적용하지 않은 경우, 기존의 데이터 분할 비율(훈련:검증:테스트 = 0.8:0.1:0.1)에서 테스트 데이터에 대한 R^2 값이 평균적으로 0.72 수준에 머무르는 반면, 증강 기법을 적용한 경우 동일한 분할 조건에서 평균 R^2 값이 약 0.85로 유의미하게 향상됨을 확인하였다. 이 결과는 제한된 원본 데이터로 인해 발생할 수 있는 모델의 불안정성과 과적합 문제를 데이터 증강을 통해 효과적으로 완화하였음을 시사하며, 증강 기법이 모델 성능 향상에 중요한 역할을 보여준다.

그림 5는 t-SNE 기법을 이용하여 생성된 데이터(●)와 실험 데이터(X)를 2개의 임의의 특성들 기준으로 시각화한 것이다. 그림 5 (a)에서는 생성된 데이터와 실험 데이터가 서로 특성이 크게 차이 나지 않으며, 유사성이 높은 것을 알 수 있다. 그림 5 (b)에서는 그림 5 (a)에 비하여 생성된 데이터와 실험 데이터 군집 간의 차이가 상대적

Table 2. Accuracy and range-specific F1-scores of the K-nearest neighbor (K-NN) method for each property

	70~90 (HV)	90~110 (HV)	25~32 (%IACS)	32~47 (%IACS)
Accuracy	0.71		0.81	
F1-score	0.78	0.59	0.76	0.85

으로 도드라지고, 구간별 데이터 간의 특성 분포 또한 뚜렷하게 관찰되지는 않으나, 실험 데이터 군집에서 벗어난 일부의 데이터의 간극을 매우면서 데이터의 다양성을 높인 것을 확인할 수 있다.

표 3~6은 각각 역설계된 조성과 공정 조건을 비커스 경도와 전기 전도도의 범위에 따라 세분화하여 제시한 데이터로, 각각의 조건이 물성에 미치는 영향을 구체적으로 보여준다. 먼저, 표 3은 비커스 경도 70~90 HV 범위에서의 데이터로 대부분 AI 함량은 90.5~92% 수준이고 용질 원자 중에서는 Mg이 0.9~2.0%로, 함량의 최대와 최소의 차이가 3%이상을 보이는 다른 원소에 비하여 비교적 적은 범위에 분포하는 편이다. 이 범주의 설계안에서는 대부분의 샘플의 전기전도도가 28.5~41%IACS값을 가지는 것으로 예측되었다.

표 4는 비커스 경도 90~110 HV 범위에서의 데이터로 대부분 AI 함량은 90~92% 수준이고 용질 원자 중에서는 Mg이 0.8~2.0%로, 표 3의 경우와 비슷하나, Si, Cu, Zn 이 세가지의 함량 분포의 범위가 상당히 좁아진 것을 관찰할 수 있다. 이 범주의 설계안에서는 레이저에 의해 가해지는 에너지(Laser power/Scan speed)가 클수록 비커스 경도가 대체로 감소하는 거동을 보이는데, 이는 분

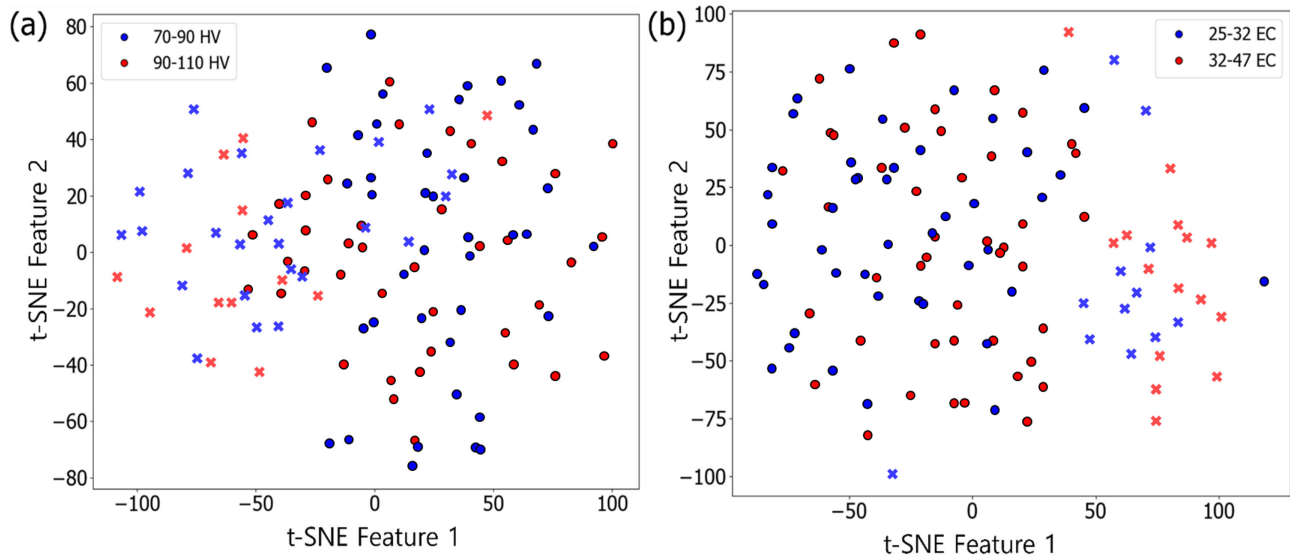


Fig. 5. t-Distributed stochastic neighbor embedding (t-SNE)-based dimensionality reduction results for experimental data (x) and generated data (•) based on (a) Vickers hardness and (b) electrical conductivity.

Table 3. Composition and processing parameter data for materials with hardness values in the range of 70 to 90 HV

70~90 HV	Al (wt.%)	Si (wt.%)	Mg (wt.%)	Cu (wt.%)	Zn (wt.%)	Scan speed (mm/min)	Laser power (W)	Vickers Hardness (HV)	Electrical Conductivity (%IACS)
1	91.3	1	0.9	4.9	1.9	550	700	89.4	31.32
2	90.7	4	2.0	1.9	1.4	850	400	85.5	37.55
3	90.9	0.5	1.5	4.7	2.4	600	500	76.4	37.2
4	91.7	0.4	1.2	2.3	4.4	550	650	70.4	31.58

Table 4. Composition and processing parameter data for materials with hardness values in the range of 90 to 110 HV

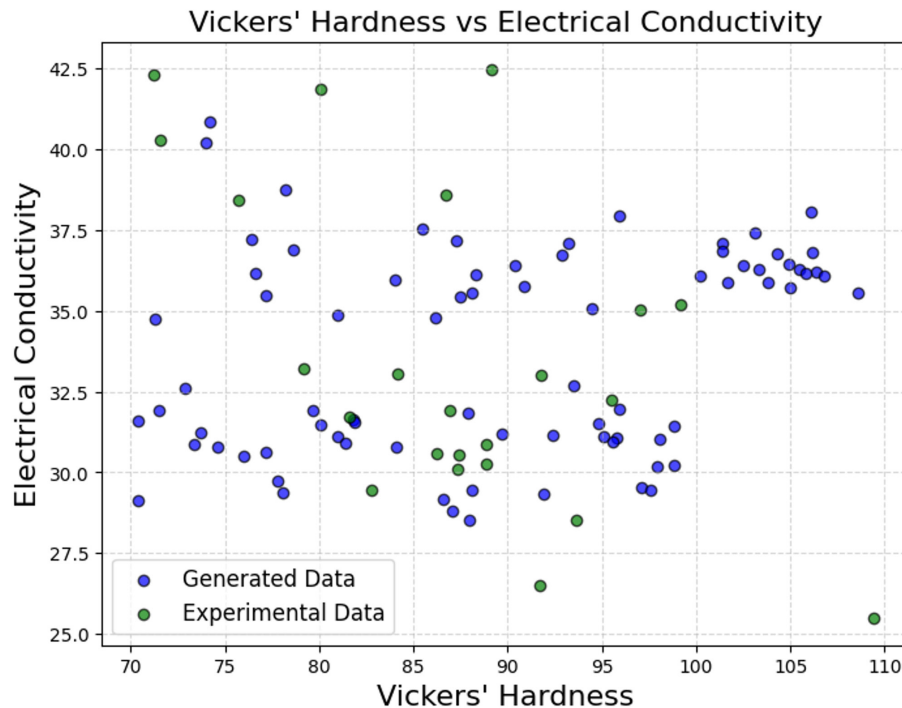
90~110 HV	Al (wt.%)	Si (wt.%)	Mg (wt.%)	Cu (wt.%)	Zn (wt.%)	Scan speed (mm/min)	Laser power (W)	Vickers Hardness (HV)	Electrical Conductivity (%IACS)
1	91.6	1.8	1.4	2.2	3	1000	500	108.6	35.5
2	91.5	2	1.7	2.7	2.1	1000	600	105.5	36.3
3	90.1	2	1.8	3.4	2.7	800	800	95.8	31.07
4	91.2	2.2	2	2.4	2.2	500	700	90.4	36.4

Table 5. Composition and processing parameter data for materials with electrical conductivity values in the range of 25 to 32 %IACS

25~32 %IACS	Al (wt. %)	Si (wt. %)	Mg (wt. %)	Cu (wt. %)	Zn (wt. %)	Scan speed (mm/min)	Laser power (W)	Vickers Hardness (HV)	Electrical Conductivity (%IACS)
1	91.6	2.9	1.7	1.7	2.1	500	750	87.9	31.82
2	91.9	2.2	1.8	0.3	3.8	950	600	95.8	31.07
3	91.9	0.7	1.9	2.2	3.3	700	800	97.9	30.18
4	90.4	1.5	1.8	1.9	4.4	800	500	87.1	28.82

Table 6. Composition and processing parameter data for materials with electrical conductivity values in the range of 32 to 42 %IACS

32~42 %IACS	Al (wt. %)	Si (wt. %)	Mg (wt. %)	Cu (wt. %)	Zn (wt. %)	Scan speed (mm/min)	Laser power (W)	Vickers Hardness (HV)	Electrical Conductivity (%IACS)
1	91.6	3.1	1.6	1.5	2.2	650	400	74.2	40.86
2	91.2	4.2	1	1.9	1.7	1000	500	106.1	38.08
3	91.4	2.1	1.9	2.6	2	900	700	104.9	36.43
4	91.7	4	1.7	0.5	2.1	600	550	93.5	32.69

**Fig. 6.** Scatter plot of Vickers' hardness and electrical conductivity for experimental data and generated data.

말에 가해지는 에너지가 너무 강하면 일부가 증발되어 물성 저하의 원인이 되는 Keyhole이 생겨 경도값이 낮아지는 것으로 추정된다. 또한, 대부분의 샘플의 전기전도도는 29.3~41 %IACS값을 가지는 것으로 예측되었는데, 이는 70~90 HV범위의 비커스 경도를 가지는 소재와 비슷한 범위의 전기 전도도를 가지는 것으로, 경도는 향상시키면서 전기 전도도의 하향은 막아 대체로 상반되는 특성을 동시에 만족하는 것을 알 수 있다.

표5는 본래 전기 전도도의 최소값이 25 %IACS로 설정되어 있었으나, 데이터 생성 결과 28.82 %IACS가 최소값이 된 28~32 %IACS 범위에서의 데이터로 대부분 Al 함량은 90~92% 수준이고 용질 원자 중에서는 Mg의 값이 크게 변동되지 않은 것을 알 수 있다. 다른 물성 구간에 비하여 값의 범위가 좁아 전기 전도도에 관한 다른 변수들 간의 뚜렷한 상관관계는 발견되지 않았다. 이 범주의 설계안에서는 대부분의 샘플의 비커스 경도는 70~99 HV값을 가

지는 것으로 예측되었다.

표 6 또한, 본래 전기 전도도의 최대값이 47 %IACS로 설정되어 있었으나, 데이터 생성 결과 40.86 %IACS가 최대값이 된 전기 전도도 32~41 %IACS 범위에서의 데이터로 대부분 Al 함량은 91% 수준으로 다른 물성범위에 비하여 Al 함량의 분포 범위가 좁으며, 용질 원자 중에서는 Mg와 더불어 Zn의 조성 값이 크게 바뀌지 않았다는 것을 알 수 있다. 이 범주의 설계안에서는 대부분의 샘플의 비커스 경도는 71~109HV값을 가지는 것 상당히 넓은 범위로 예측되었다. 이는 표5와 같은 이유로 물성의 범위 자체가 넓게 설정된 것도 있으나, 높은 비커스 경도와 전기 전도도를 동시에 가지는 소재가 생성된 것이 가장 큰 이유로 추측된다.

또한, 표5와 표6에서 실험 데이터의 전기 전도도 범위와 생성된 데이터의 전기 전도도 범위가 다른 이유는, 실험 데이터에서 최소값과 최대값의 물성을 가지는 데이터의 수가 다른 값에 비하여 적

어 모델이 학습하기 어렵기에 모든 전기 전도도 값에 관한 균등한 예측이 어려울 것이라 추측된다.

그림 6은 비커스 경도와 전기 전도도를 각각 X축, Y축으로 하여 생성된 데이터와 실험 데이터를 시각화한 산점도다. 생성 데이터의 경도 및 전기전도도 값은, 실제 실험 데이터를 기반으로 학습된 모델을 통해 예측된 결과이며, 이후 수행된 추가 실험에서도 해당 예측값과 유사한 수준의 물성이 재현됨을 확인하였다. 특히, 주요 조성 조건에서의 경도 및 전기전도도는 각각 $\pm 5\%$ 이내의 오차 범위 내에서 실험값과 일치하여, 생성 데이터의 신뢰성과 본 모델의 예측 정확도가 검증됨을 보여준다. 실험 데이터에서 경도와 전기 전도도 두 개의 물성을 전부 가지고 있는 데이터를 선정하였으며, 생성된 데이터의 비커스 경도 범위인 70~110HV의 범위를 기준으로 한정하여 나타내었다. 시각화 결과, 실험 데이터가 다른 구간에 비하여 매우 적은 100HV~110HV범위에 많은 데이터가 생성되었을 뿐만 아니라, 생성된 데이터의 전기 전도도가 주변 범위에서의 실험 데이터와 비교하여 상당히 높게 나타난 것을 확인할 수 있었다. 이는 두개의 상반되는 특성이 동시에 향상된 소재의 데이터를 제공함과 동시에 불균형한 물성 구간 별 데이터 분포를 보완할 수 있다는 것이다.

4. Conclusion

본 연구에서는 경도와 전도도라는 상반되는 두 물성을 동시에 만족하는 DED 적층제조용 알루미늄 합금을 기계학습을 통해 개발하였다. 이를 위해 VAE를 이용해 데이터 분포를 학습하고 새로운 데이터를 생성하였으며, 인공신경망ANN과 그라디언트 부스팅 회귀GBR 모델을 통해 물성을 예측하였다. 결론적으로, VAE로 생성한 데이터는 실험 데이터와 90% 이상의 유사도를 보여 데이터의 신뢰성을 입증하였으며, ANN과 GBR 모델은 각각 테스트 데이터에서 결정계수 0.91과 0.94를 기록하여 높은 예측 성능을 보였다. 이로써 비커스 경도와 전기 전도도의 트레이드오프 관계를 극복하는 최적의 소재가 설계 가능함을 확인하였다. 본 연구는 적층 제조 공정에 필요한 데이터 생성과 물성 예측의 효율성을 크게 향상시킬 수 있는 기초를 제공하며, 향후 다양한 산업 분야에서 데이터 보강과 새로운 소재 개발에 폭넓게 활용될 가능성이 있다.

Funding

This work was also supported by a National Research Foundation of Korea (NRF) grant funded by the Korean government (MSIT) (NRF-2022R1A5A1030054, RS-2025-00562104).

Conflict of Interest

Hyunjoo Choi serves as an editor of the Science editing, but has no role in the decision to publish this article. Except for that, no potential conflict of interest relevant to this article was reported.

Data Availability Statement

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

Author Information and Contribution

First Author: Undergraduate student; Implementation, writing – original draft

Second Author: PhD student; Review & Editing

Third Author: Master's student; Review & Editing

Fourth Author: Undergraduate student; Review & Editing

Corresponding Author: Professor; Conceptualization, writing–original draft, supervision

Acknowledgments

None.

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SnF₂-Induced LiF Interphase for Stable Lithium Metal Anodes with Suppressed Dendrite Growth

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Lithium (Li) metal is a promising anode for next-generation batteries due to its high capacity, low redox potential, and low density. However, dendrite growth and interfacial instability limit its use. In this study, an artificial solid electrolyte interphase layer of LiF and Li-Sn (LiF@Li-Sn) was fabricated by spray-coating SnF₂ onto Li. The LiF@Li-Sn anode exhibited improved air stability and electrochemical performance. Electrochemical impedance spectroscopy indicated a charge transfer resistance of 25.2 Ω after the first cycle. In symmetric cells, it maintained a low overpotential of 27 mV after 250 cycles at 2 mA/cm², outperforming bare Li. In situ microscopy confirmed dendrite suppression during plating. Full cells with NMC622 cathodes and LiF@Li-Sn anodes delivered 130.8 mAh/g with 79.4% retention after 300 cycles at 1 C and 98.8% coulombic efficiency. This coating effectively stabilized the interface and suppressed dendrites, with promising implications for practical lithium metal batteries.

Keywords: Tin fluoride; Lithium fluoride; Li metal anodes; Artificial SEI layer; Lithium dendrite

Received: May 26, 2025

Accepted: June 13, 2025

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1. Introduction

In response to increasing global efforts toward carbon neutrality and environmental sustainability, numerous policies and initiatives targeting CO₂ emission reductions have been implemented worldwide. Secondary batteries have emerged as a pivotal enabling technology in this transition. Since the commercialization of lithium-ion batteries (LIBs) by Sony in 1991, LIBs have dominated the secondary battery market, gradually replacing lead-acid, nickel-cadmium (Ni-Cd), and nickel-metal hydride (Ni-MH) batteries. Today, LIBs are widely utilized in smartphones, drones, electric vehicles, and energy storage systems (ESSs). However, for applications such as electric vehicles and ESSs, an energy density of at least 300 Wh/kg is required, which is challenging to achieve with conventional LIB systems employing metal oxide cathodes and graphite anodes. Consequently, research into next-generation batteries offering higher

energy and power densities has rapidly accelerated [1-5].

Lithium (Li) metal is considered a highly promising anode material for next-generation batteries owing to its high theoretical specific capacity (3680 mAh/g), low redox potential (−3.04 V vs. SHE), and low density (0.534 g/cm³). Nevertheless, the practical implementation of Li metal anodes is severely hindered by the growth of Li dendrites during repeated cycling. These dendrites originate from non-uniform Li⁺ deposition and lead to continuous side reactions with the electrolyte, resulting in the formation of electrically isolated “dead Li.” Over time, uncontrolled dendrite growth may penetrate the separator, ultimately causing internal short circuits and catastrophic cell failure [6-12]. To address these challenges, significant efforts have been devoted to suppressing dendrite formation and stabilizing the Li metal surface. For example, He et al. [13] fabricated a LiF-rich solid electrolyte interphase (SEI) by reacting NF₃ gas with Li metal, thereby enhancing mechanical robustness and ionic conductivity. Wang et al. [14] constructed a three-dimensional Li host structure on a Cu current collector to facilitate homogeneous Li⁺ flux. Cheng et al. [15] introduced nanoscale additives

to promote uniform Li deposition and suppress dendritic growth. Despite extensive research into various strategies for suppressing Li dendrite growth, formidable technical challenges remain that hinder the reliable and practical application of Li metal anodes.

In this study, SnF_2 was spray-coated onto Li metal to form an artificial SEI layer comprising LiF and Li-Sn phases (LiF@Li-Sn). This composite layer significantly enhanced the air stability of Li metal and reduced interfacial resistance, as confirmed by electrochemical impedance spectroscopy (EIS). Furthermore, in situ optical microscopy analysis demonstrated that the composite layer effectively suppressed Li dendrite growth, ensuring uniform Li deposition during cycling. Full cells incorporating NMC622 cathodes and LiF@Li-Sn anodes exhibited excellent cycling stability, retaining over 79.4% of their initial capacity after 300 cycles at 1 C, thereby validating the efficacy of the proposed surface modification strategy. These results clearly highlight the potential of SnF_2 -based surface modification in achieving stable and durable Li metal anodes, providing a facile and scalable approach for next-generation Li metal batteries (LMBs).

2. Experimental Section

2.1 Preparation of composite coating layer on lithium metal

To prepare LiF@Li-Sn composite layer, a coating solution was first prepared. SnF_2 and KPF_6 were dissolved at a weight ratio of 1:5 in 40 mL of dimethyl ether (DME). The solution was sonicated for 1 hour to ionize the SnF_2 . Subsequently, the solution was centrifuged at 4000 rpm for 10 minutes. The resulting coating solution was then spray-coated onto the Li metal surface at a dry room. After spray coating, the Li metal was washed with dimethyl carbonate (DMC) to remove any unreacted residues and dried in a convection oven at 60°C for 30 minutes.

2.2 Electrochemical measurements

For electrochemical performance test of LMBs, NMC622 electrodes were firstly prepared. The cathode slurry was composed of NMC622, Super P (carbon black, Timcal), and PVDF binder (polyvinylidene fluoride, KF1300, Kureha) in a weight ratio of 90:5:5, and mixed using a Thinky mixer (ARE-310, Thinky) at 2000 rpm for 12 minutes. The prepared slurry was cast onto Al foil (Welcos) with a thickness of 120 μm and dried in a convection oven at 110°C for 1 hour and in 110°C vacuum oven for 24 hours. Two types of coin cells (CR2032, Welcos) were assembled in a glove box filled with argon gas to evaluate

the electrochemical performance. For the Li//Li symmetric cells, Li metals with a thickness of 200 μm (Honjo metal) were used as both anode and cathode with 1 M LiTFSI in DOL/DME (1:1, v/v) as the electrolyte. In the NMC622 full cells, as-prepared NMC622 electrode, Li metal, and 1 M LiPF_6 in EC/EMC (1:2, v/v) were employed as cathode, anode, and electrolyte, respectively. Chronoamperometry (CA), Tafel analysis, and EIS were conducted using potentiostat (VSP, Biologics) in a two-electrode configuration. Galvanostatic charge and discharge tests were performed using a battery cycler (SERIES 4000, MACCOR).

2.3 Materials characterization

Field-emission scanning electron microscopy (FE-SEM) was used to observe the surface morphology of the composite coating layer on Li metal. Measurements were carried out with an electron beam at 15 kV and 10 mA. The Li dendrite growth behavior during plating was monitored in real time using a digital optical microscope under a current density of 3 mA/cm^2 . Elemental composition of the composite coating layer was analyzed using X-ray photoelectron spectroscopy (XPS), with all data calibrated to the C 1s peak at 284.5 eV.

3. Results and Discussion

Fig. 1 shows the surface and cross-sectional morphology of bare Li metal and LiF@Li-Sn metal. The bare Li metal surface (Fig. 1a) is smooth with low roughness, as confirmed by the 3D topography image. This smooth surface is susceptible to localized Li deposition, which can result in dendrite growth. In contrast, the LiF@Li-Sn metal surface (Fig. 1b) is rough and covered with granular structures. The 3D topography image shows that the surface roughness is much higher than that of bare Li metal. This roughness is due to the formation of the LiF@Li-Sn layer created by the reaction between SnF_2 and Li. The cross-sectional images further illustrate the difference. The bare Li metal (Fig. 1c) has no protective layer, leaving it exposed to the electrolyte, which increases the risk of dendrite formation. On the other hand, the LiF@Li-Sn metal (Fig. 1d) has a uniform coating layer with a thickness of about 7.85 μm . This layer is composed of two main components: LiF, which is an ion-conductive but electronically insulating material, and Li-Sn, which provides good electrical conductivity and mechanical strength [16]. The LiF layer acts as a barrier against dendrite growth, while the Li-Sn layer maintains electrical contact. This dual-layer structure improves the stability of the Li metal surface by preventing direct contact with the electrolyte and distributing the current density more

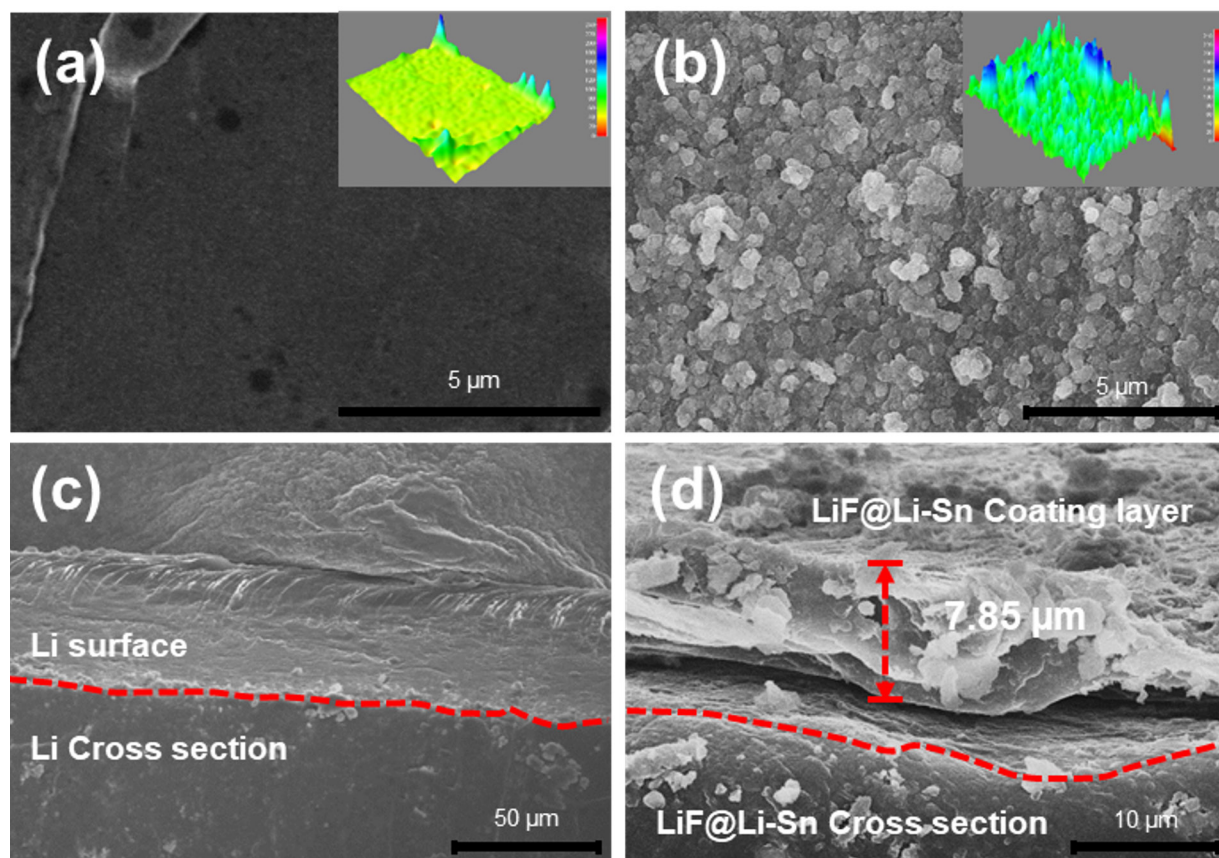
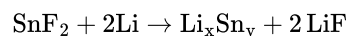


Fig. 1. Field-emission scanning electron microscopy images of (a, c) bare Li metal and (b, d) LiF@Li-Sn metal, with 3D surface topography maps shown as insets.

evenly. This structure is expected to enhance the cycling performance of Li metal anodes.

Fig. 2 provides elemental analysis of the LiF@Li-Sn composite layer through EDS, confirming the chemical composition and the spatial distribution of key elements. The EDS spectrum shows prominent peaks for tin (Sn) and fluorine (F), indicating that Sn and LiF are present in the composite layer. A peak for phosphorus (P) is also detected, which is likely due to the use of KPF_6 in the SnF_2 solution preparation. Despite thorough washing, P remains detectable, which suggests that PF_6^- ions are either strongly adsorbed onto the LiF surface or chemically transformed during the SnF_2 treatment process. PF_6^- can decompose on the Li surface, forming phosphate or other phosphorus-containing compounds [17]. The EDS mapping images show that Sn (green) and F (red) are uniformly distributed across the composite layer, indicating a homogeneous structure. However, the exact chemical state of P cannot be determined through EDS alone. Further analysis using XPS is necessary to confirm whether P exists as PF_6^- , phosphate, or other species.

Fig. 3 presents the XPS analysis of the LiF@Li-Sn composite layer, confirming the chemical composition and the transformation of the SnF_2 precursor into a stable structure. In Fig. 3a, the P 2p XPS spectrum exhibits a major peak at 136.3 eV, which is attributed to P-F bonding in Li_xPF_y species or undecomposed PF_6^- residues. A minor peak at 133.8 eV is ascribed to lithium phosphate compounds ($\text{Li}_x\text{PF}_y\text{O}_z$) formed on the lithium surface [18, 19]. The Sn 3d XPS spectrum (Fig. 3b) reveals two distinct peaks at 485.0 eV ($\text{Sn } 3d_{5/2}$) and 493.4 eV ($\text{Sn } 3d_{3/2}$), consistent with metallic Sn (Sn^0) or a Li-Sn alloy (Li_xSn_y) [20]. These energies are significantly lower than that of SnF_2 ($\text{Sn } 3d_{5/2}$ at ~487.0 eV), confirming that the SnF_2 precursor has been fully converted according to [20]:



This transformation produces a conductive Li-Sn alloy while generating LiF as an ion-conductive, electronically insulating protective layer. The formation of LiF and Li-Sn alloy is also confirmed by the Li 1s and F 1s XPS spectra in Fig. 3c and 3d,

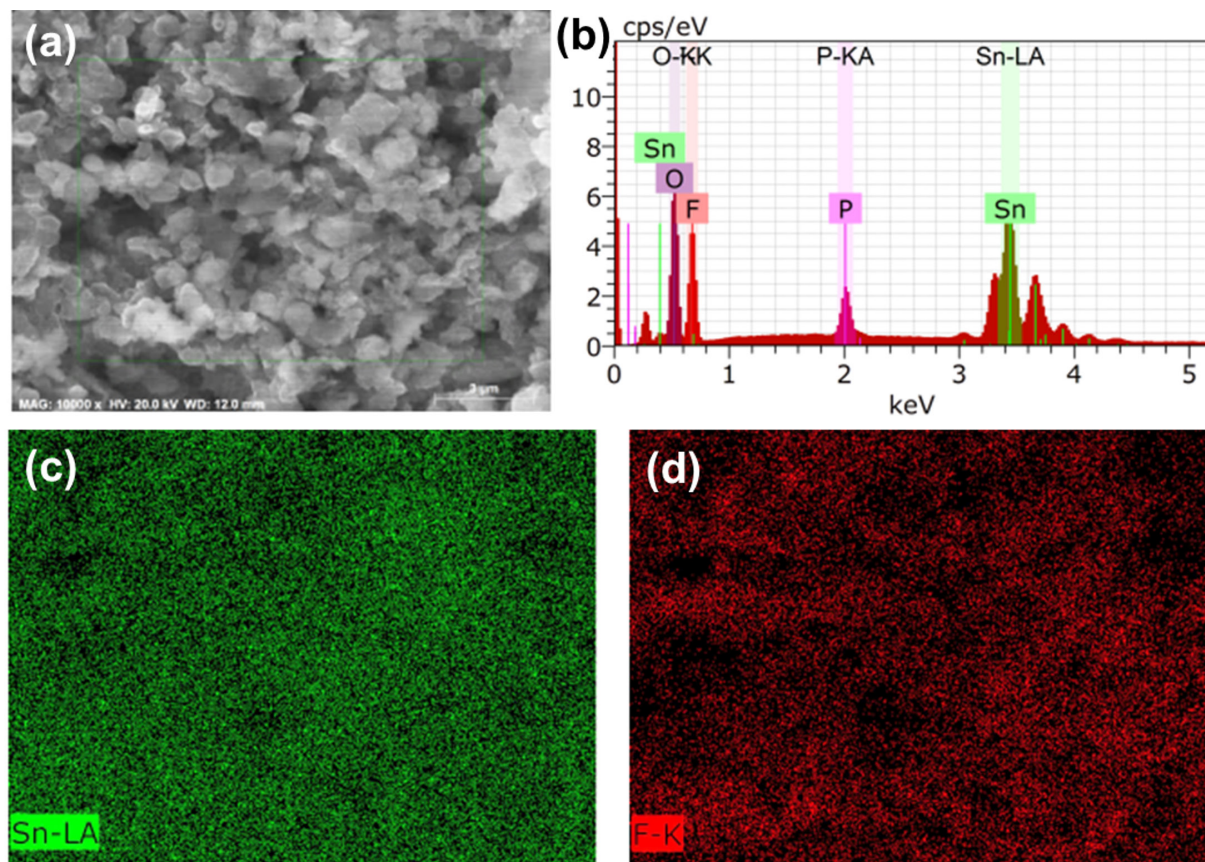


Fig. 2. Energy-dispersive X-ray spectroscopy (EDS) analysis of the LiF@Li-Sn metal surface: (a) Scanning electron microscopy image and (b) corresponding EDS spectrum. Elemental mapping images of (c) Sn and (d) F.

where peaks at 55.5 eV (Li 1s) and 684.3 eV (F 1s) correspond to LiF, and a peak at 55.9 eV (Li 1s) indicates the presence of Li-Sn alloy [21]. These findings demonstrate that the LiF@Li-Sn composite layer is composed of an electron-conductive Li-Sn alloy and an ion-conductive LiF layer, collectively providing enhanced interfacial stability for Li metal anodes.

Fig. 4 presents the comparative air stability of bare Li metal and LiF@Li-Sn composite over a period of 30 minutes of air exposure. The bare Li metal shows rapid surface degradation upon exposure to air. Initially, the clean metallic surface quickly begins to discolor within 1 minute, indicating the onset of oxidation. This discoloration intensifies over time, becoming progressively darker at 3 to 5 minutes. After 10 minutes, the surface exhibits a darkened and uneven appearance, and by 30 minutes, it is almost completely black. This severe discoloration is attributed to the formation of lithium oxide (Li_2O), lithium hydroxide (LiOH), and potentially lithium carbonate (Li_2CO_3), caused by the reaction of lithium with atmospheric oxygen, moisture, and CO_2 [22]. This result clearly demonstrates the poor air stability of bare Li

metal. In contrast, the LiF@Li-Sn composite (bottom row) shows significantly enhanced air stability. The surface maintains a relatively uniform appearance for the first 5 minutes, with only minimal discoloration appearing after 10 minutes. Even after 30 minutes of exposure, the surface remains largely intact, with only slight darkening in some regions. This enhanced stability is attributed to the protective function of the LiF@Li-Sn layer. The LiF component provides an ion-conductive but electronically insulating barrier, effectively blocking direct contact between the reactive lithium and atmospheric species.

Fig. 5a and 5b shows the CA curves of bare Li and LiF@Li-Sn electrodes, which were used to determine the Li^+ diffusion coefficients. Using Cottrell equation [23], the diffusion coefficients of Li^+ at bare Li and LiF@Li-Sn were calculated as $1.08 \times 10^{-7} \text{ cm}^2/\text{s}$ and $1.28 \times 10^{-6} \text{ cm}^2/\text{s}$, respectively. The enhanced diffusion in the LiF@Li-Sn electrode is attributed to its porous surface structure and the lithiophilic properties of LiF. The Tafel plots (Fig. 5c) further highlight the superior electrochemical activity of LiF@Li-Sn. The LiF@Li-Sn composite exhibits an ex-

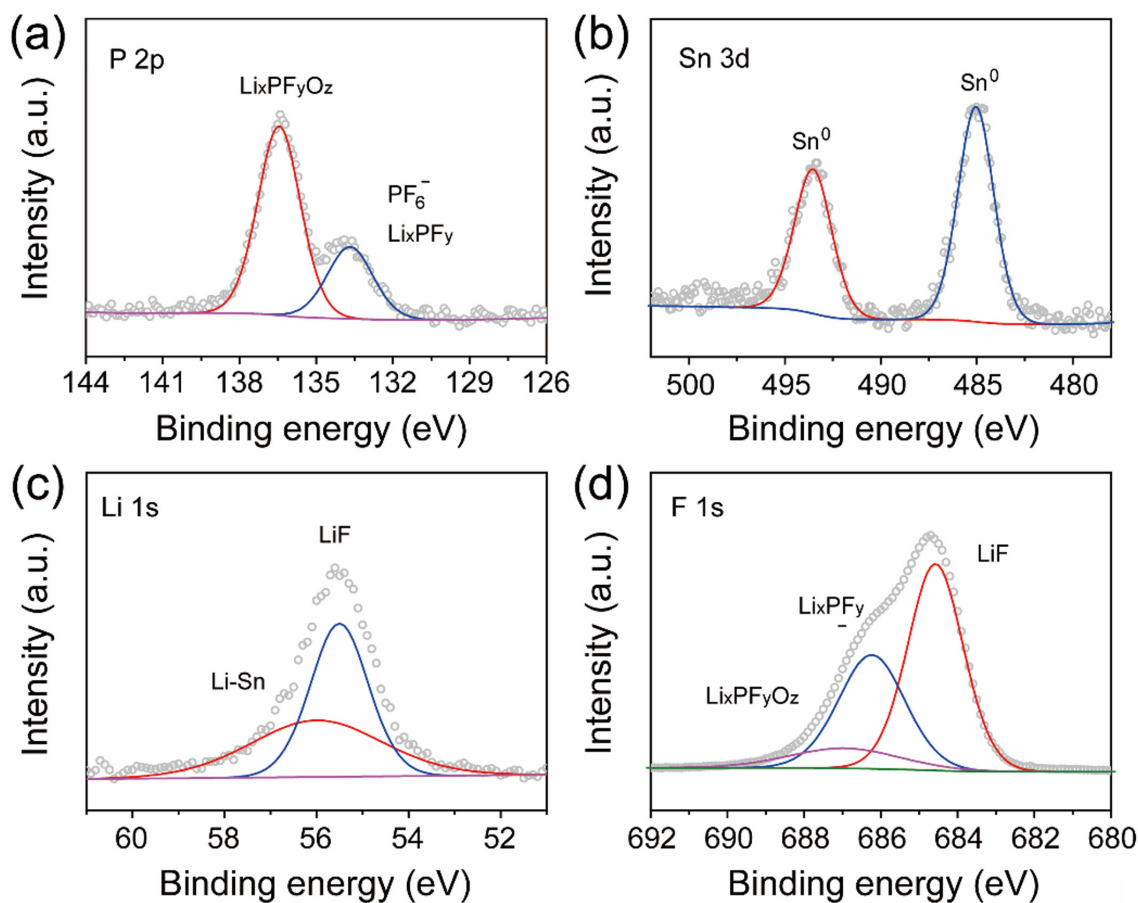


Fig. 3. X-ray photoelectron spectra of LiF@Li-Sn: (a) P 2p, (b) Sn 3d, (c) Li 1s, and (d) F 1s.

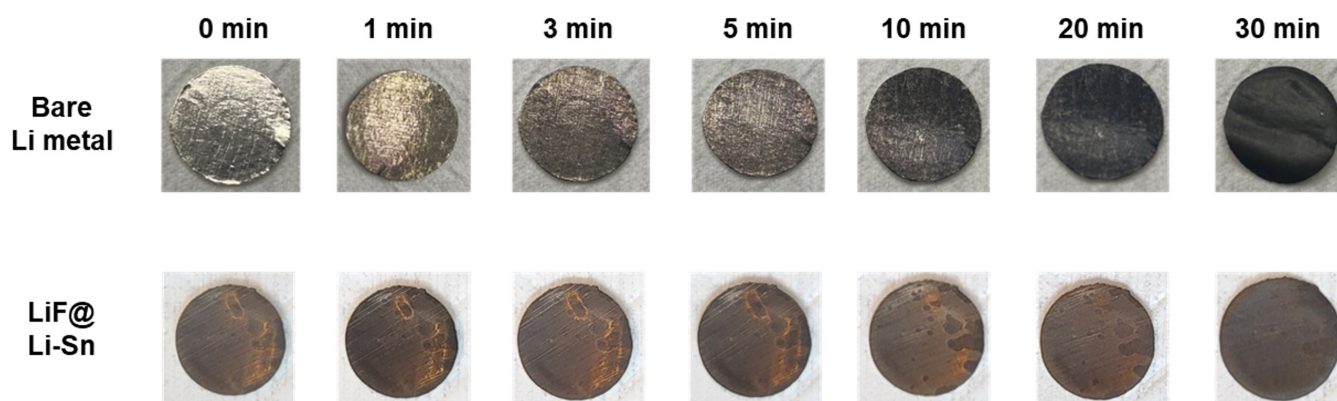


Fig. 4. Optical images showing the air stability of (top) bare Li metal and (bottom) LiF@Li-Sn metal.

change current density (i_0) of 0.242 A/cm^2 , which is significantly higher than that of bare Li metal (0.042 A/cm^2). This indicates faster charge transfer kinetics at the LiF@Li-Sn interface, attributed to the conductive Li-Sn alloy and the stable, ion-conductive LiF layer. In contrast, bare Li exhibits a lower i_0 due to

unstable surface reactions and limited active area for charge transfer. Nyquist plots in Fig. 5d strongly support these Tafel analysis findings. After the cycle, the charge transfer resistance (R_{ct}) of LiF@Li-Sn is 25.2Ω , significantly lower than that of bare Li (164.3Ω). This low R_{ct} directly aligns with the high exchange

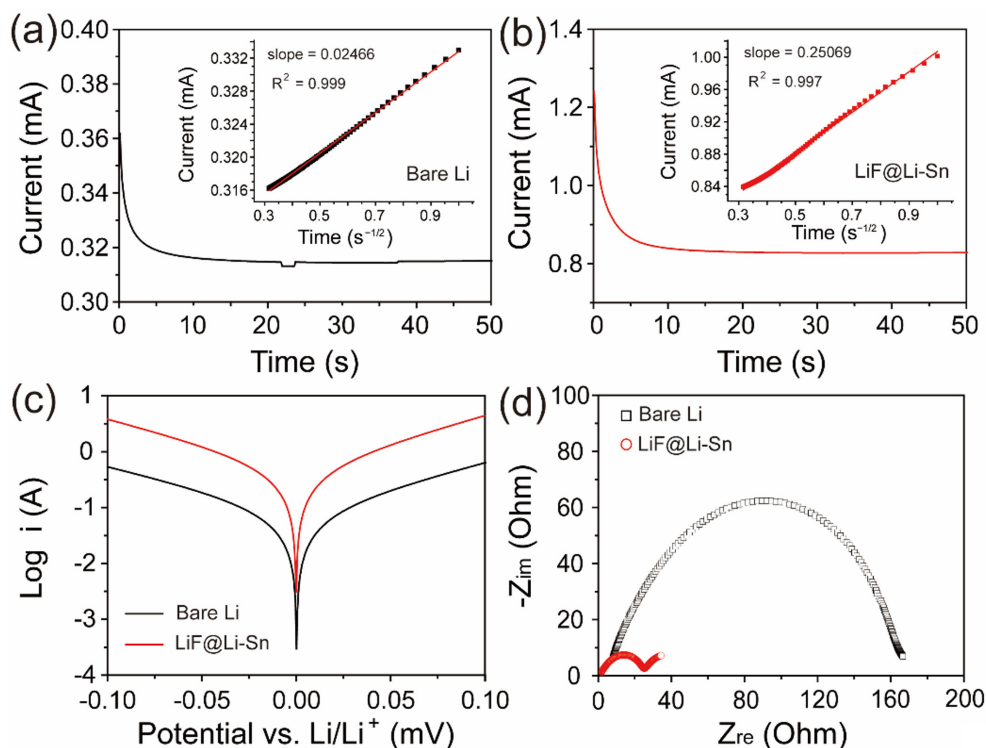


Fig. 5. Chronoamperometry analysis results of (a) bare Li metal and (b) LiF@Li-Sn metal. (c) Tafel plot of bare Li metal and LiF@Li-Sn metal. (d) Nyquist plot of lithium symmetric cells after the first cycle with bare Li metal and LiF@Li-Sn metal.

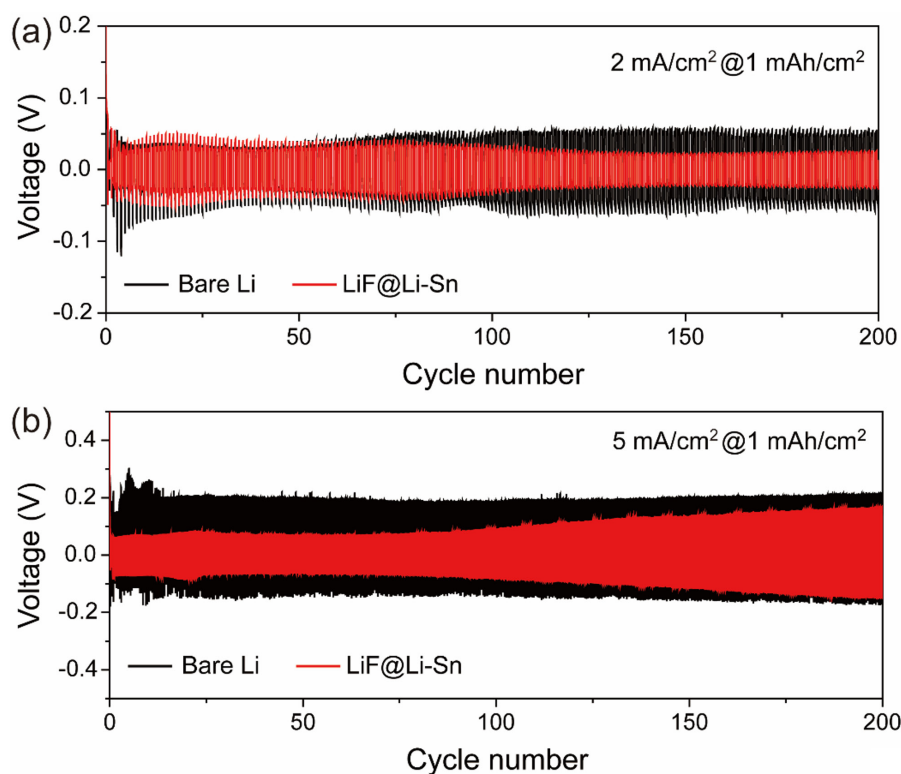


Fig. 6. Lithium symmetric cell data of bare Li and LiF@Li-Sn at (a) a current density of 2 mA/cm^2 with a capacity of 1 mAh/cm^2 and (b) a current density of 5 mA/cm^2 with a capacity of 1 mAh/cm^2 .

current density observed in the Tafel plots, confirming that LiF@Li-Sn provides a more efficient charge transfer pathway.

Fig. 6 presents the cycling performance of Li symmetric cells with bare Li metal and LiF@Li-Sn at two current densities: 2 mA/cm² (Fig. 6a) and 5 mA/cm² (Fig. 6b). In Fig. 6a, the LiF@Li-Sn cell starts with an initial overpotential of 40 mV, which decreases to 27 mV after 250 cycles, indicating stable and efficient Li plating/stripping. In contrast, the bare Li cell shows a high and unstable overpotential, which increases rapidly, reflecting poor interfacial stability due to continuous SEI formation and dendrite growth. In Fig. 6b, the differences are more pronounced. The bare Li cell starts with a high overpotential of 200 mV, which further rises during cycling, indicating severe interfacial degradation. In contrast, the LiF@Li-Sn cell maintains a low initial overpotential of 50 mV, which only increases to 150 mV after 200 cycles, demonstrating superior stability. These re-

sults confirm that the LiF@Li-Sn composite effectively suppresses dendrite formation and maintains low interfacial resistance, providing consistent Li plating/stripping even under high current conditions.

Fig. 7 provides direct visual evidence of the Li deposition behavior on bare Li metal (Fig. 7a) and LiF@Li-Sn (Fig. 7b). In Fig. 7a, bare Li metal rapidly develops dendrites within 1 minute, which grow significantly over time, forming dense, thick structures by 10 minutes. This rapid dendrite formation indicates poor interfacial stability, where uncontrolled Li deposition leads to continuous SEI formation and severe surface roughening. In contrast, Fig. 7b shows that LiF@Li-Sn maintains a smooth and stable surface without any visible dendrite formation, even after 20 minutes. The absence of dendrites demonstrates that the LiF@Li-Sn composite effectively suppresses uncontrolled Li growth. The LiF layer acts as an ion-conductive

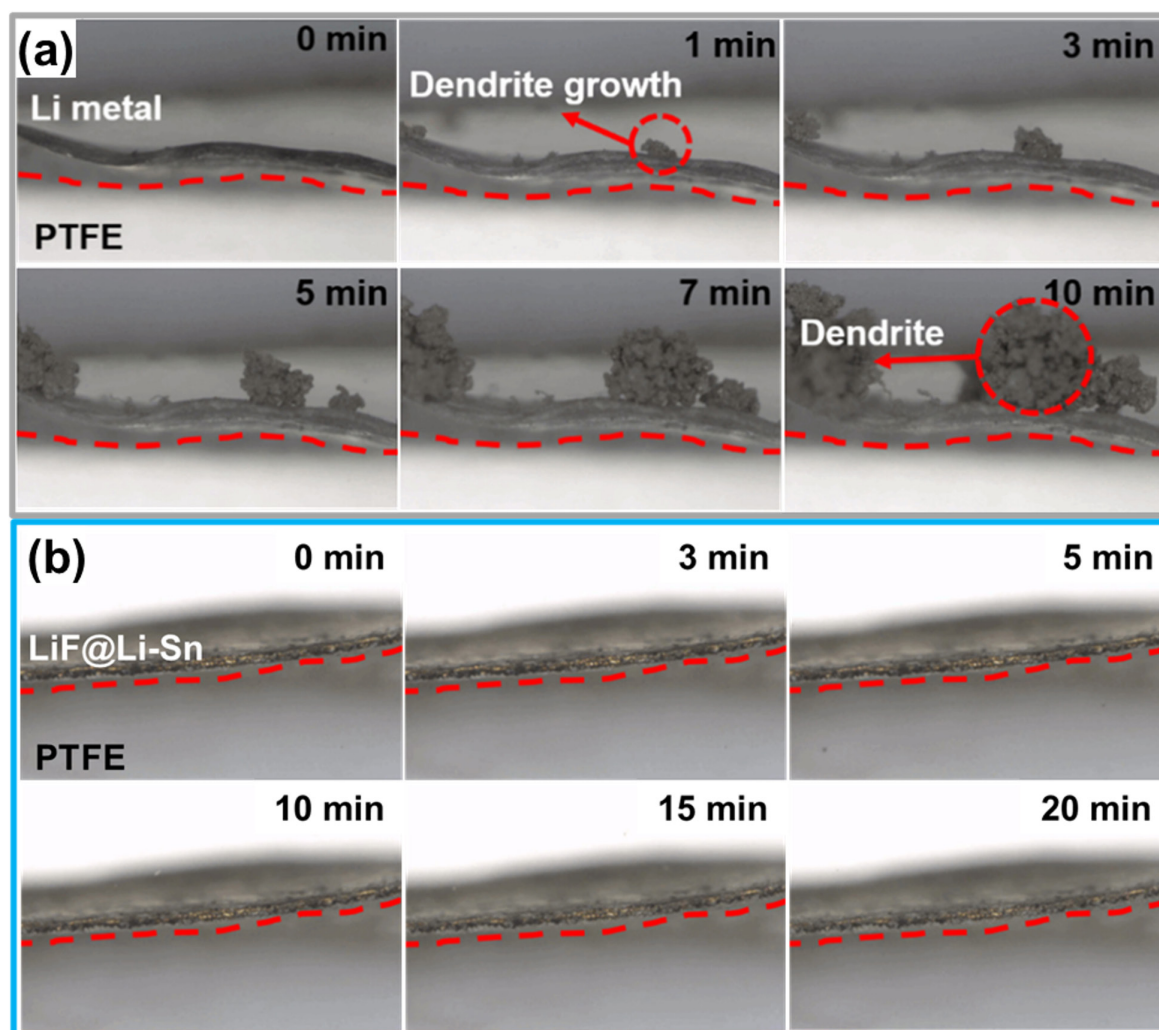


Fig. 7. In situ optical microscopy images of lithium deposition behavior on (a) bare Li and (b) LiF@Li-Sn over time.

but electronically insulating barrier, preventing direct Li-electrolyte contact, while the Li-Sn alloy promotes uniform Li deposition. These observations confirm that the LiF@Li-Sn composite not only enhances surface stability but also ensures safe and uniform Li deposition, making it an effective protective layer for Li metal anodes.

Fig. 8 shows the electrochemical performance of NMC622 full cells with bare Li metal and LiF@Li-Sn metal. In Fig. 8a and 8b, both cells show similar initial capacities around 170 mAh/g, but the Li//NMC622 cell rapidly decays to 9.8 mAh/g after 300 cycles, while the LiF@Li-Sn//NMC622 cell maintains 130.8

mAh/g (79.4%), indicating superior cycling stability. This improvement is attributed to the LiF@Li-Sn layer, which prevents direct Li-electrolyte contact and minimizes side reactions. Fig. 8b further supports this result, where the Li//NMC622 cell shows erratic coulombic efficiency (CE) and a sharp capacity drop after 215 cycles, caused by dendrite formation and electrolyte depletion. In contrast, the LiF@Li-Sn//NMC622 cell maintains a stable CE around 98.8%, reflecting consistent Li plating/stripping. The rate performance in Fig. 8c reveals that the LiF@Li-Sn//NMC622 cell maintains high capacities of 184.6, 181.2, 174.5, 186.7, 157.8, and 150.2 mAh/g at 0.1 C to 5 C, outper-

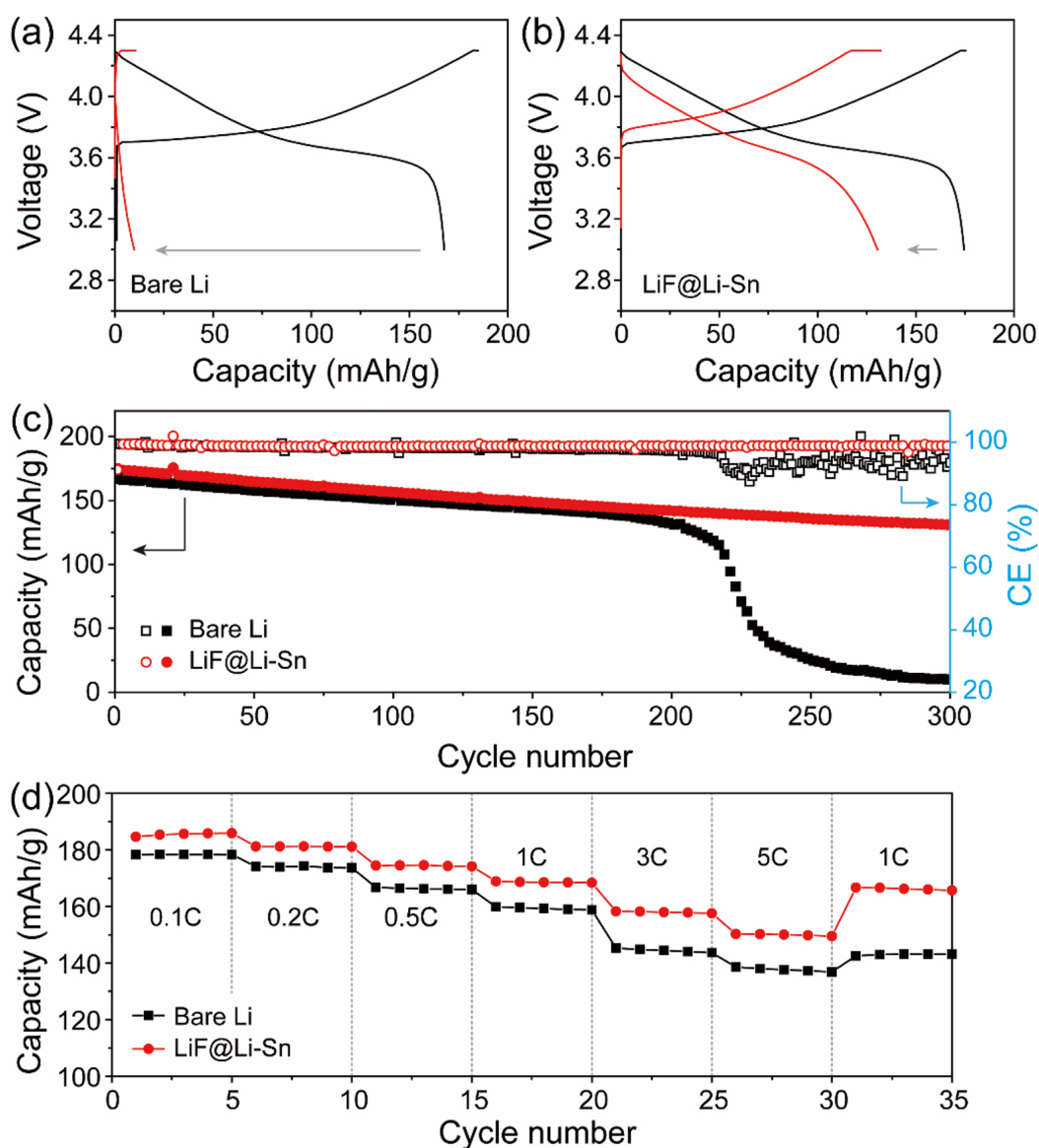


Fig. 8. Electrochemical performance of NMC622 full cells with bare Li and LiF@Li-Sn: (a and b) Galvanostatic charge and discharge profiles after the first and 300th cycle. (b) Cycling performance at 1 C. (c) Rate performance at various rates.

forming the Li//NMC622 cell, which suffers greater capacity loss at high rates. These results confirm that the LiF@Li-Sn layer significantly enhances cycling stability, CE, and rate performance.

4. Conclusion

In this study, a scalable SnF_2 -based spray coating method was used to form a LiF@Li-Sn as artificial SEI layer on Li metal, significantly enhancing the electrochemical performance of LMBs. The artificial SEI layer, composed of ion-conductive LiF and conductive Li-Sn alloy, effectively suppressed Li dendrite growth and maintained a stable interface. This dual protective structure not only provided efficient ion transport but also ensured uniform Li plating and stripping, preventing continuous SEI formation and interfacial degradation. Electrochemical analysis confirmed the superior performance of the LiF@Li-Sn electrode. In symmetric cells, the LiF@Li-Sn electrode maintained a stable overpotential without visible dendrite formation, demonstrating excellent interfacial stability. In NMC622 full cells, the LiF@Li-Sn//NMC622 cell achieved a high capacity retention of 79.4% (130.8 mAh/g) after 300 cycles, significantly outperforming the Li//NMC622 cell, which rapidly decayed to 9.8 mAh/g. The LiF@Li-Sn//NMC622 cell also exhibited high coulombic efficiency (~98.8%) and superior rate performance, delivering high capacities across various current densities, including 150.2 mAh/g at 5 C. These results highlight the potential of the SnF_2 based composite coating as a practical strategy for stabilizing Li metal anodes for high energy density LMBs.

Funding

This research was supported by the National Research Foundation of Korea (NRF) grant funded by the Korea government (MSIT) (No. 2022R1C1C1006536 and No. RS-2023-00221237).

Conflict of Interest

Minho Yang serves as an editor of the Journal of Powder Materials editing but has no role in publishing this article. Except for that, the authors declare no competing financial interests or personal relationships.

Data Availability Statement

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

Author Information and Contribution

Yeong Hoon Jeon: MS candidate; writing-original draft, visualization. Seul Ki Choi: Ph.D candidate; writing-original draft, visualization. Yun Seung Nah: conceptualization, investigation. Wonil Shin: Ph.D candidate; writing-review & editing. Yong-Ho Choa: Professor, supervision, writing-review & editing. Minho Yang: Professor; conceptualization, writing-review & editing, writing-original draft, supervision, funding acquisition.

Acknowledgments

None.

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고청정 Ni-Cr-Co계 초내열 합금 분말 제조를 위한 플라즈마 회전 전극 공정 연구

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The Manufacturing Process of Clean Ni-Cr-Co-Based Superalloy Powder Using a Plasma Rotating Electrode

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Ni-based superalloys are widely used for critical components in aerospace, defense, industrial power generation systems, and other applications. Clean superalloy powders and manufacturing processes, such as compaction and hot isostatic pressing, are essential for producing superalloy discs used in turbine engines, which operate under cyclic rotating loads and high-temperature conditions. In this study, the plasma rotating electrode process (PREP), one of the most promising methods for producing clean metallic powders, is employed to fabricate Ni-based superalloy powders. PREP leads to a larger powder size and narrower distribution compared to powders produced by vacuum induction melt gas atomization. An important finding is that highly spheroidized powders almost free of satellites, fractured, and deformed particles can be obtained by PREP, with significantly low oxygen content (approximately 50 ppm). Additionally, large grain size and surface inclusions should be further controlled during the PREP process to produce high-quality powder metallurgy parts.

Keywords: Plasma rotating electrode process; Ni-based superalloy; Clean powder; Microstructure

Received: June 2, 2025

Revised: June 18, 2025

Accepted: June 18, 2025

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1. Introduction

니켈계 초내열 합금은 우수한 화학적, 내식성, 고온 기계적 안정성을 나타냄에 따라 우주/항공, 발전, 국방 분야에서 주요 핵심 고온 부품으로 적용되고 있다[1-3]. 니켈계 초내열 합금에서 40% 이상의 높은 석출상 분율을 가지는 경우, 성형 가공 및 절삭이 어려워 부품과 유사한 형태로 제작이 가능한 분말야금 및 주조 공정이 주요 제조 공정으로 제작되고 있다. 그 중에서 분말야금 공정으로 제조되는 초내열 합금은 주조 공정으로 제조되는 초내열 합금의 대표적인 미세조직학적 특성인 조대하고 불균일 주조조직(수지상, 편석, 공정상 등) 없이 균일하고 미세한 조직을 구현할 수 있다. 분말

야금 공정으로 제조되는 대표적인 니켈계 초내열 합금은 Udimet 720, Rene 95, Rene 88DT, FGH95 등의 소재가 있으며 주로 고온과 반복적인 응력에 노출되는 터빈 엔진 디스크 소재로 적용되고 있다[1, 3].

분말야금 공정을 위한 니켈계 초내열 합금 분말을 제조하기 위해서는 진공 또는 아르곤 불활성 분위기에서 제작이 되어야 한다. 이에 진공 유도 용해 가스 분무(Vacuum Induction Melting Gas Atomization, 이하 VIGA), 전극 유도 용해 가스 분무(Electrode Induction Melting Gas Atomization, 이하 EIGA), 플라즈마 분무(Plasma Atomization, 이하 PA) 공정이 적용되고 있다. 특히, VIGA는 현재 가장 많이 적용되고 있는 분말 제조 공정으로 가스 압력에 따라서 분말의 크기를 제어할 수 있다. 또한 VIGA 공정은 넓은 크기 범위의 분말을 제작할 수 있어 분말 야금, 적층 제조, 용사 코팅 등 다양한 공정에 적용 가능한 분말을 한 번의 공정으로 제

<https://doi.org/10.4150/jpm.2025.00171>

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작이 가능하다[4-7]. 하지만 모합금 용융을 위하여 용해 도가니를 사용함에 따라서 비금속 개재물의 혼입 위험이 있다. 이와 같은 문제를 해결하기 위한 방안으로 도가니 접촉없이 모합금을 직접 용해하여 분무하는 EIGA 공정이 관심을 받았다[8, 9]. 또한 플라즈마 에너지를 활용하여 모합금을 용융시킴과 동시에 환원 분위기를 조성하여 더욱 청정하고 미세하고 균일한 분말을 제조하기 위한 PA 공정도 개발되었다[10, 11].

그럼에도 불구하고 전술한 공정들은 분말 제작을 위하여 용융 금속으로 고속의 불활성 가스를 분무함에 따라 분말내 기공 간헐으로 인한 분말 진밀도 감소, 높은 위성분말, 분말 겉보기 밀도 감소 등의 현상을 나타내고 있다. 이러한 분말 특성은 분말 야금 부품의 미세조직 및 결합 형성에 영향을 주는 것으로 연구자들에 의해 결과들이 제시되고 있다[4, 7]. M. Chen 등에 따르면 분말의 치밀화를 위하여 적용하는 고온 등압 성형(Hot Isostatic Pressing)을 적용한 부품은 분말의 용융이 발생하지 않기 때문에 초기 분말에 존재하는 기공에 의하여 최종 부품에서도 기공이 관찰되며 기계적 특성의 저하를 나타낸다고 발표하였다 [12]. S. J. Wolff 등은 분말 용융이 일어나는 적층 제조 공정에서도 초기 분말의 진밀도에 따라 적층 소재의 결합으로 잔류할 수 있다고 제시한 바 있다[13]. 그 외에도 높은 위성분말, 낮은 구형도는 분말 야금을 위한 근사정형 부품을 제조시 낮은 흐름도 및 다짐 밀도(tap density) 저하로 고온 등압 성형 수축량이 증가됨에 따라 분말 야금 부품의 크기, 변형을 제어하는데 어려움이 발생한다. 이와 함께 G. Appa Rao 등은 분말의 산소 및 질소 함량이 분말 야금 초내열 합금의 기계적 특성을 감소시킬 수 있어 고청정 분말을 제조하는 것이 중요한 것으로 제시한 바 있다[14].

최근 플라즈마 에너지를 활용하여 고청정 금속 분말을 제조할 수 있는 플라즈마 회전 전극 공정(Plasma Rotating Electrode Process, 이하 PREP)이 제시되고 있다. 현재까지 플라즈마 회전 전극의 공정 변수를 제어하여 제작된 분말의 형상, 크기, 제조 공정 등에 대한 연구 결과들이 주로 제시되고 있다[15-17]. 플라즈마 회전 전극 공정의 생산성 향상을 위해서는 전극 직경 증가가 요구되고 있으며 회전력을 크게 할 수 있어야 미세한 분말 제작이 가능하다. 하지만 초내열 합금은 높은 밀도 (8 g/cm^3 이상)를 나타내고 있어 대형 전극으로 제작하고 회전시키는데 있어서 회전 진동 문제가 발생할 수 있다. 이에 따라 전극과 장비 사이에 기계 누출로 인하여 챔버 분위기 제어가 어려워 분말의 산소, 질소 등의 가스 함량에 대한 문제가 발생할 수 있다. 그럼에도 불구하고 플라즈마 회전 전극 공정을 활용하는 경우, 고속 가스에 의한 분무 저동 및 강제 냉각이 없어 기존 분말에서 발생하고 있는 분말 내 기공을 최소화할 수 있으며 높은 구형도, 플라즈마로 인한 환원 분위기로 인하여 고청정 분말을 제조할 수 있는 것으로 알려지고 있다.

따라서 본 연구에서는 상기의 문제를 해결하기 위하여 기개발 PREP 장비, 직경 70mm 이상의 잉곳을 활용한 Ni-Cr-Co계 초내열 합금 고청정 분말 제조를 시도하였다. 제작된 PREP 초내열 합금 분말의 입도 분포, 형상, 특성, 밀도, 청정도, 미세조직 등의 특징을 VIGA 분말과 비교 분석하고자 하였으며 고청정 분말의 활용 분야에 맞는 분말 제작 방안에 대하여 고찰하고자 하였다.

2. Experimental Methods

본 연구에서는 분말 야금 합금으로 적용되고 있는 Ni-Cr-Co계 초내열 합금의 고청정 분말 제조 공정을 연구하기 위하여 2종의 잉곳 모합금을 적용하였으며 A 모합금은 질소, 산소, 수소가 각각 70 ppm, 130 ppm, 5 ppm 이 포함되어 있었고 B 모합금은 4 ppm, 10 ppm 0.4 ppm을 가지는 것으로 분석되었다. 분말 제조 공정이 분말의 미량원소 변화에 미치는 영향을 확인하기 위하여 A 모합금은 PREP 공정으로 분말을 제작하였으며 B 모합금은 VIGA 공정에 각각 적용하여 분말을 제작하였다.

PREP 공정은 그림 1에서 제시한 기 개발 양산급 장비를 활용하였다. PREP 공정을 위하여 $\phi 75 \text{ mm}$ 으로 정밀 가공하여 잉곳을 세척 후 적용하였다. 초내열 합금 분말 양산을 위하여 잉곳의 끝단 중심에 잉곳을 연결할 수 있도록 나사산을 가공하여 280 mm 길이의 잉곳이 서로 연결되어 챔버의 분위기를 유지하면서 연속 공정이 될 수 있도록 설계되었다. 플라즈마 회전 전극 공정 조건은 사전 시험을 통하여 선정된 최적 조건으로 플라즈마 파워는 180 kW, 전극 회전 속도는 12,000~15,000 r/min, 플라즈마 건과 전극 사이의 거리는 50~60 mm, 전극 중심과 플라즈마 중심은 15 mm 이격하여 수행했다. 분말 청정도 비교를 위한 VIGA 공정은 100 kg급 장비를 활용하였으며 챔버 압력이 $5 \times 10^{-4} \text{ torr}$, 약 1,500 °C로 소재를 용해를 하였으며 아르곤 가스를 활용하여 분무 압력을 15 kgf/cm^2 이상으로 설정하여 분무하였다.

분말 야금 소재로 활용하기 위해서는 산소, 질소 등의 가스 성분이 중요함에 따라서 분말을 제작한 후, 가스 성분의 변화를 NO분석기(LECO, ONH836)를 활용하여 분석하였다. 제조된 분말의 특성을 평가하기 위하여 PSA (Particle size analyzer, Malvern Mastersizer 3000)를 활용하여 분말 평균 입도와 입도 분포를 분석하였다. 분말 형상은 주사전자현미경(Scanning Electron Microscope, 이하 SEM, JEOL, JSM-7900F)를 활용하여 PREP, VIGA 분말의 표면을 분석하여 산화물과 같은 비금속 개재물의 유무를 확인하였다. 분말 및 잉곳의 미세조직을 관찰하기 위하여 각 공정으로 제조된 분말과 잉곳을 마운팅하였으며 SiC 페이퍼 #400~2000을 활용하여 폴리싱을 수행하였으며 정밀 연마는 다이아몬드 페이스트와 콜로이달 실리카 용액으로 정밀연마 했다. 이 후, SEM 및 EBSD(Electron

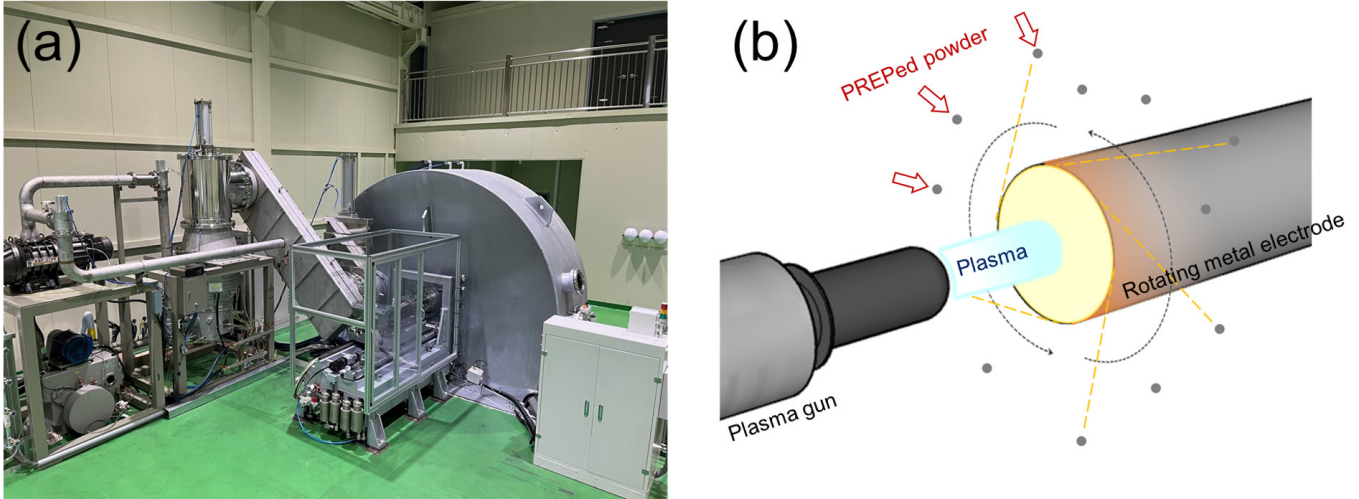


Fig. 1. (a) Plasma rotating electrode process equipment used in this study and (b) schematic diagram of an atomization mechanism for the plasma rotating electrode process powder manufacturing process.

Backscatter Diffraction, 이하 EBSD) 분석을 수행하여 분말의 내부 기공도 및 결정 구조를 확인하였다. EBSD (TESCAN, MIRAI LMH EDAX Velocity)는 20 kV, step size 500 nm 조건으로 측정하여 결과를 분석하였다.

3. Results and Discussion

PREP 공정은 플라스마 에너지에 의한 금속 소재의 용융 속도와 전극의 원심력에 따라서 DDF (Direct Drop Formation), LD (Ligament Disintegration), FD (Film Disintegration)으로 3가지의 분말 형성 기구가 있는 것으로 알려지고 있다[17]. DDF 거동은 용융 금속량이 상대적으로 적은 경우, 용융 금속이 원심력에 의하여 금속 액적(melt droplet)으로 탈락되어 금속 분말이 형성되는 원리이다. LD의 경우, DDF보다는 금속 용융량이 많으며 전극의 회전에 의하여 용융 금속의 미세한 액상선을 형성하여 액적으로 분리되어 분말이 형성되는 기구로 DDF와 비교시 상대적으로 미세한 분말을 형성할 수 있다는 특징이 있다. 반면, 금속 용융 속도가 너무 빠른 경우(FD)에는 용융 금속이 막 형태로 형성되며 막이 원심력에 의해 탈락됨에 따라서 분말의 형태가 불규칙해질 수 있으며, 큰 분말 크기를 가지는 것으로 알려지고 있다.

전술한 것과 같이 PREP 공정에서 금속의 용융 속도는 금속 분말 형성 기구를 변화시키는 중요한 공정 변수이며, 이는 Hinze-Millborn Number(Hi) 값으로 표현 및 구분될 수 있다[17].

$$Hi = \frac{\mu^{0.17} Q \rho^{0.71} \omega^{0.6}}{\gamma^{0.88} D^{0.68}} \quad (1)$$

$\mu(\text{Pa} \cdot \text{s})$ 는 용융 금속의 유동도(viscosity of the liquid metal), $Q(\text{m}^3 \cdot \text{s}^{-1})$ 는 용융 속도(melting rate), $\rho(\text{kg} \cdot \text{m}^{-3})$ 는 밀도, $\omega(\text{rad} \cdot \text{s}^{-1})$ 는 각속도, $\gamma(\text{N} \cdot \text{m}^{-1})$ 는 용융 금속의 표면장력(surface tension of the liquid metal), $D(\text{mm})$ 는 전극 직경이다. Hi값이 0.07 이하인 경우, DDF 거동을 따르게 되며 $0.07 < Hi < 1.33$ 인 경우는 LD, 1.33 이상의 값을 가지면 FD 거동을 따르는 것으로 알려지고 있다. 온도에 따라 변화하는 소재의 유동도($0.00272 \sim 0.00702 \text{ Pa} \cdot \text{s}$), 밀도($6.76 \sim 7.29 \text{ g/cm}^3$), 표면장력($155 \sim 177 \text{ N/cm}$), 전극 직경(75 mm)를 각각 적용하였다. 이 관계를 이용하여 본 연구에서 적용한 소재의 분말 형성 거동의 기준이 되는 금속 용융 속도를 구해보면 약 0.10 kg/min 이하의 용융 속도의 경우에는 DDF가 주요 분말 형성 기구이며, $0.10 \sim 2.02 \text{ kg/min}$ 의 용융 속도의 경우에는 LD, 2.02 kg/min 이상의 용융 속도에는 FD 거동이 활성화되는 것으로 예측된다. 본 연구에서는 용융 속도를 1.16 kg/min 속도로 제어하였으며 이에 따라 LD 거동이 주요 분말 형성 거동이 되는 것으로 판단되었다.

각각의 분말 형성 기구를 통하여 형성되는 평균 분말 입도는 금속의 용융속도, 전극 직경, 회전량 등의 공정 변수에 따라서 아래와 같은 경험식으로 예측할 수 있다 [17].

$$\text{DDF : } D_{50} = \frac{1}{\omega} \sqrt{\frac{12\gamma}{\rho D}} \quad (2)$$

$$\text{LD : } D_{50} = \frac{2}{\omega} \sqrt{\frac{\gamma}{\rho D}} \quad (3)$$

그림 2에서 제시한 결과는 본 연구에서 적용한 니켈계 초내열 합금의 전극 직경, 회전수에 따른 평균 입도 변화 수식 (2)~(3)을 활용하여 예측한 결과이다. 그림에서 확인할 수 있는 것과 같이 회전 속도와 전극 직경의 변화로 25 μm 이하 및 150 μm 이상의 분말을 제조할 수 있는 것으로 예측된다. 하지만 전극 직경이 커지는 경우, 고속 회전을 수행하기 위한 공정 시스템의 구조적 안정성(진동, 전극 동심도, 회전 모터 안정성 등)이 확보되어야 한다. 또한 전극 직경이 작은 경우에는 회전은 빠르게 할 수 있으나 생산량의 감소가 크게 발생함에 따라서 경제적인 분말 제조 공정이 될 수 있도록 적절한 공정 변수를 설정하여야 한다. 본 연구에서는 12,000 ~ 15,000 rpm 및 75 mm의 전극 직경을 적용하여 시간 당 60 kg 이상의 분말을 제조할 수 있는 조건을 설정하였다. 이를 통하여 평균 입도는 LD 기구를 통하여 68 ~ 86 μm , DDF 기구를 통하여 227 ~ 284 μm 범위의 분말을 제조할 수 있는 것으로 예측되었다 (그림 2 (b)). 다만, PREP 공정에서는 공정 환경(플라즈마 에너지 밀도, 전극 중심과의 이격도, 플라즈마와 전극 거리, 전극 형상 변화, 용융 금속 온도가 변화되어 용융 금속의 밀도, 유동도, 표면 장력이 변화 등)에 따라서 계산된 값과 다소 차이를 나타낼 수 있다.

그림 3에서는 본 연구에서 제작한 PREP 및 VIGA 분말 크기 및 분포를 분석한 결과를 나타냈다. 그림에서 제시한 것과 같이 -140 mesh (100 μm 이하)의 분말은 PREP와 VIGA 공정 조건으로 제조하는 경우, 각각 84.1 % 및 58.5 %의 수율을 나타내었다. 그리고 PREP 분말의 경우, 분말의 크기가 증가함에 따라서 분율이 10.2 % (약 100~150 μm), 5.7 % (150 μm 이상)으로 순차적으로 감소하고 있으나 VIGA 분말은 17 % (약 100~150 μm), 24.5 % (150 μm

이상)으로 분석됨에 따라서 bi-modal 형태의 분말 크기 분포를 나타내었다. 이 결과는 분말 크기 균일도가 PREP 분말이 더욱 높다는 것을 의미한다. PREP 분말의 평균 입도는 계산으로 예측된 분말 크기보다 다소 작은 값을 나타냈으나, D10이 36.8 μm , D50이 58.6 μm , D90이 95.1 μm 로 측정됨에 따라 VIGA 분말 보다 상대적으로 큰 분말 크기를 나타냈다. 본 연구에서 적용한 Ni-Cr-Co 합금 분말은 분말 야금으로 제작되는 부품으로 적용을 고려하고 있으며 주로 -140 mesh 이하의 분말을 적용함에 따라서 PREP 공정을 적용하는 경우 높은 수율의 분말 제작성을 나타낼 수 있다. 하지만 현재 공정 조건으로 제조되는 PREP 분말은 상대적으로 미세한 분말이 필요한 분말베드용융법(powder bed fusion)으로 적용하기에는 다소 어려움이 있을 것으로 판단된다. 반면 PREP로 제작된 균일한 분말을 분말 야금 부품 제작에 사용하는 경우, 부품을 만들기 위한 용기 추진도를 향상시킬 수 있다. 이를 통하여 근사정형의 분말 부품을 제작함에 있어 분말 크기 또는 위치별 층진 밀도 차이에 의한 불균일한 수축을 발생시키지 않고 균일한 미세조직을 가지는 부품을 제작할 수 있을 것으로 판단된다.

그림 4에서는 PREP 및 VIGA 공정으로 제작된 분말의 대표적인 형상을 제시하였다. PREP 분말은 높은 구형도를 가지며, 분말 크기 분포가 크지 않은 균일한 입도 분말이 제작되었음을 확인할 수 있다 (그림 4 (a)). PREP 분말은 대부분 독립적 구형의 분말로 제작되었으며 일부 분말에서 위성 분말(satellite)과 연신 형태(elongated)의 분말이 관찰되었다. 대표적 형태를 가지는 분말을 확대하여 관찰하면 액적이 응고가 됨에 따라서 발생하는 수지상 형태의 조직이 관찰되었으며 매우 깨끗한 분말 표면 상태를 나타내고

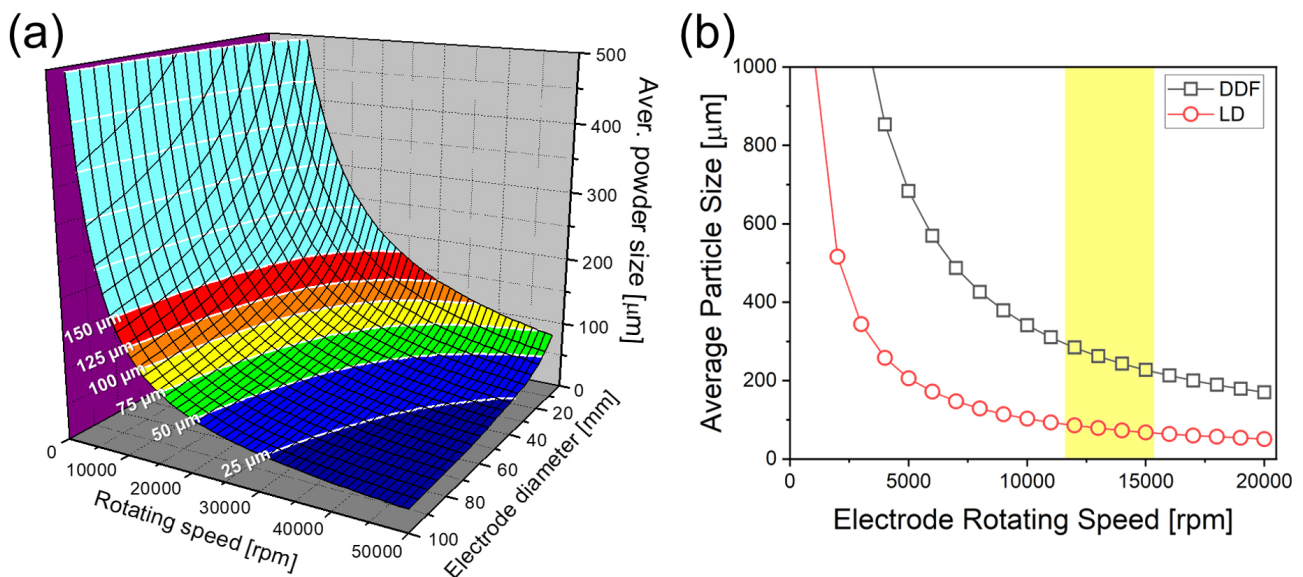


Fig. 2. (a) Effect of rotating speed and electrode diameter, and (b) effect of the atomizing mechanism of the plasma rotating electrode process on the average powder size of Ni-Cr-Co-based superalloy.

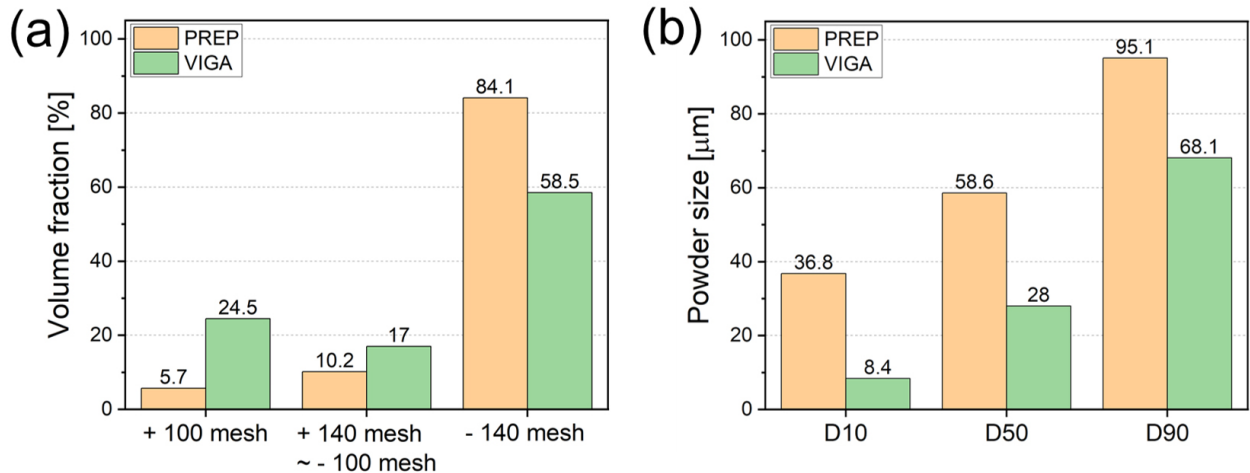


Fig. 3. Results of (a) size distribution and (b) D10, D50, and D90 powder size according to manufacturing processes.

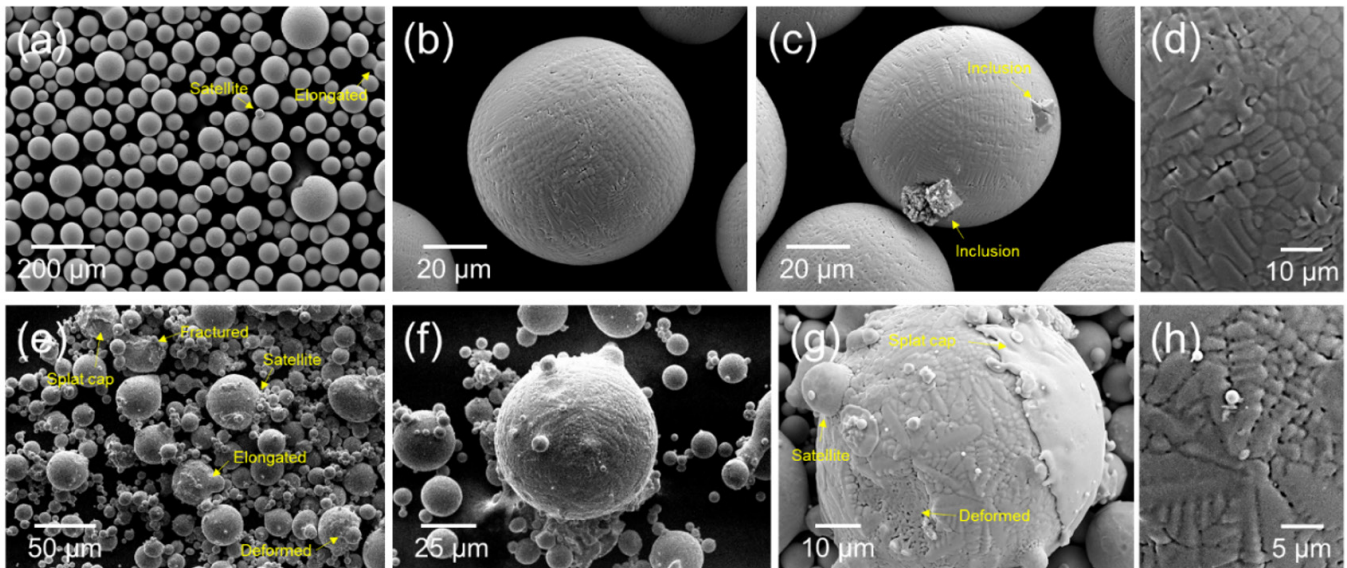


Fig. 4. Scanning electron microscope images of powder size distribution, powder morphology, surface characteristics of (a-d) plasma rotating electrode process-prepared powder and (e-h) vacuum induction melting gas atomization-prepared powder.

있었다(그림 4 (b)). 하지만 일부 분말에서 비금속 개재물로 유추되는 입자들이 분말 표면에서 관찰되었다(그림 4 (c)). VIGA 분말은 PREP 분말과 비교하여 상대적으로 넓은 분말 크기 분포를 가지는 것으로 확인되었으며 위성분말(satellite), 연신된 분말(elongated), 변형된 분말(deformed), 파괴된 분말(fractured), 겹쳐진 분말(splat cap) 등 다양한 형태의 분말이 관찰되었다(그림 4 (d)). 대표적 형태를 가지는 분말을 관찰해 보면, PREP 분말과 동일하게 수지상 형태의 조직이 표면에서 관찰되었으나 위성분말이 많이 관찰되었으며 위성분말의 크기는 약 1~10 μm로 확인되었다(그림 4 (e)). 특히 그림 4 (f)에서 제시한 것과 같이 VIGA 분말에서는 금속 액적이 응

고된 분말과 충돌을 발생시켜 나타날 수 있는 겹침(splat cap) 현상, 분말의 충돌로 발생하는 변형, 파괴 등의 현상이 PREP 분말에 비해 두드러지게 관찰되었다.

전술한 것과 같이 PREP와 VIGA 분말의 형상 차이는 분말이 형성되는 거동과 관계가 있는 것으로 이해해 볼 수 있다. PREP의 경우, 전극의 모서리 부분에서 액적이 순차적으로 분리되고, 분리된 액적은 전극 회전에 의한 원심력으로 인하여 직선적인 비행 운동을 하면서 응고가 발생함에 따라 액적-액적 사이에서 충돌 확률이 낮을 것으로 기대해 볼 수 있다. 반면, VIGA는 고속 가스를 이용하여 분말을 제작함에 따라서 가스의 유동(난류)에 의하여 액적 분리

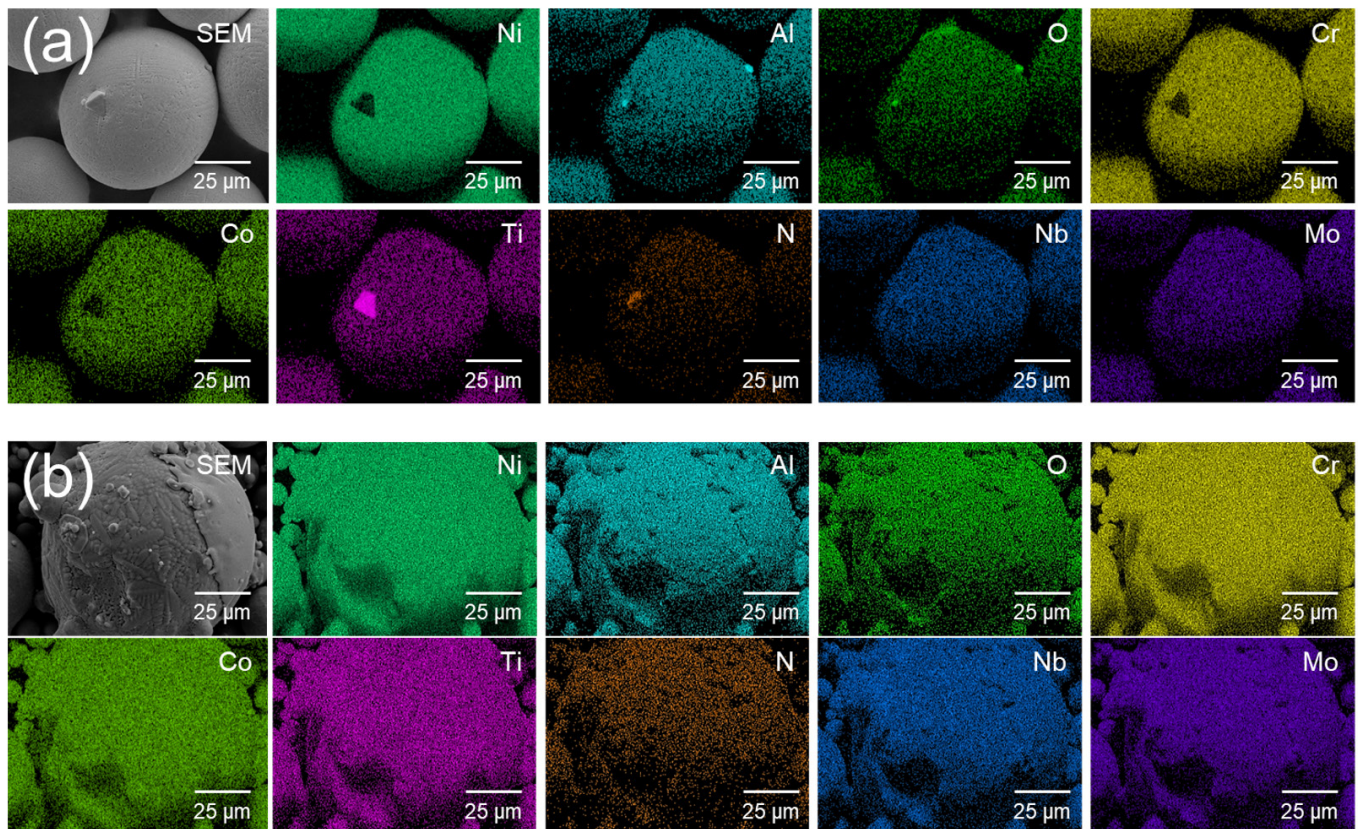


Fig. 5. Elemental distributions of (a) plasma rotating electrode process-prepared powder and (b) vacuum induction melting gas atomization-prepared powder.

및 액적 비행에 영향을 주게 되며, 가스의 난류가 심하게 발생하는 경우에는 액적-액적(불균일 형태 분말), 반응고 분말-액적(불균일 형태 분말), 반응고 분말-반응고 분말(연신된 분말), 고체-액적 분말(splat cap), 고체-반응고 분말(위성 분말), 고체-고체(파괴 또는 변형 분말) 분말 사이의 충돌 확률이 증가되어 다양한 형태의 분말이 형성되는 것으로 사료된다.

그림 5에서는 PREP 및 VIGA 공정으로 제작된 분말의 표면 성분 분석 결과를 나타냈다. 그림에서 제시된 것과 같이 PREP 공정으로 제작된 분말의 표면에서 관찰되었던 입자 위치에서 타이타늄, 질소, 알루미늄, 산소의 분포가 높게 나타남에 따라서 TiN 및 Al_2O_3 등의 입자일 것으로 예측할 수 있다. 이러한 비금속 개재물 입자는 플라스마의 높은 열에 용융이 일어나지 않아 모합금 잉곳에서 존재하던 개재물이 분말에서 동일하게 관찰된 것으로 예측해 볼 수 있다. 또한 이와 같은 입자들이 분말의 표면에서 관찰되는 것은 전극 회전에 따라서 액적이 분리되어 비행하게 되는데 이때 액적 또한 회전(자전)하게 된다. 액적의 자전에 의하여 밀도 분리가 발생할 수 있으며 상대적으로 높은 밀도를 나타내는 금속 액체는 분말은 내부로 낮은 밀도를 나타내는 개재물은 분말의 표면으로 이동하

Table 1. Gas and carbon contents in two different ingots used in this study: PREP-prepared and VIGA-prepared superalloy powders

	N (ppm)	O (ppm)	H (ppm)	C (ppm)
Ingot A for PREP	70	130	5	760
PREP-prepared powder	60	50	5	650
Ingot B for VIGA	4	10	0.4	640
VIGA-prepared powder	10	130	10	640

PREP, plasma rotating electrode process; VIGA, vacuum induction melting gas atomization.

게 되고 응고에 의하여 표면에서 관찰되는 것으로 이해할 수 있다. 반면 VIGA 공정으로 제조된 분말의 표면에서는 PREP에서 관찰된 것과 같은 개재물은 관찰되지 않았으며 모든 원소가 균일하게 분포하고 있는 것으로 확인되었다.

이러한 차이는 분말을 제조하기 위한 모합금의 성분 차이에 기인한 것으로 판단할 수 있으며 이에 따라 표 1에서는 모합금 잉곳과 분말의 미량 원소를 측정하여 제시했다. PREP 공정으로 분말을 제조한 경우, 모합금과 비교하여 질소와 산소의 함량이 감소하는 결

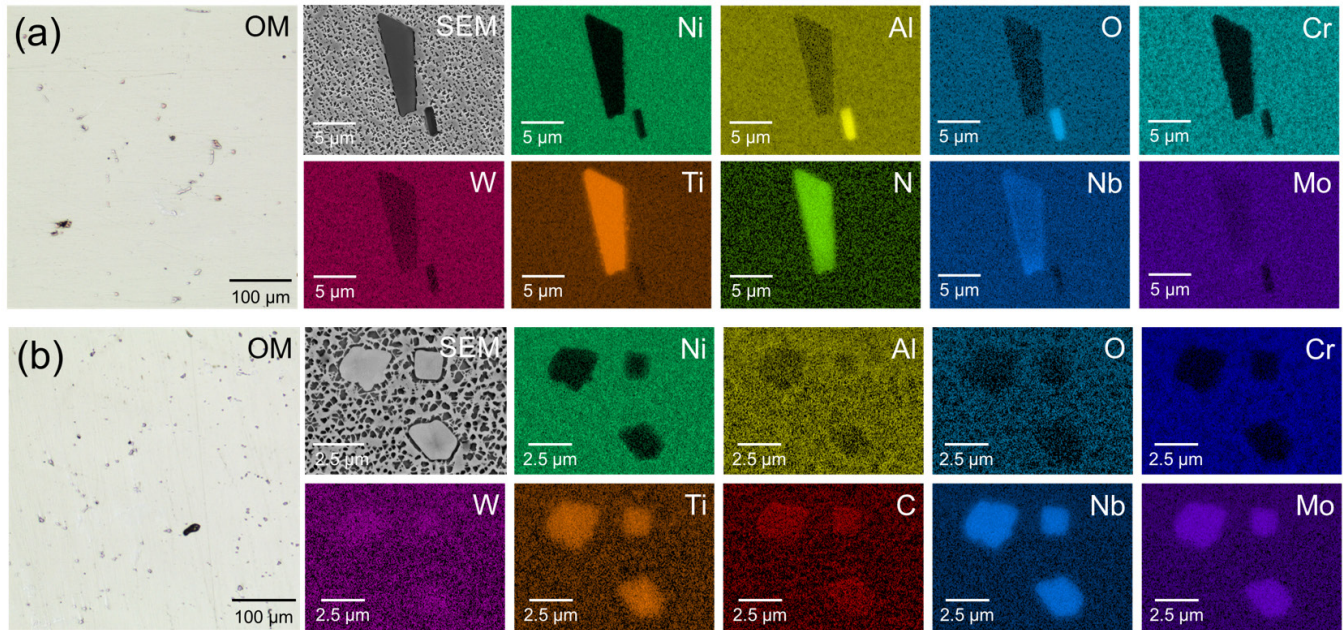


Fig. 6. Results of microstructure and phase analysis of (a) ingot A for plasma rotating electrode process and (b) ingot B for VIGA vacuum induction melting gas atomization.

과를 보이고 있었다. V.I. Kalita 등의 결과에 따르면 플라즈마를 활용하여 분말 제조시 환원 분위기를 구축할 수 있으며 이에 따라 분말의 산소 함량이 감소할 수 있다[18]. 본 연구에서 적용한 PREP 공정에서도 이와 같은 현상이 나타난 것으로 판단되며 표면적이 넓은 분말로 제조되었음에도 모합금 보다 낮은 산소 함량을 나타낼 수 있는 것으로 판단된다. 반면 상대적으로 낮은 질소 및 산소 함량을 가진 B 모합금으로 VIGA 공정을 적용하여 제작한 분말의 경우, 모합금의 산소 함량과 비교하여 분말의 산소함량이 크게 증가하는 것으로 확인되었다. 이 현상은 분말 크기가 미세함에 따라서 산소 함량이 증가하는 일반적인 결과로 판단할 수 있다. 분말의 크기가 작아질수록 표면적이 크게 증가하며 이에 따라 대기 중 또는 분위기에서 존재하는 산소를 흡착하여 분말 표면에 자연 산화물을 형성하게 된다[19]. 이에 따라서 그림 5 (b)에서 제시한 것과 같이 입자 형태의 개재물이 관찰되지 않는 것으로 판단해 볼 수 있다.

전술한 것과 같이 산소 및 질소 함량이 상대적으로 높더라도 VIGA 분말에서는 개재물이 관찰되지 않는 것을 확인하였으며, 이는 분말 형성 거동의 차이와 관계없이 모합금의 청정도가 분말 청정도와 직접적인 관계가 있는 것으로 사료되는 결과이다. 이를 확인하기 위하여 그림 6에서는 분말을 제작하기 위한 모합금 잉곳의 미세조직을 분석하여 제시하였다. A 모합금은 B 모합금과 비교하여 높은 질소 및 산소 함량을 나타낸다. 이에 따라 그림 6 (a)에서 제시한 것과 같이 분말을 제작하기 전 모합금 내에서 B 모합금과 비교하여 높은 비율의 질화물 및 산화물을 관찰할 수 있었다. 이 질

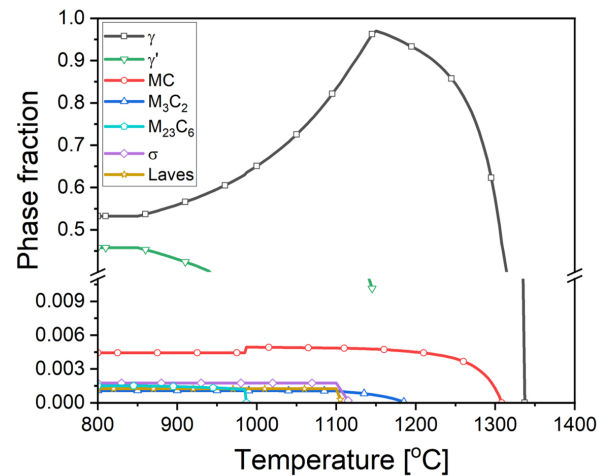


Fig. 7. Phase fraction changes according to temperature, calculated by JMatPro.

화물과 산화물은 대부분 동일 위치에서 관찰되었으며 각형을 나타냈다. 반면, B 모합금에서도 그림 6 (b)에서 나타난 것과 같이 입자상이 관찰되고 있었으나 이는 탄화물로 분석되었다. 그럼에도 불구하고 VIGA 분말에서는 탄화물, 산화물, 질화물 등의 개재물이 관찰되지 않는 것은 각 분말을 제조하기 위한 제조 공정의 특징에 의한 것으로 사료된다.

그림 7에서 제시한 것과 같이 모합금에 존재하는 석출물 및 탄화

물은 잉곳 온도 증가와 함께 용융 금속으로 용해되는 것으로 판단해 볼 수 있다. 하지만 질화물(TiN 등) 및 산화물(Al_2O_3 등)은 각각 2930 °C, 2072 °C로 높은 용점을 나타냄에 따라서 용해되지 않고 분말에서 비금속 개재물이 그대로 존재할 가능성이 높아진다. 즉, 본 연구에서 적용한 VIGA 공정의 경우, 금속을 약 1,500 °C로 용융됨에 따라 탄화물 및 석출물은 모두 용해되는 것으로 판단되며, 낮은 질소 및 산소 함량을 가지는 모합금 B를 사용하더라도 일부 질화물 및 산화물은 용탕내에서 존재할 것으로 사료된다. 하지만 VIGA 공정시 가스 분무를 위하여 용융 금속을 턴디시로 이동하게 되는데 이때, 개재물(질화물, 산화물)을 물리적으로 걸러내는 세라믹 필터를 적용하여 분말의 청정도를 더욱 높일 수 있다. 반면, 플라스마 회전전극 공정으로 분말을 제조하는 경우, 플라스마 에너지에 의하여 일부 산소 함량을 감소시킬 수는 있으나 VIGA와 같이 용융된 금속내 개재물을 물리적으로 걸러낼 수 있는 필터를 적용할 수 없다. 결과적으로 VIGA 공정과 비교하여 PREP 공정이 모합금의 청정도가 분말 청정도에 더욱 큰 영향을 주는 것이 중요한 공정적 특징으로 판단된다.

PREP 및 VIGA 제조 공정 특징은 분말의 물성, 미세조직에도 큰 영향을 미칠 수 있다. PREP 분말의 겉보기 밀도는 4.88 g/cm^3 로 측정되었으며 VIGA 분말은 4.33 g/cm^3 로 측정되었다. S. E. Brika 등의 결과에 따르면 분말의 구형도는 분말의 겉보기 밀도를 변화시키는 주요한 인자로 언급하였다[20]. 그림 3에서 제시한 것과 같이 PREP 및 VIGA 공정으로 제조된 분말은 높은 구형도를 나타내고 있으나 VIGA 분말은 위성 분말이 다수 관찰됨에 따라서 분말이 높은 밀도로 쌓일 수 없어 PREP 분말과 비교할 경우에는 상대적으로 낮은 겉보기 밀도를 나타내는 것으로 판단된다. 또한 그림 8에 제시한 것과 같이 PREP와 VIGA 분말 내 존재하는 결함 종류 및 분율에서도 큰 관계가 있다. 그림에서 나타난 것과 같이 PREP 공정으로 제작된 분말은 원심력에 의하여 액적으로 탈락됨

에 따라 액적의 내부에 기체가 갇히게 되는 확률은 매우 낮을 것으로 판단된다. 하지만 분말 부피(입도)는 VIGA 분말과 비교하여 상대적으로 크게 나타남에 따라 분말의 내부에서 상대적으로 불균일한 형태의 큰 수축공이 관찰되었다(그림 8 (a)). VIGA 분말의 경우에도 PREP 분말에서 관찰되는 수축공이 관찰되었으나 그 크기는 상대적으로 작은 것을 알 수 있으며 이는 액적의 부피가 작아, 액체에서 고체로 응고됨에 따라 발생하는 수축량이 작기 때문으로 해석할 수 있다(그림 8 (b)). 이와 함께 그림 8 (c)에서 제시한 것과 같이 VIGA 분말은 액적을 탈락시키기 위하여 고속 비활성 기체(아르곤, Ar)를 적용함에 따라 아르곤이 액적의 내부에 갇혀 있는 경우가 종종 관찰되었다. 이와 같은 결함은 겉보기 밀도를 크게 감소시킬 수 있으며 또한 분말의 진밀도 감소에도 영향을 준다.

PREP 및 VIGA 제조된 분말의 대표적인 미세조직을 그림 9에 제시했다. 그림에서 제시한 것과 같이 PREP 분말의 평균 결정립 크기는 약 34 μm 의 크기를 나타내고 있었으며 VIGA 분말의 결정립 크기는 약 4.1 μm 를 나타냈다. 분말에서 나타난 결정립의 크기는 냉각속도와 관계가 있으며 결정립이 큰 것은 그림 4에서 제시한 것과 같이 응고에 의해 형성된 수지상의 크기가 큰 것으로 이해할 수 있다. 수지상 크기를 활용하여 경험식을 통하여 분말이 응고될 때의 냉각 속도를 유추해 볼 수 있다[21].

$$\lambda = kt^n \quad (4)$$

여기서 λ 는 수지상 너비(dendrite arm spacing), t 는 냉각 속도(cooling rate), n 은 일반적으로 $1/3 \sim 1/2$ 값을 가지는 냉각 속도 지수, k 는 냉각속도를 나타낸다. 이 수식에서 나타나는 것과 같이 동일한 소재의 경우, n 과 k 는 동일한 것으로 가정해 볼 수 있으므로 PREP (λ : 약 1.31 μm) 보다 VIGA (λ : 약 0.74 μm) 분말의 냉각속도가 상대적으로 큰 것으로 예측된다. 이러한 차이는 VIGA 공정에

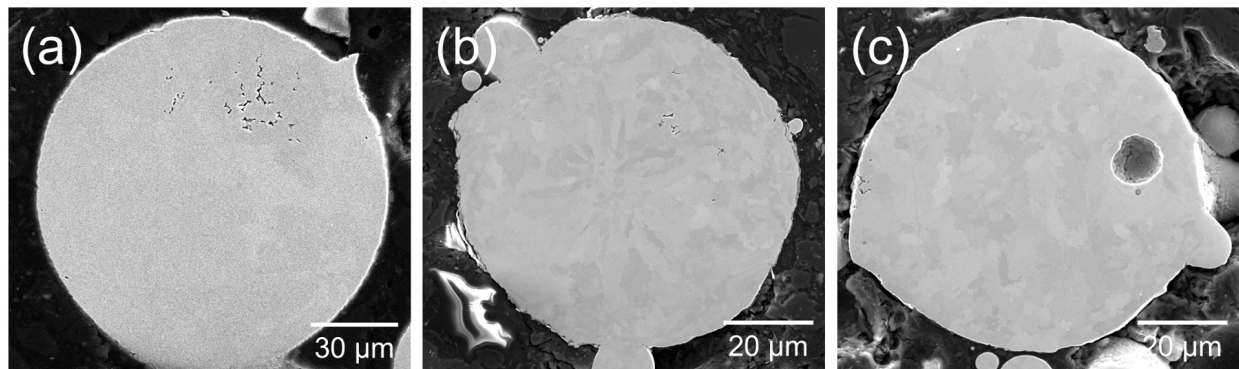


Fig. 8. Scanning electron microscope images of defects in (a) plasma rotating electrode process-prepared powder (shrinkage), (b) vacuum induction melting gas atomization-prepared powder (shrinkage), and (c) vacuum induction melting gas atomization-prepared powder (gas pore), respectively.

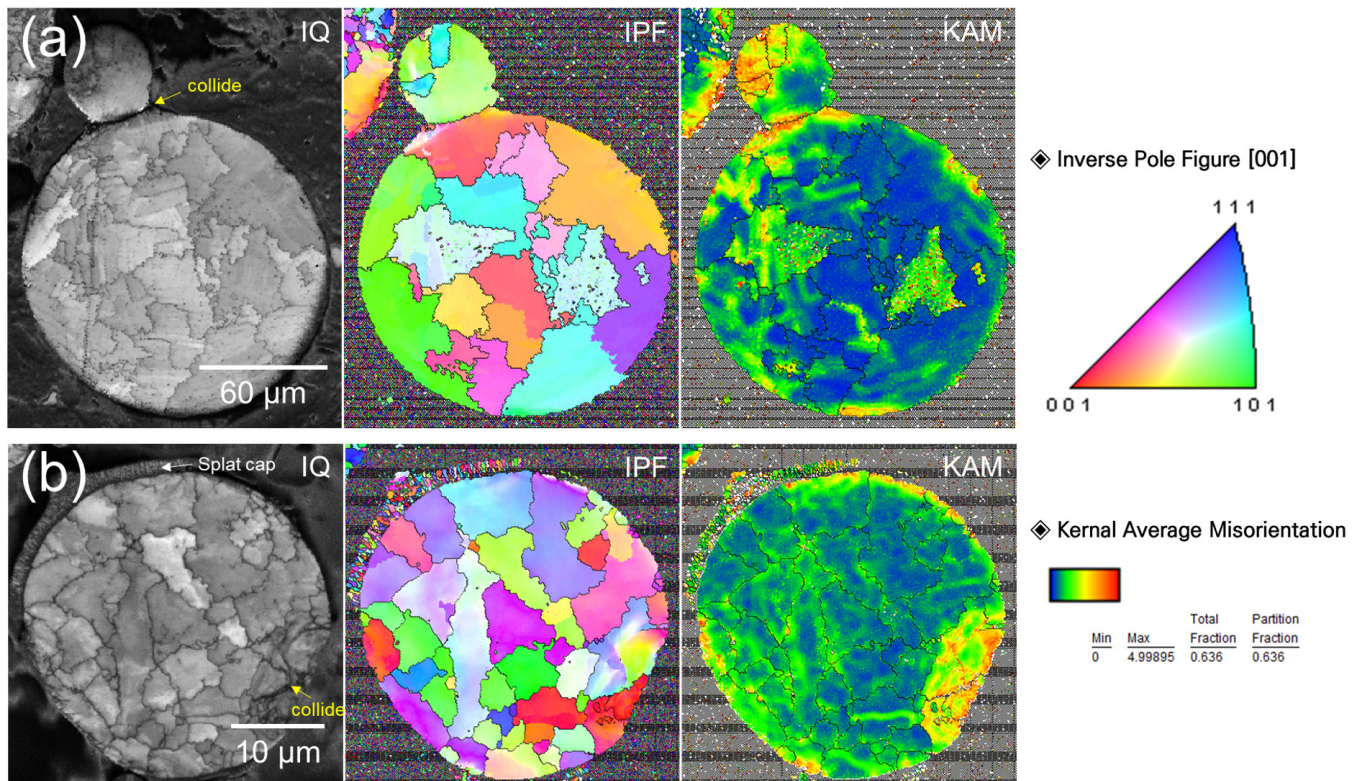


Fig. 9. Image quality map, inverse pole figure map, kernel average misorientation map of (a) plasma rotating electrode process-prepared powder and (b) vacuum induction melting gas atomization-prepared powder, respectively.

서 액적을 분리시키기 위한 아르곤 가스의 분무가 액적의 냉각 속도가 더욱 빠르기 때문이다. 냉각 속도가 빠르기 때문에 그림 9 (b)에서 나타난 것과 같이 높은 KAM 분포를 보이고 있다. 반면, PREP 분말은 가스에 의한 강제 냉각이 발생하지 않아 상대적으로 낮은 KAM 분포(그림 9 (a))를 나타내고 있으며 상대적으로 큰 결정립 크기를 가지게 된다. 또한 그림의 노란색 화살표로 표시된 영역을 확인해 보면, 그림 4에서 언급한 것과 같이 위성분말이 분말 사이의 충돌에 의해 발생하는 것으로 확인할 수 있으며 이는 각 분말에서 변형 조직을 야기함에 따라서 불균일한 분말 조직을 나타내게 한다. 또한 VIGA 분말에서 관찰되는 새로운 조직은 액적이 분말에 충돌함에 발생하는 분말 겹침(splat cap) 조직(그림 9 (b) 흰색 화살표)이며 이 조직의 경우, 열 방출 방향의 반대 방향으로 조직이 응고되어 주상정(columnar) 구조를 나타내었다. 이와 같은 불균일 조직은 HIP 등의 공정시 회복이 발생하지 않는 온도 조건에서 수행할 경우에 분말 야금 부품의 미세조직 불균일을 야기할 수 있으며 이는 부품의 기계적 특성, 신뢰성에 큰 영향이 있을 수 있을 것으로 판단된다. 반면 PREP 분말의 미세조직은 VIGA 분말보다 상대적으로 조대하지만 균일한 미세조직 나타내고 있음을 확인하였다.

4. Conclusions

본 연구에서는 플라즈마 회전 전극 공정을 적용하여 고청정 초내열 합금 분말을 제조하고자 하였으며 그 분말의 특성 및 미세조직을 기존 진공 유도용해 가스 분무 법으로 제조된 분말과 비교하여 아래와 같은 결과를 도출할 수 있었다.

1. 각각의 공정으로 제조된 분말의 가스 함량을 비교한 결과, PREP 분말이 약 50 ppm, VIGA 분말이 130 ppm로 측정됨에 따라 양질의 Ni-Cr-Co계 초내열 합금 분말을 제조할 수 있는 공정으로 확인되었다.
2. PREP 분말의 겉보기 밀도는 4.88 g/cm^3 , VIGA 분말의 겉보기 밀도는 4.33 g/cm^3 로 측정되었으며 이는 PREP 분말 내부에 낮은 결함(shrinkage, gas pore)과 높은 구형도, 낮은 위성 분말에 의한 높은 적층 밀도에 기인한 것으로 판단된다. VIGA 공정에서는 고속의 가스로 강제 냉각이 됨에 따라서 28 μm의 결정립 크기를 나타냈으며, PREP 분말의 평균 결정립 크기는 약 58 μm로 상대적으로 크게 나타났다. VIGA 공정으로 제조된 분말은 PREP 공정과 비교하여 상대적으로 빠른 냉각 속도를 가지는 것으로 예측되었으며, 이에 따라 상대

적으로 작은 결정립 크기, 높은 KAM 값, 불균일한 미세조직을 나타내었다.

3. 플라즈마 회전전극 공정으로 분말을 제조하는 경우, 플라즈마 에너지에 의하여 일부 산소 함량을 감소시킬 수는 있으나 VIGA와 같이 용융된 금속내 개재물을 물리적으로 걸러낼 수 있는 필터를 적용할 수 없으므로 모합금의 청정도가 분말 청정도에 직접적인 영향을 주는 것으로 확인되었다.

Funding

본 연구는 정부(방위사업청)의 재원으로 국방과학연구소(511LL5-912955101)에서 수행되었으며, 이에 감사드립니다.

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

Kyu-Sik Kim: Senior Researcher; Writing-original draft, Supervision, Conceptualization

Dae Woong Kim: Senior Researcher; Methodology, Investigation

Yeontae Kim: Senior Researcher; Methodology, Investigation

Jung Hyo Park: Senior Researcher; Supervision

Acknowledgment

None.

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The Effect of Aluminum Powder Size on the Structure and Mechanical Properties of Foam

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In this study, we analyzed the structural and mechanical properties of aluminum foams fabricated using aluminum powders of varying sizes and mixtures. The effects of sintering and pore structure at each size on the integrity and mechanical properties of the foams were investigated. Structural characteristics were examined using scanning electron microscopy and micro-computed tomography, while mechanical properties were evaluated through compression testing. The experimental results demonstrated that smaller powder sizes improved foam integrity, reduced porosity and pore size, and resulted in thinner cell walls. In combination, these effects increased compressive strength as the powder size decreased. The findings of this study contribute to the understanding and improvement of the mechanical properties of aluminum foams and highlight their potential for use in a wide range of applications.

Keywords: Aluminum foam; Spark plasma sintering; Space holder technique; Powder metallurgy; Mechanical properties

Received: May 26, 2025

Revised: June 19, 2025

Accepted: June 20, 2025

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1. Introduction

Metal foam is a lightweight material with unique physical, chemical, and mechanical properties that can replace solid metals to achieve weight reduction, cost savings, and increased efficiency [1]. These materials exhibit high specific strength, excellent energy absorption, low density, and effective acoustic damping, making them suitable for lightweight structural applications across various industries. [2-4]. Metal foam is a unique lightweight material that can be fabricated from a variety of metals and alloys, offering weight reduction, cost savings, and enhanced efficiency by replacing solid metals. Common raw materials for metal foams include pure metals such as aluminum, titanium, nickel, and copper, as well as alloys like Cu-Zn-Al, Ni-Ti, Ti-Mg, and stainless steel [5-12]. Among them, aluminum is widely used in engineering due to its abundant availability, low density, good ductility, and high corrosion resistance. These properties make aluminum foam one of the

most popular and actively researched types of porous metals [13, 14]. While retaining the intrinsic properties of aluminum, the internal porous structure of aluminum foam provides high specific strength and excellent energy absorption. Additionally, it offers distinctive features such as low weight, good thermal and electrical conductivity, vibration damping, and acoustic absorption [14-17]. Aluminum foams, in particular, have attracted increasing attention due to their low density, high surface area, excellent thermal and electrical conductivity, high mechanical strength, and electromagnetic interference (EMI) shielding capabilities. These characteristics make them suitable for a wide range of industrial applications, including heat exchangers, exhaust mufflers, catalyst carriers in chemical reactors, high temperature filters, sound barriers, and EMI shielding materials [18-20]. The internal pore structure of aluminum foam allows it to absorb large amounts of energy as the cell walls deform under external loads. This makes it especially valuable in applications such as improving crashworthiness in automobiles, providing shock protection in aerospace and military equipment, enhancing seismic resistance and vibration damping in architectural structures, and serving as packaging

<https://doi.org/10.4150/jpm.2025.00157>

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or soundproofing material [13–15, 21, 22]. Furthermore, aluminum foam is considered environmentally friendly due to its recyclable, fire resistance, and durability in various weather conditions [13].

Aluminum foam can be manufactured using various methods, including gas injection, melt foaming, and powder metallurgy [23–26]. Among these, the powder sintering method produces porous structures by compressing and sintering metal powders, where the arrangement of the powder particles determines the size and shape of the pores [27].

Spark plasma sintering (SPS) is an innovative powder metallurgy technique that enables the rapid densification of samples by applying electric current and pressure directly to a mold containing metal powder. This method is widely utilized in the fabrication of nanocrystalline structures, porous materials, ceramics, and iron-based materials due to its advantages, including low sintering temperatures and voltages, fast heating rates, and short holding times [28, 29]. In SPS, particle size has a direct influence on sintering density. Smaller particles lead to higher relative density and hardness due to their larger surface area, which facilitates faster sintering neck formation. Conversely, larger particles tend to create larger interparticle pores, which can decrease the final density and degrade mechanical properties. These characteristics make SPS an especially effective sintering technique for producing nanocrystalline materials and dense metal foams [30–35].

Aluminum foam is typically fabricated by mixing aluminum powder with a space holder, followed by compaction and sintering. After compaction — often with the addition of small amounts of sintering aids and binders — sintering forms a bonded aluminum matrix, and the space-holders are removed through pre- or post-sintering heat treatment, yielding an open-pore aluminum foam. In the sinter-dissolve process, inorganic salts such as NaCl and CaCl_2 are used as space-holders due to their higher melting points than aluminum. Process parameters in the space-holder method significantly influence the microstructure and performance of the final foam. Key variables include the size, shape, volume fraction of the space-holders, compaction pressure, and sintering temperature. The volume fraction directly determines porosity, while compaction pressure and sintering temperature affect interparticle bonding and mechanical properties. Despite its advantages, the space-holder method has certain limitation. First, porosity is constrained when the packing density of the space holders is below 65%, and residual particles may reduce porosity and cause corrosion. Second, large space-holder particles (over 1 mm) are

prone to breakage during compaction, making it difficult to produce foams with large pores. Nevertheless, due to its ability to precisely control pore size and shape, the space-holder method remains a widely adopted technique for producing highly porous and functional aluminum foams [13, 36].

In compression tests of aluminum foams, a characteristic stress-strain curve is typically observed, which can be divided into three distinct regions. The first region is the linear elastic region, where stress increases almost linearly with strain due to the elastic bending of the cell walls. The second region is the plateau region, during which the stress remains nearly constant or increases slightly as the cell structure progressively collapses. In this region, the cell walls act as plastic hinges, allowing large deformations without a significant increase in stress. The final region is the densification region, where the stress rises sharply as the collapsed cell walls come into full contact and the structure can no longer deform without significant resistance [13, 21, 37]. The mechanical properties of aluminum foams are governed by the interplay of several factors, including cell structure and relative density, cell wall thickness, and pore size and shape. By optimizing these parameters, aluminum foams can be tailored to meet the specific performance requirements of various applications [13].

This study aims to investigate the effect of aluminum powder size on mechanical properties and microstructure of aluminum foam. Although many studies have explored the processing and performance of aluminum foams, the specific influence of powder particle size—particularly across a wide size range—has not been sufficiently addressed. Since particle size directly affects sintering behavior, pore morphology, and mechanical performance, a systematic investigation is essential to better understand and control foam characteristics. In this work, porous aluminum foam was fabricated using the space-holder method, in which aluminum powder was mixed with sodium chloride (NaCl) particles (500 μm) as space-holders and then sintered. The results confirmed that aluminum powder size significantly influences both the mechanical properties and microstructure of the foam, suggesting that optimizing powder size can enhance performance and versatility. Furthermore, this fabrication approach is not limited to aluminum, but can potentially be extended to a broad range of metal or alloy systems, contributing to the design of lightweight and energy-absorbing materials for structural and functional applications.

2. Experimental Procedure

2.1 Foam Manufacturing

Aluminum foams were fabricated using the space-holder process, and a schematic of the process is shown in Fig. 1. Sodium chloride (NaCl) was used as the space-holder material. Specifically, 500 μm NaCl (purity 99%, particle size 500 μm , COMSCIENCE) was used, and four types of aluminum powders were prepared: 1 μm (purity 99.9%, particle size 1 μm , AVENTION), 50 μm (purity 99.0%, particle size 200 mesh, SAMCHUN), 100 μm (purity 99.9%, particle size 100 μm , AVENTION), and a 1:1 weight ratio mixture of 1 μm and 100 μm powders. The aluminum powder and NaCl were mixed in a volume ratio of 1:5 using a vortex mixer (IKA, Vortex 3) for approximately 1 minute. The mixed powder was then placed into a graphite mold (35 mm outer diameter, 10 mm inner diameter, 40 mm height), and a uniaxial pressure of 1 MPa was applied using a hydraulic press prior to sintering. Sintering was carried out using spark plasma sintering (SPS) under the following conditions: a heating rate of 50°C/min, sintering temperature of 500°C, holding time 10 minutes, applied pressure of 50 MPa, vacuum level of 150 mTorr, and air cooling. The sintered sample were cylindrical, with a diameter of 10 mm, height of 4.1–4.3 mm, and a weight of approximately 0.8 g. To remove the NaCl space-holder, the sintered samples were immersed in distilled water heated to 60°C for 1 hour. Following this, ultrasonic cleaning was performed in two steps: first in distilled water and then in ethanol, with sonication lasting approximately 15 minutes for each step. The cleaned samples were then dried in a drying oven at 120°C for 1 hour. After drying, the final

foam samples had a diameter of 10 mm, a height of 4.1–4.3 mm, and a weight of approximately 0.16g. For each condition, four samples were prepared.

2.2 Microstructure Analysis

The microstructure of the powders and aluminum foams were analyzed using a variable pressure scanning electron microscope (Hitachi, SU3900). The powders were examined to determine the size and morphology of aluminum powder and NaCl, while the foams were analyzed for pore morphology, size and distribution. A particle size analyzer (Malvern Panalytical, Mastersizer 3000) was used to measure the particle sizes of both aluminum and NaCl. X-ray micro-computed tomography (Micro CT; Bruker, SKYSCAN 1272) was employed to characterize the foam in terms of pore size, porosity, cell thickness, overall morphology, and pore structure.

2.3 Mechanical Properties

To evaluate the compressive strength of the aluminum foams, compression tests were conducted at room temperature using a universal testing machine (Instron, 5569). The foam specimens had a diameter of 10 mm and a height ranging from 4.1 to 4.3 mm. Four types of aluminum foams were tested: (1) foam fabricated with 1 μm aluminum powder (hereafter referred to as 1 μm foam), (2) foam fabricated with 50 μm powder (50 μm foam), (3) foam fabricated with 100 μm powder (100 μm foam), and (4) foam fabricated with a 1:1 weight ratio mixture of 1 μm and 100 μm powders (Mix foam). Each test was performed in triplicate for statistical reliability. The strain rate was set at $1 \times 10^{-3} \text{ s}^{-1}$, and the compression was applied up to 70% strain.

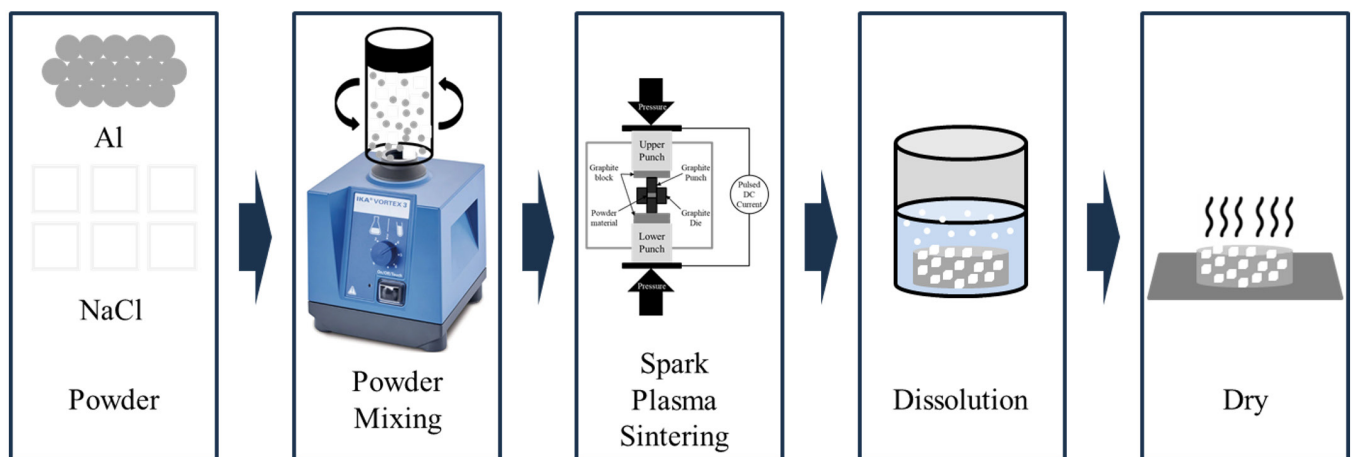


Fig. 1. Schematic of aluminum foam manufactured using the space-holder method.

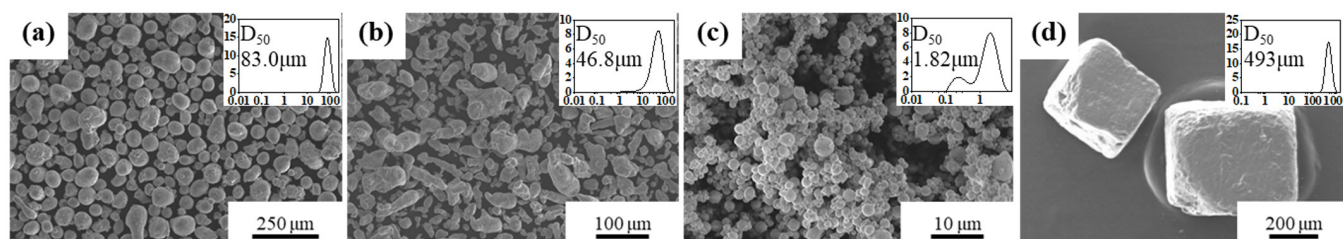


Fig. 2. Scanning electron microscopy images and particle size analysis results of aluminum powders and NaCl powder: (a) 100 μm aluminum powder, (b) 50 μm aluminum powder, (c) 1 μm aluminum powder, (d) 500 μm NaCl powder.

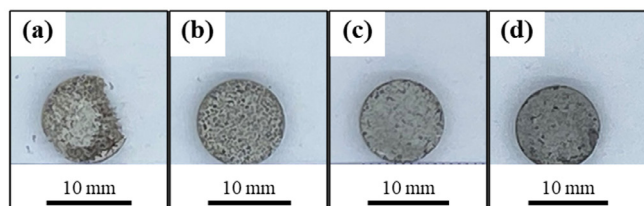


Fig. 3. Images of aluminum foams fabricated with different aluminum powder sizes: (a) 100 μm foam, (b) 50 μm foam, (c) 1 μm foam, (d) Mix foam.

3. Results and Discussion

3.1 Powder and Foam Measurement

Fig. 2. a–d show SEM images and particle size analysis results of the aluminum powders and NaCl. The SEM images illustrate the size and morphology of the aluminum powder and NaCl particles. As observed by SEM, the aluminum powders were approximately 1 μm , 50 μm , and 100 μm in size, with spherical or cylindrical shapes, while the NaCl particles were about 500 μm and exhibited a cubic morphology. To accurately determine particle sizes, a particle size analyzer was used. The D50 values obtained were as follows: 1.82 μm for the 1 μm aluminum powder, 46.8 μm for the 50 μm powder, 83.0 μm for the 100 μm powder, and 493 μm for the 500 μm NaCl. These values were consistent with the observations made from the SEM images, indicating good agreement between the two measurement methods.

Fig. 3. a–d show images of the fabricated aluminum foams. The foams were categorized based on the aluminum powder used: 100 μm foam (fabricated using 100 μm aluminum powder), 50 μm foam (using 50 μm powder), 1 μm foam (using 1 μm powder), and Mix foam (using a 1:1 weight ratio mixture of 100 μm and 1 μm powders). All foam had a cylindrical shape with a diameter of 10 mm and a height ranging from 4.1 to 4.3 mm. The relative density of each foam was calculated prior to

NaCl removal. The densities of aluminum and NaCl are 2.70 g/cm³ and 2.16 g/cm³. Respectively, In the green compact with a 1:5 volume ratio of aluminum to NaCl, 0.16 g of aluminum corresponds to a volume of 0.05926 cm³, and 0.64 g of NaCl corresponds to a volume of 0.2963 cm³. The total volume is therefore 0.35556 cm³, and the total weight is 0.80 g, yielding an overall density of 2.25 g/cm³ for the compact. The measured densities of the sintered foams were: 100 μm foam is 2.15 g/cm³, 50 μm foam is 2.15 g/cm³, 1 μm foam is 2.20 g/cm³, and Mix foam is 2.15 g/cm³. The corresponding relative densities were: 100 μm foam is 95.6%, 50 μm foam is 95.8%, 1 μm foam is 97.6%, and Mix foam is 95.7%. All samples exhibited relative densities greater than 95%, indicating successful sintering. Among them, the 1 μm foam showed highest density, suggesting enhanced particle packing and bonding.

$$\rho = \frac{m}{v}, \rho_{Relative} = \frac{\rho_{Experiment}}{\rho_{Theoretical}} \quad (1)$$

To confirm the removal of NaCl, the NaCl removal rate was measured and calculated using Eq. (2). The measured removal rates were as follows: the 100 μm foam was not measurable due to peripheral breakage during the NaCl removal process; the 50 μm foam showed 100% removal; the 1 μm foam, 95.24%; and the Mix foam, 96.27%. Incomplete removal of NaCl can be attributed to several factors. First, as the aluminum powder size decreases, the number of aluminum particles surrounding each NaCl particle increases, and the voids between the aluminum powders become smaller. These two factors restrict access to distilled water and hinders the dissolution of NaCl. Second, the height and porosity of the foam also play a critical role. In initial trials, aluminum foams with a height of 10 mm exhibited residual NaCl in the center of the sample. To address this issue, the sample height was reduced to 4 mm and the porosity was increased, which enhanced NaCl removal by improving pore interconnectivity and creating more effective diffusion path-

ways. Third, increased relative density reduce pore connectivity, further preventing the complete removal of NaCl. Fourth, breakage of NaCl particles during compaction or sintering may result in their entrapment within the matrix. Wan, Tan, et al. reported that space-holder particles are susceptible to breakage during compaction, which can impede their complete elimination [13]. For these reasons, the NaCl removal rate tends to decrease as the aluminum powder size decreases.

(2)

$$\text{NaCl removal rate (\%)} = \left(\frac{\text{NaCl}_{\text{removal weight}}}{\text{NaCl}_{\text{weight}}} \right) \times 100$$

(NaCl removal weight = weight before removal NaCl - weight after removal NaCl)

Fig. 3. Shows a full image of the fabricated aluminum foams, which were used to evaluate the structural integrity of the foams. For the 100 μm foam, all four samples exhibited partial collapse during the NaCl removal process, with approximately 10% of the total volume affected. In contrast, no collapse was observed in the 50 μm foam, 1 μm foam, or Mix foam. In terms of structural integrity, the 100 μm foam showed the poorest performance while the other foams maintained good integrity. Factors affecting the integrity of the foam include the ratio of aluminum powder size to NaCl size, the volume ratio of aluminum to NaCl, and the sintering conditions. In this study, the sintering conditions and the volume ratio of aluminum to NaCl (1:5) were kept constant across all samples. Therefore, the primary influencing factor was the relative particle size ratio between aluminum powder and the NaCl. The NaCl particle size was fixed at 500 μm , while the aluminum powder sizes were 100 μm , 50 μm , and 1 μm , corresponding to size ratio of aluminum powder to NaCl of 1:5 (100 μm foam), 1:10 (50 μm foam), and 1:500 (1 μm foam), respectively. Fig. 4. Illustrates the relative sizes. When converted to volume ratios, these become approximately 1:125 (100 μm foam), 1:1000 (50 μm foam), and 1:125,000,000 (1 μm foam). Given the 1:5 aluminum-to-NaCl volume ratio, the number of aluminum particles per NaCl particle increases significantly with decreasing aluminum powder size (approximately 25 for 100 μm , 200 for 50 μm , and 25 million for 1 μm). As the aluminum particle size decreases, the number of aluminum particles surrounding each NaCl particle increase, and the interparticle void size decrease. This reduces the diffusion pathways for distilled water, which is essential for dissolving and removing the NaCl. Consequently, smaller aluminum particles can hinder NaCl removal. Additionally, smaller particles have a higher surface area, promoting faster sinter-

ing neck formation and leading to increased relative density [9–14]. While this improves structural integrity, it can also trap NaCl within the matrix, as observed in the 1 μm foam and Mix foam, where NaCl was not completely removed.

3.2 Microstructure Measurement Using SEM

Fig. 5. Shows an SEM image of aluminum foam. The image reveals the size and morphology of the pores, as well as the shape and thickness of the cell walls. The pores can be classified into three types based on their formation mechanisms: (1) pores formed during powder sintering, (2) pores generated by the removal of NaCl, and (3) pores formed by the partial collapse or destruction of the cell wall during NaCl removal. Pores formed during powder sintering are typically smaller than 50 μm and exhibit irregular shapes. As the aluminum powder size decreases, the size of these pores also decreases, owing to the reduced interparticle voids in powders. Pores resulting from NaCl removal are approximately 300–500 μm in size and generally cubic in shape. The fact that they are smaller than the original NaCl particles (500 μm) is attributed to deformation of the NaCl under pressure during sintering [13]. Pores caused by the destruction of the cell walls are irregular in both shape and size, and their occurrence is more noticeable in 50 μm and Mix foams. Overall, the average pore size decreases as the aluminum powder size decreases. Examination of the cell walls shows that aluminum powders are well bonded. In the 100 μm

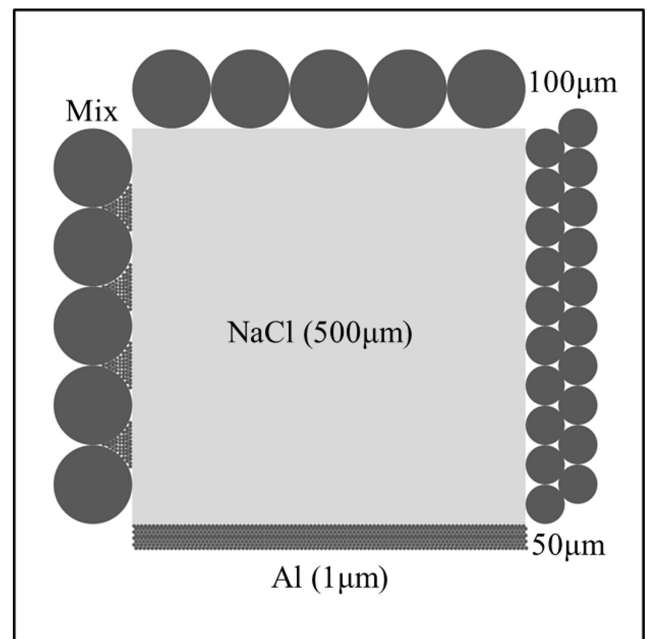


Fig. 4. Comparison of the sizes of NaCl and aluminum powders.

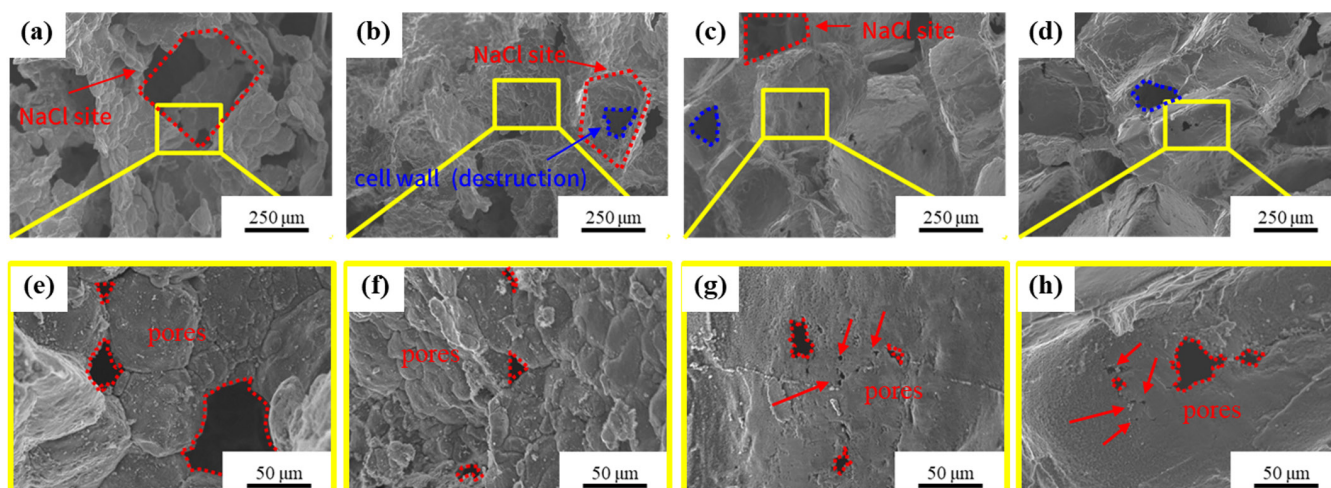


Fig. 5. Scanning electron microscopy images of aluminum foams fabricated with different powder sizes: [(a), (e)] 100 μm foam, [(b), (f)] 50 μm foam, [(c), (g)] 1 μm foam, [(d), (h)] Mix foam. [($\times 100$), ($\times 500$)].

and 50 μm foams, the boundaries between particles are clearly visible, while the 1 μm foam exhibits blurred boundaries or smooth surface. This indicates that finer aluminum powders, with their higher surface area, promote rapid neck formation during spark plasma sintering, leading to improved densification and higher relative density. The thickness of the cell walls also tends to decrease as the aluminum powder size decreases. This is consistent with increased densification achieved through enhanced particle bonding in smaller powders [30–35].

3.3 Microstructure Measurement Using Micro-CT

Fig. 6. a–d shows full 3D images of the aluminum foams, Fig. 6. e–h presents the 2D cross-sectional images and Fig. 6. i–l displays 3D cropped images ($3 \times 3 \times 3 \text{ mm}^3$) of each foam. In all images, the aluminum cell walls appear as white or gray regions, while the pores are shown in black. Comparison of the 3D images revealed that the 50 μm , 1 μm , and Mix foams maintained good structural integrity, whereas the 100 μm foam exhibited partial collapse and compromised structure. The 2D cross-sectional image clearly show the morphology of the cell walls and pores. The cell walls are formed by the sintering of aluminum powders, and their thickness is influenced by the powder size, which determines the surface area and sintering behavior. As the aluminum powder size decreases, the cell wall thickness tends to decrease due to enhanced densification. In the 100 μm foam, collapse and poor bonding between cell walls were observed, along with reduced interconnectivity. In contrast, the 50 μm , 1 μm , and Mix foams showed well-bonded cell walls and good structural interconnectivity. Pore shapes

and sizes were found to be irregular and varied, primarily due to deformation of the NaCl particles under pressure during sintering [13]. The 3D cropped images provided detailed visualization of pore morphology and cell wall structure. Porosity, pore size, and cell wall thickness were quantitatively analyzed using Micro-CT. Porosity was calculated from the full 3D image, while pore size and cell wall thickness were calculated using the 3D cropped image data. This approach was taken because, in the full 3D image of the 100 μm foam, collapsed regions were recognized as pores, which led to overestimation of pore size and inaccurate measurements. By using the 3D cropped images ($3 \times 3 \times 3 \text{ mm}^3$) and excluding the damaged areas, more accurate and representative values were obtained. The measured porosities of the aluminum foams were $89.70\% \pm 1.64$ for the 100 μm foam, $85.20\% \pm 1.77$ for the 50 μm foam, $76.10\% \pm 0.28$ for the 1 μm foam, and $81.50\% \pm 3.60$ for the Mix foam. The predicted porosity based on the volume ratio of aluminum to NaCl (1:5) was 83.3%. The 100 μm and 50 μm foams showed higher porosities than predicted, while the 1 μm and Mix foams showed lower porosities. In the 100 μm foam, collapsed areas were recognized as pores, resulting in a higher than predicted porosity. For 50 μm foam, all NaCl was removed, but the porosity was higher than the predicted porosity due to internal pores identified by the relative density after sintering. The Mix foam, despite a relative density similar to the 50 μm foam, retained some NaCl, lowering its porosity. The 1 μm foam exhibited the lowest porosity due to both its high relative density and is retained some NaCl. The average pore sizes obtained from micro-CT were $315.01 \pm 10.615 \mu\text{m}$ for 100 μm

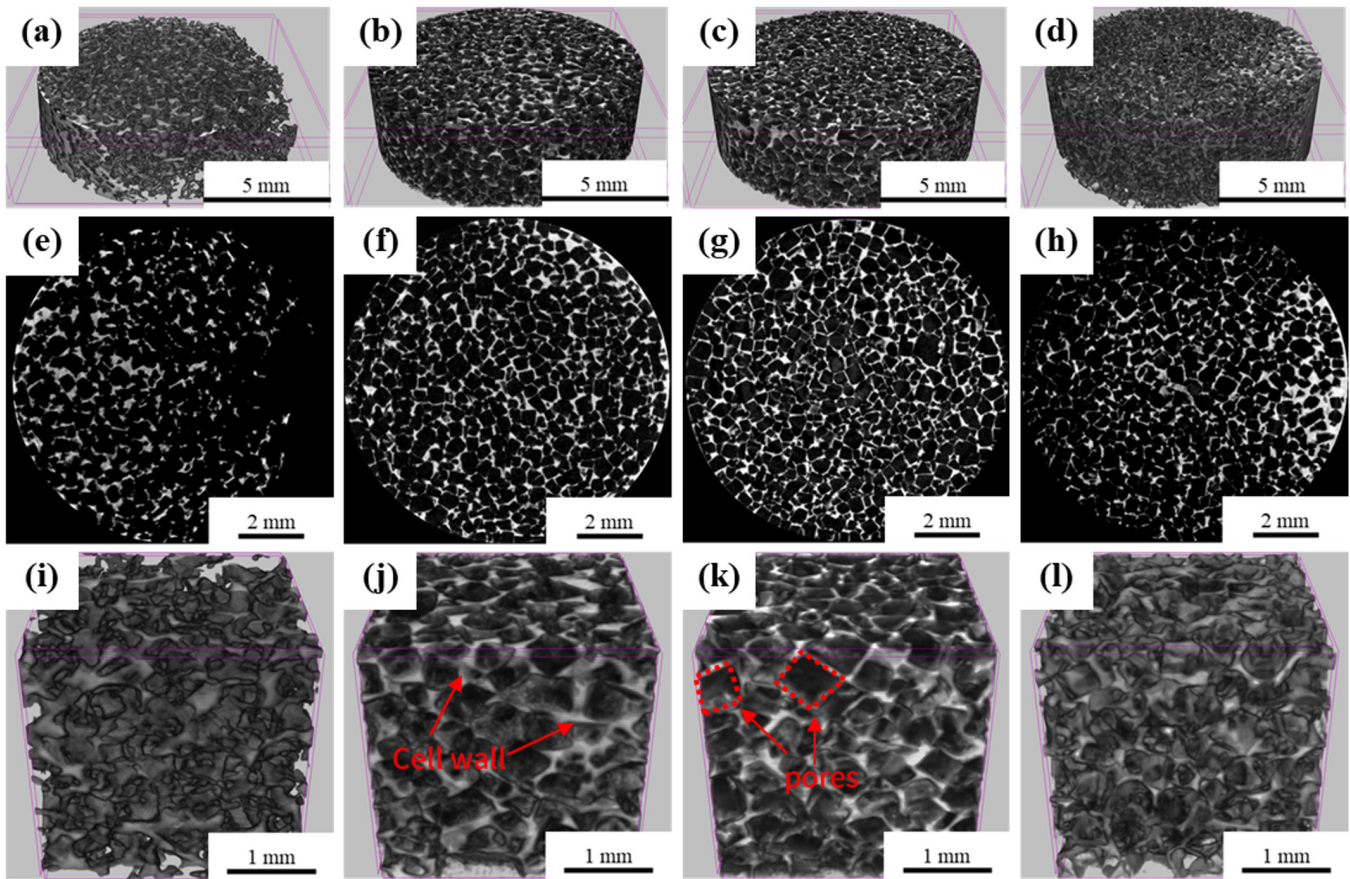


Fig. 6. Micro-computed tomography visualization of aluminum foams fabricated with different powder sizes: [(a)–(d)] 3D models, [(e)–(h)] 2D cross-sectional images, [(i)–(l)] 3D cropped images, [(a), (e), (i)] 100 μm foam, [(b), (f), (j)] 50 μm foam, [(c), (g), (k)] 1 μm foam, and [(d), (h), (l)] Mix foam.

foam, $291.37 \pm 9.954 \mu\text{m}$ for 50 μm foam, $262.34 \pm 9.866 \mu\text{m}$ for 1 μm foam, and $290.85 \pm 10.373 \mu\text{m}$ for Mix foam. In all cases, the pore sizes were smaller than the original NaCl particle size (500 μm), primarily due to deformation under pressure during sintering, partial destruction of cell walls during NaCl removal, and additional pores formed during sintering. SEM analysis confirmed that pore size decreases with decreasing aluminum powder size, consistent with the micro-CT results. The measured cell wall thicknesses were $104.45 \pm 4.363 \mu\text{m}$ for 100 μm foam, $92.06 \pm 4.094 \mu\text{m}$ for 50 μm foam, $71.51 \pm 3.085 \mu\text{m}$ for 1 μm foam, and $91.26 \pm 4.144 \mu\text{m}$ for Mix foam. Cell wall thickness is affected by both the number and size of aluminum powders, as well as the degree of densification during sintering. Smaller powders result in larger surface areas, which accelerate neck formation and enhance densification, thereby reducing cell wall thickness. SEM images supported this trend, showing blurred boundaries and smoother surface as the powder size decreased. In summary, as the aluminum powder size decreases,

pore size, porosity, pore size, and cell wall thickness all decrease, reflecting enhanced densification and sintering behavior, as confirmed by both SEM and micro-CT analysis.

3.3 Compression Test

Fig. 7. a–d shows the compression test curves of the aluminum foams. The stress-strain behavior of aluminum foam under compression can be divided into three regions: the elastic region, the plateau region, and the densification region [21, 37]. Region 1 corresponds to the elastic region, which is characterized by a linear elastic region with very low strain. Region 2 is the plateau region, where the pores collapse occurs and strain increases with little to no increase in stress. In this region, both the 1 μm foam and Mix foam exhibit noticeable fluctuations, which are attributed to the presence of unremoved NaCl particles. The residual NaCl induced localized fracture during compression, resulting in fluctuations in the curve. The 1 μm foam exhibits greater fluctuations than the Mix foam, indicating a

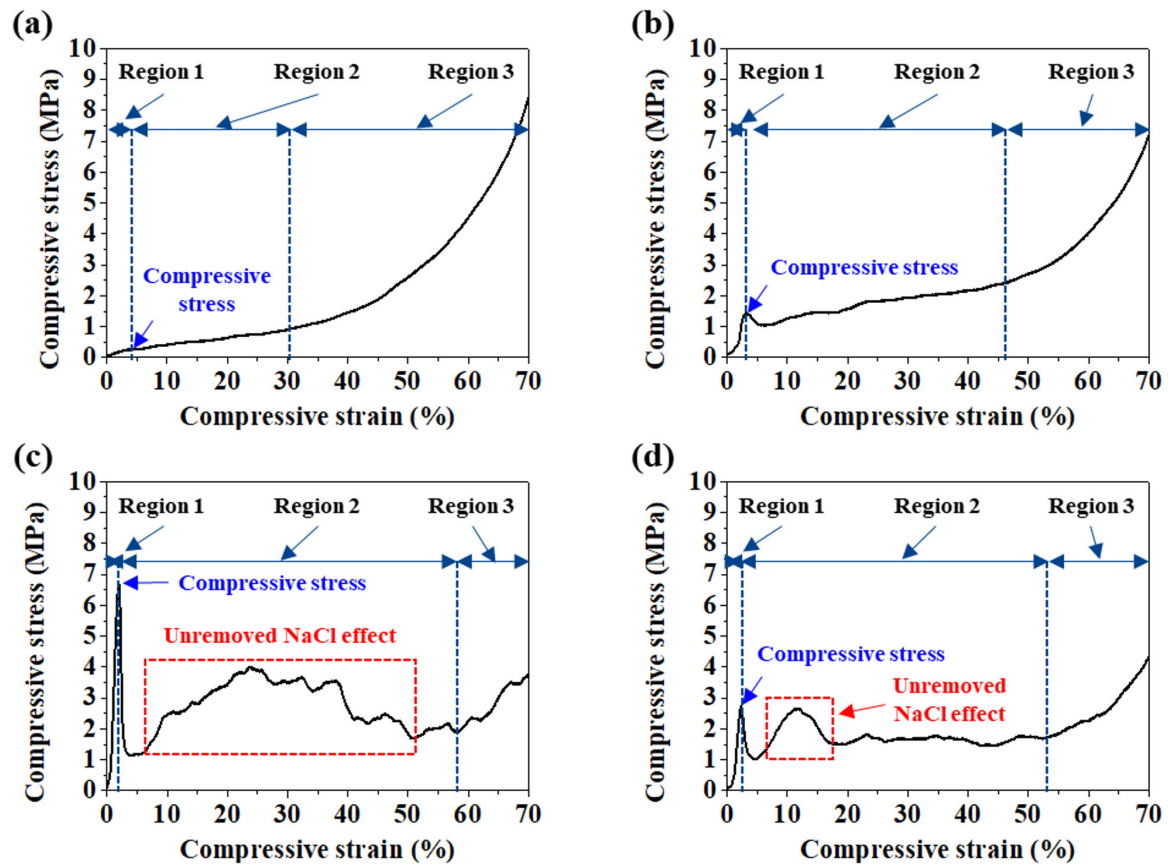


Fig. 7. Stress–strain curves of aluminum foams fabricated with different powder sizes: (a) 100 μm foam, (b) 50 μm foam, (c) 1 μm foam, (d) Mix foam.

larger amount of residual NaCl. Region 3 is the densification region, where the previously collapsed pores are compacted, leading to a rapid increase in compressive stress. The compressive strength was determined as the average of the maximum values in region 1, and the Young's modulus was calculated from the slope of the stress–strain curve in region 1 just before reaching the compressive strength [38]. The measured compressive strengths and Young's modulus of the foams were 0.523 ± 0.198 MPa and 0.023 ± 0.0036 GPa for 100 μm foam, 1.386 ± 0.099 MPa and 0.735 ± 0.184 GPa for 50 μm foam, 5.804 ± 0.822 MPa and 3.841 ± 0.917 GPa for 1 μm foam, and 2.419 ± 0.297 MPa and 1.761 ± 0.290 GPa for Mix foam. As the aluminum powder size decreases, the compressive strength increases. Notable, the Mix foam exhibits a higher compressive strength than the 50 μm foam, indicating a synergistic effect from combining fine and coarse powders. This enhancement is likely attributed to improved particle packing, where fine powders fill the voids between coarse powders, resulting in better interparticle contact and more uniform pore wall formation

during sintering. Therefore, the mixed powder approach provides an effective strategy to enhance mechanical performance while maintaining microstructural stability. The compressive strength of aluminum foam is influenced by several factors, including porosity, pore size, and cell wall thickness, as reported in previous studies [4, 39–41].

Fig. 8. a–d shows the relationships between aluminum powder size and four key parameters: porosity, pore size, cell thickness, and compressive strength. As the aluminum powder size decreases, the porosity, pore size, and cell wall thickness also decrease, whereas compressive strength increases. To evaluate the effects of these parameters on compressive strength, predictive equations were employed. Based on the classical and widely accepted Gibson–Ashby model, the relationship between porosity and strength was formulated using an exponential or powder–law function. The remaining variables — pore size, cell wall thickness, and powder size — were incorporated according to their physical relevance, as represented in Eq. (3). Regression analysis using the Ordinary Least Squares (OLS)

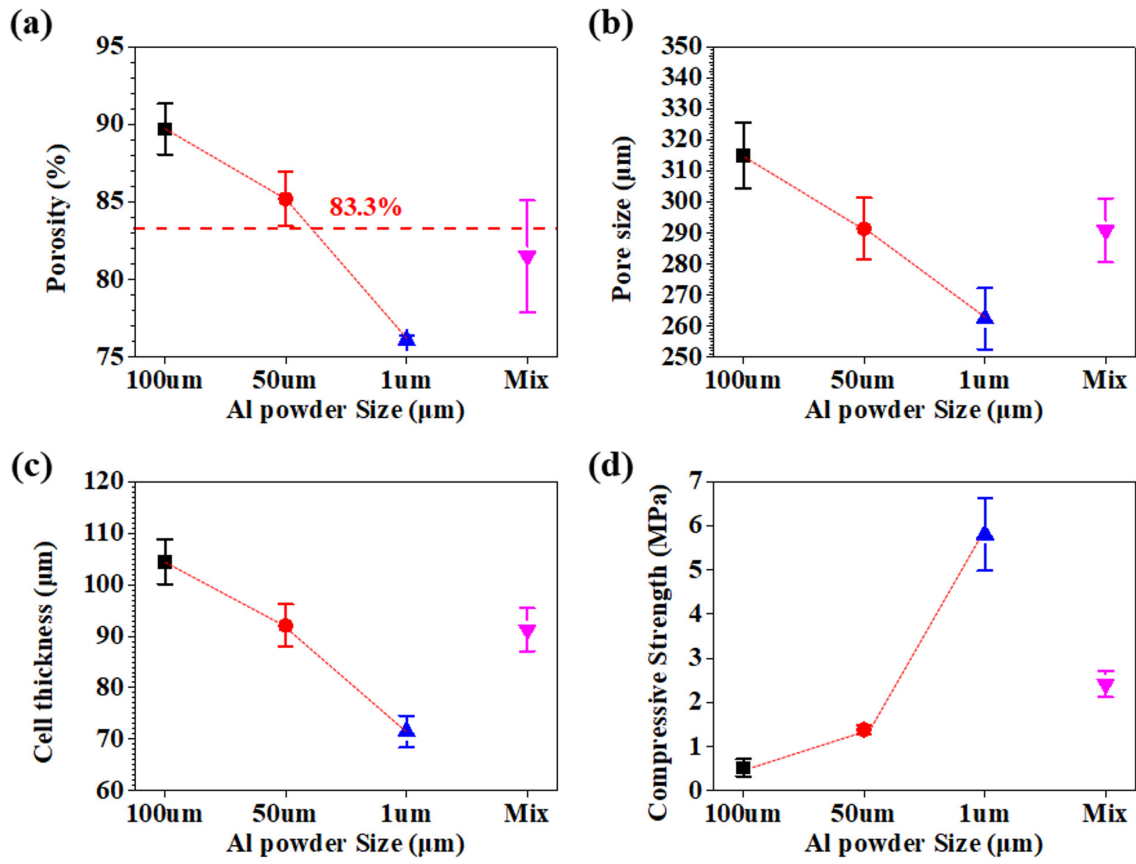


Fig. 8. Effect of aluminum powder size on the structural and mechanical properties of aluminum foams: (a) porosity, (b) pore size, (c) cell thickness, and (d) compressive strength.

method conducted to calibrate the coefficients A , n , α , and β in Equation 3 based on the experimental data. These coefficients quantitatively describe the influence of each variable on compressive strength. The results of the regression analysis indicate that strength increases with lower porosity, thicker cell walls, smaller powder size, and smaller pore size. Among these, porosity has the most significant influence, followed by pore size, with cell wall thickness and powder size exhibit relatively minor effects. In addition to its direct influence, aluminum powder size indirectly affects strength by altering microstructural features such as porosity, pore size, and cell thickness. Therefore, mechanical properties of the foam can be effectively controlled by tuning the relative size of aluminum powder to NaCl in the space-holder method. This approach can be extended to a wide range of metallic materials, not limited to aluminum, offering a flexible and scalable strategy for optimizing the mechanical performance of metal foams.

$$\sigma_c \approx A \cdot \left(1 - P\right)^n \cdot \left(\frac{t}{d_p}\right)^\alpha \cdot \left(\frac{1}{d_{po}}\right)^\beta \quad (3)$$

σ_c : predicted compressive strength of the foam (MPa), A : 3390 (constant)

P : $\frac{\text{porosity (\%)}}{100}$, d_p : powder size (μm), t : cell thickness (μm), d_{po} : pore size (μm)

n , α , β : indexes estimated by regression based on experimental data

$n = 2.50$, $\alpha = 0.05$, $\beta = 0.54$

The compressive strengths calculated using Eq. (3) were compared with the experimental results presented in Table 2. For the 100 μm foam, the calculated strength was 0.518 MPa, while the experimental value was 0.523 MPa, resulting in an error of 0.96%. For the 50 μm foam, the calculated strength was 1.376 MPa, while the experimental value was 1.386 MPa, resulting in an error of 0.72%. For the 1 μm foam, the calculated strength was 5.788 MPa, while the experimental value was

Table 1. Comparison of densities and NaCl removal rate of aluminum foams with varying aluminum powder sizes

	100 μm foam	50 μm foam	1 μm foam	Mix foam
Experiment density (g/cm^3)	2.15	2.15	2.2	2.15
Theoretical density (g/cm^3)			2.25	
Relative density (%)	95.6	95.8	97.6	95.7
NaCl removal rate (%)	X	100	95.24	96.27

100 μm foam: foam fabricated using 100 μm aluminum powder. 50 μm foam: foam fabricated using 50 μm aluminum powder. 1 μm foam: foam fabricated using 1 μm aluminum powder. Mix foam: foam fabricated by mixing 100 μm aluminum powder with 1 μm aluminum powder.

Table 2. Comparison of porosity, pore size, cell thickness, and compressive strength of foams with different aluminum powder sizes

	100 μm foam	50 μm foam	1 μm foam	Mix foam
Porosity (%)	89.70 ± 1.64	85.20 ± 1.77	76.10 ± 0.28	81.50 ± 3.60
Pore size (μm)	315.04 ± 10.612	291.37 ± 9.954	262.34 ± 9.866	290.85 ± 10.373
Cell thickness (μm)	104.45 ± 4.363	92.06 ± 4.094	71.51 ± 3.085	91.26 ± 4.144
Compressive strength (MPa)	0.523 ± 0.198	1.386 ± 0.099	5.804 ± 0.822	2.419 ± 0.297
Young's modulus (GPa)	0.023 ± 0.0036	0.735 ± 0.184	3.841 ± 0.917	1.761 ± 0.290

100 μm foam: foam fabricated using 100 μm aluminum powder. 50 μm foam: foam fabricated using 50 μm aluminum powder. 1 μm foam: foam fabricated using 1 μm aluminum powder. Mix foam: foam fabricated by mixing 100 μm aluminum powder with 1 μm aluminum powder.

5.804 MPa, resulting in an error of 0.28%. For the Mix foam, the calculated strength was 2.403 MPa, while the experimental value was 2.419 MPa, resulting in an error of 0.66%. With relative errors ranging from 0.28% to 0.96%, the predicted values are in good agreement with the experimental results, supporting the applicability of Eq. (3) for modeling compressive behavior in open-cell aluminum foams.

4. Conclusion

In this study, the effects of porosity, pore size, and cell wall thickness on mechanical properties of aluminum foams were investigated in relation to aluminum powder size and powder mixing, using NaCl as a space-holder.

1. Densification, structural integrity, and NaCl removal efficiency were compared as a function of aluminum powder size. As the powder size decreased, the relative density increased, indicating enhanced densification. Conversely, larger aluminum powders exhibited lower structural integrity due to insufficient sintering. However, a decrease in powder size also resulted in NaCl removal rate, attributed to the increased densification, which hinders diffusion pathways.

2. SEM analysis was conducted to compare the pore structures and cell walls with different aluminum powder sizes. Three types of pores were identified: (1) pore formed by the removal of NaCl, (2) pores generated by the destruction of cell walls during the NaCl removal, and (3) pores originating from

interparticle voids during sintering. Pore size was found to decrease with decreasing aluminum powder size. Cell wall morphology also varied with powder size: clear boundaries between particles were observed in the 100 μm and 50 μm foams, while blurred boundaries and smoother surfaces appeared in the 1 μm foam. These results suggest that smaller powders increase surface area, and enhance neck formation during sintering, promoting densification.

3. Micro-CT analysis was used to quantitatively assess porosity, pore size, and cell wall thickness. All three parameters decreased as the aluminum powder size decreased. These trends were consistent with SEM observations and are influenced by factors such as densification, NaCl removal rate, interparticle voids, and pressure-induced NaCl deformation. The results align well with relative density measurements and visual evaluations of structural integrity.

4. Compression testing was performed to evaluate mechanical properties across the different foams. The stress-strain curves revealed three characteristic regions. In the plateau region (Region 2) fluctuations were observed in the 1 μm and Mix foams due to incomplete NaCl removal, with more pronounced fluctuations in the 1 μm foam. Compressive strength increased with decreasing aluminum powder size. A regression analysis was performed to determine the influence of each microstructural parameter on strength. The results showed that strength increases with decreasing porosity, decreasing pore size, decreasing powder size, and increasing cell wall thickness.

Among these, porosity had the most significant effect, followed by pore size, with cell wall thickness and powder size exhibit relatively minor effects.

This study demonstrates that aluminum powder size plays a critical role in determining the microstructure and mechanical performance of aluminum foams. By optimizing powder size and mixing strategies, the mechanical properties of aluminum foams can be significantly improved. Moreover, the finding and methodology of this study can be extended to a wide range of metals and alloys beyond aluminum.

Funding

This work was supported by the Agency for Defense Development of the Korean Government (UI230016TD).

Conflict of Interest

The corresponding author (Prof. Seok-Jae-Lee) currently serves on the editorial board of JPM, but was not involved in any part of the publication process. Other than this, the authors declare that they have no relevant potential conflicts of interest.

Data Availability Statement

Data will be made available on request.

Author Information and Contribution

Seunghyeok Choi: PhD candidate; writing—original draft.

Sungjin Kim: PhD candidate; experiment.

Tae-Young Ahn: Senior Researcher; formal analysis.

Yu-Song Choi: Principal Researcher; formal analysis.

Jae-Gil Jung: Professor; investigation.

Seung Bae Son: Research Professor; writing-review & editing, supervision.

Seok-Jae Lee: Professor; writing-review & editing, funding acquisition, supervision.

Acknowledgments

None.

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LPBF 공정으로 적층제조된 Ti-6Al-4V 합금 조형체의 서포트 형상에 따른 잔류응력 분포

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Effect of Support Structure on Residual Stress Distribution in Ti-6Al-4V Alloy Fabricated by Laser Powder Bed Fusion

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Ti-6Al-4V alloy is widely utilized in aerospace and medical sectors due to its high specific strength, corrosion resistance, and biocompatibility. However, its low machinability makes it difficult to manufacture complex-shaped products. Advancements in additive manufacturing have focused on producing high-performance, complex components using the laser powder bed fusion (LPBF) process, which is a specialized technique for customized geometries. The LPBF process exposes materials to extreme thermal conditions and rapid cooling rates, leading to residual stresses within the parts. These stresses are intensified by variations in the thermal history across regions of the component. These variations result in differences in microstructure and mechanical properties, causing distortion. Although support structure design has been researched to minimize residual stress, few studies have conducted quantitative analyses of stress variations due to different support designs. This study investigated changes in the residual stress and mechanical properties of Ti-6Al-4V alloy fabricated using LPBF, focusing on support structure design.

Keywords: Laser powder bed fusion; Ti-6Al-4V alloy; Residual stress; Contour method; Support design

Received: April 5, 2025

Revised: May 19, 2025

Accepted: June 12, 2025

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1. Introduction

레이저 분말 베드 용융(Laser powder bed fusion, LPBF) 공정

은 대표적인 금속 적층 제조(additive manufacturing, AM) 공정 중 하나로, 고에너지 레이저를 이용해 금속 분말을 선택적으로 용융하여 한층씩 적층하는 방식으로 기존 공법으로는 구현하기 어려운 복잡한 형상의 부품을 한번에 제조할 수 있는 공정기술이다[1-5]. 이러한 공정 특성으로 인해 LPBF 공정은 항공우주, 모빌리티, 의료산업 등 다양한 첨단산업 분야에서 널리 활용되고 있으며, 특

<https://doi.org/10.4150/jpm.2025.00087>

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히 형상 자유도가 높은 부품 설계가 가능하다는 점에서 경량화, 고강도, 고정밀 특성이 요구되는 맞춤형 다품종 부품 제작에 효과적으로 활용되어지고 있다[6-11].

한편, LPBF 공정 도중 특유의 가혹한 열환경과 높은 냉각속도 ($10^6 \sim 10^8$ K/s)로 인해 제도가 이루어지는 부품은 반복적인 열팽창 및 수축이 발생하며, 이 과정에서 필연적으로 부품 내부 과도한 잔류응력이 축적된다[12-14]. 이러한 잔류응력의 축적은 LPBF로 제조된 부품의 균열, 변형, 뒤틀림과 같은 품질 저하 문제를 초래할 수 있으며, 부품의 치수 정밀도 및 기계적 안정성을 저하하는 주요 원인으로 작용한다[15-17]. 이러한 LPBF 적용 소재의 잔류응력을 효과적으로 제어하기 위해서는 응력 축적을 완화할 수 있는 LPBF 공정조건의 최적화와 부품의 형상 설계 및 서포트 구조 설계 전략이 필수적이다[18-21]. 특히, LPBF로 제조되는 부품 내부 열 전달 경로를 제어하고 기계적 지지 역할을 수행하는 서포트 구조의 설계 최적화는 잔류응력 완화를 위한 핵심 요소로 작용한다[22-24].

본 연구에서는 LPBF 공정으로 적층 제조된 Ti-6Al-4V 합금 조형체의 서포트 형상에 따른 잔류응력 분포를 정량적으로 분석하였다. 이를 위해, 서포트 구조의 차이가 열 전달 및 냉각 속도에 미치는 영향을 고찰하고 잔류응력 완화와의 상관관계를 분석하였다. 본 연구 결과는 LPBF 기반 부품 제작 시 잔류응력을 최소화할 수 있는 최적의 서포트 구조 설계 방안을 도출하는 데 기여할 것으로 기대되며, 이를 통해 실제 산업에서 사용되는 중·대형 부품의 형상 안정성을 확보하고 적층 제조 공정의 품질 신뢰성을 향상시키는 데

활용될 수 있다[18].

2. Experimental

2.1. Ti-6Al-4V 분말

본 연구에서는 미국 AP&C社에서 가스 분무법(gas atomization)으로 제조된 구형의 Ti-6Al-4V Gr.5 분말이 활용되었다. Fig. 1(a)는 전계방출 주사전자현미경(field emission scanning electron microscopy, FE-SEM, JEOL, Japan)을 통해 촬영한 분말 SEM 이미지를 나타내며, 해당 결과와 같이 활용분말은 우수한 구형도를 나타냄을 확인할 수 있다. 본 분말에 대해 입도분석기 LA-960V2 (HORIBA, Japan)를 사용하여 분말 입도분포 분석을 진행하였으며, 그 결과는 Fig. 1(b)에 도시하였다. 분말 입도 분포 측정 결과 D₅, D₅₀, D₉₀은 각각 22.74 μ m, 32.47 μ m, 44.60 μ m 값을 나타내었으며 LPBF 공정에 적합한 입도분포를 나타냄을 확인할 수 있었다. 분말 유동도 측정을 위해 겉보기 밀도와 탭 밀도를 측정한 후 이를 기반으로 Hausner ratio값을 계산하였으며 Hall Flow-meter (Tokyo rikakikai, Japan)를 통해 흘 유동도를 특정하였다. Table 1은 활용분말의 유동도 값을 보여주며, 본 결과를 통해 해당 분말이 LPBF 공정에 적합한 유동도를 나타냄을 확인하였다[25].

2.2. LPBF 기반 조형체 제조

본 연구에서는 상용 LPBF 장비(M2, GE additive, U.S.A)를 활

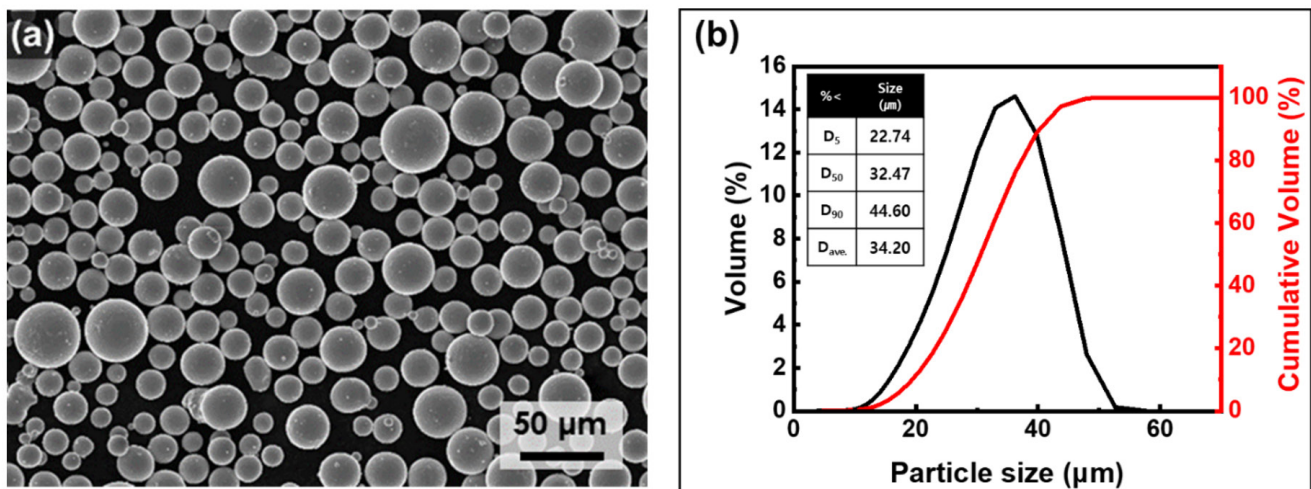


Fig. 1. (a) Scanning electron micrograph and (b) particle size distribution of the Ti-6Al-4V alloy powder.

Table 1. Physical properties of the Ti-6Al-4V alloy powder

Apparent density [g/cm ³]	Tap density [g/cm ³]	Flow rate [s/50g]	Hausner ratio
2.62 ± 0.02	2.83 ± 0.02	4.39 ± 0.16	1.08

용하여 적층을 진행하였고, 해당 분말에서 상대밀도 99 % 이상의 고밀도 조건을 획득할 수 있는 공정조건인 Laser power 300 W, Scan speed 1800 mm/s, Hatching space 100 μ m, Layer thickness 30 μ m 조건에서 Ar 분위기 하에 조형체 제조가 수행되었다[26]. Fig. 2(a)와 같이 스캔패턴은 지그재그 형태인 Meander 패턴으로 설정되었으며 층간 회전각은 소재 내부 이방성과 잔류응력을 최소화할 수 있는 67° 회전 조건으로 설정하였다[27]. 본 연구에서는 너비 72 mm, 높이 30 mm, 두께 4 mm인 직육면체 형상의 조형체를 제작하였으며 서포트 형상에 따른 잔류응력 차이를 명확하게 관측하기 위해 서포트 형상은 잔류응력의 영향을 많이 받는 구조인 트윈 캔틸레버 구조로 디자인하였다[22]. 또한, 서포트 홀(Hole) 크기에 따른 조형체 잔류응력 변화를 관측하기 위해, Fig. 2(b)와 같이 서포트 홀 크기가 각각 4 mm 및 2.75 mm인 2가지 타입(Type)의 조형체를 제조하였다.

2.3. 잔류응력 측정

잔류응력 측정은 크게 파괴적 방법과 비파괴적 방법으로 나뉘며, 본 연구에서는 Contour 법과 X-ray diffraction (XRD) 법을 활용하였다. 각 방법의 특징과 측정 절차는 다음과 같다.

(1) Contour 법

Contour 법은 시편을 절단한 후, 절단 과정에서 발생하는 내부 응력 풀림으로 인한 절단면 변형을 측정하고, 이를 유한요소 해석(finite element method, FEM)을 통해 절단 전 시편의 초기 응력을 역으로 계산하는 파괴적 방법이다[28]. 특히, 시편 절단 방식에 따라 잔류응력 분포가 달라질 수 있으며, 기판(substrate)의 유무가 이에 중요한 영향을 미치는 것으로 알려져 있다. 본 연구에서는 시편을 기판에 부착된 상태로 유지한 채 절단을 수행하였으며, 이는 기판이

조형체를 구속함으로써 절단 과정 중 발생할 수 있는 탄성 복원 및 응력 재분포를 억제하고, 적층 제조 중 형성된 본래의 잔류응력 분포를 보다 정확히 측정하기 위함이다. 실제로 기판 없이 절단할 경우, 부품의 자유 변형으로 인해 응력 분포가 왜곡될 수 있음이 기존 연구에서 보고된 바 있으며[29], 본 연구 또한 이러한 점을 고려하여 외부 변형을 최소화하고 보다 신뢰성 있는 내부 응력 측정을 수행하였다[30–32]. 잔류응력 측정은 Contour 법 전용 장비인 SPSM-10 (Fusion ENG, Korea) 장비를 사용하여 수행되었다. 시편 절단은 초저속 와이어 방전가공(wire electrical discharge machining, WEDM)으로 진행되었으며, 절단면의 변형은 정밀 레이저를 이용해 측정하였다. 측정된 데이터는 Contour Transform Program을 이용한 유한요소법으로 분석되었으며, Contour FEM 시뮬레이션 프로그램을 활용해 시편 내부의 잔류응력을 예측하였다.

(2) XRD 법

XRD 법은 다결정체 표면에 X선을 입사하여 브래그 법칙에 따라 X선 회절 각도와 격자 면간격 변화를 분석하여 잔류응력을 계산하는 방식이다[33]. 이 방법은 재료의 손상을 유발하지 않으므로 비파괴적 방법에 속하며, 표면 잔류응력 측정에 용이하다. 본 연구에서는 Xstress3000 G3 (Stresstech, Finland) 장비를 사용하여 잔류응력 측정을 수행하였으며, Ti tube를 이용해 데이터를 수집하였다. 측정의 신뢰도를 높이고 표면 잔류응력 측정의 정확도를 확보하기 위해, 시편의 거칠기를 줄이며 산화층을 제거하는 표면 처리를 진행하였다. 표면처리는 2000 grit 폴리싱 후, Voltage 50 V, Flow rate 12, Time 5 s 조건으로 전해연마를 수행하였다. 전해연마 용액은 과염소산(HClO_4) 60 ml, 메탄올(CH_3OH) 600 ml, 2-부톡시 에탄올($\text{C}_6\text{H}_{14}\text{O}_2$) 360 ml를 혼합한 용액을 사용하였다. XRD 법 측정은 결과 데이터를 mapping 방식으로 표현하기 위해

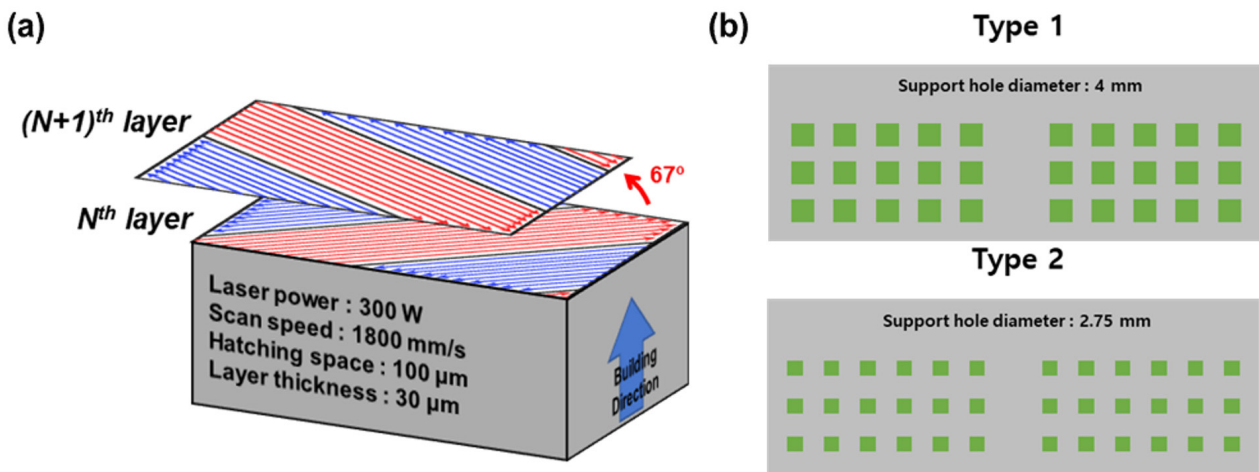


Fig. 2. (a) Scanning strategy of the LPBF process and (b) the schematics of support design for the present samples.

측정 지점이 겹치지 않도록 0.3 ϕ tip을 사용하여 0.3 mm 간격으로 전체 영역을 스캔하였다. 정확한 분석을 위해 tile angles는 -45° 에서 $+45^\circ$ 까지 설정하였고, 각 포인트는 +방향과 -방향으로 총 5회 측정하였다. exposure time은 16초로 설정하였으며, 측정방법은 ASTM E2860-20 규격을 준수하였다[34].

Fig. 3는 LPBF 공정을 통해 제조된 조형체의 위치 별 잔류응력 측정법을 나타낸 모식도이다. 본 연구에서는 조형체의 X Plane은 XRD 법, Y-Z Plane은 Contour 법을 활용해 잔류응력 분포를 분석하였으며, 두 가지 측정 기법을 조합하여 조형체 내에서 위치별 잔류응력 분포 및 경향성을 보다 정밀하게 분석하였다.

2.4. 열전도도 측정

서포트 홀 크기에 따른 기판과의 열전달 차이를 실험적으로 검증하기 위해, 시편 Type별로 열전도도 측정 실험을 수행하였다. 열확산계수 측정을 위해 적층제조된 시편에서 샘플을 가공한 위치와

측정 샘플의 이미지를 Fig. 4에 도시하였다. 열확산계수는 LFA 467 HyperFlash (NETZSCH, Germany)장비를 활용하여 측정하였으며, Fig. 4(a)에서 보이는 것과 같이 시편의 중앙부에서 가공한 10 mm \times 10 mm \times 1.5 mm (길이 \times 너비 \times 두께)크기의 샘플로 수행되었다. 열전도도 측정에 사용한 실제 샘플은 Fig. 4(b)에 나타내었으며, ASTM E1461규격에 따라 laser flash analysis 법을 사용하여 측정하였다. 측정된 열확산계수와 밀도, 비열을 이용하여 열전도도를 계산하였으며, 다음 식(1)에 따라 산출하였다[35, 36].

$$k = \alpha \cdot \rho \cdot C_p \quad (1)$$

3. Results and Discussion

3.1. 육안 검사

Fig. 5는 LPBF 공정으로 적층제조된 직육면체 조형체의 외형 결

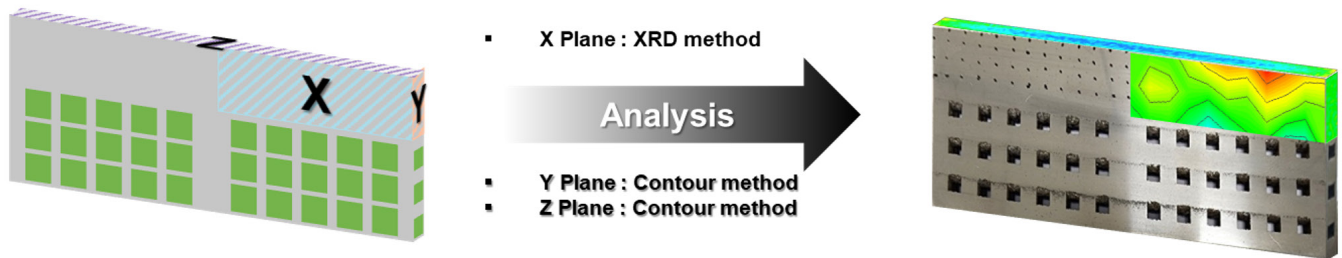


Fig. 3. Measurement positions of residual stress in the LPBF-processed samples.

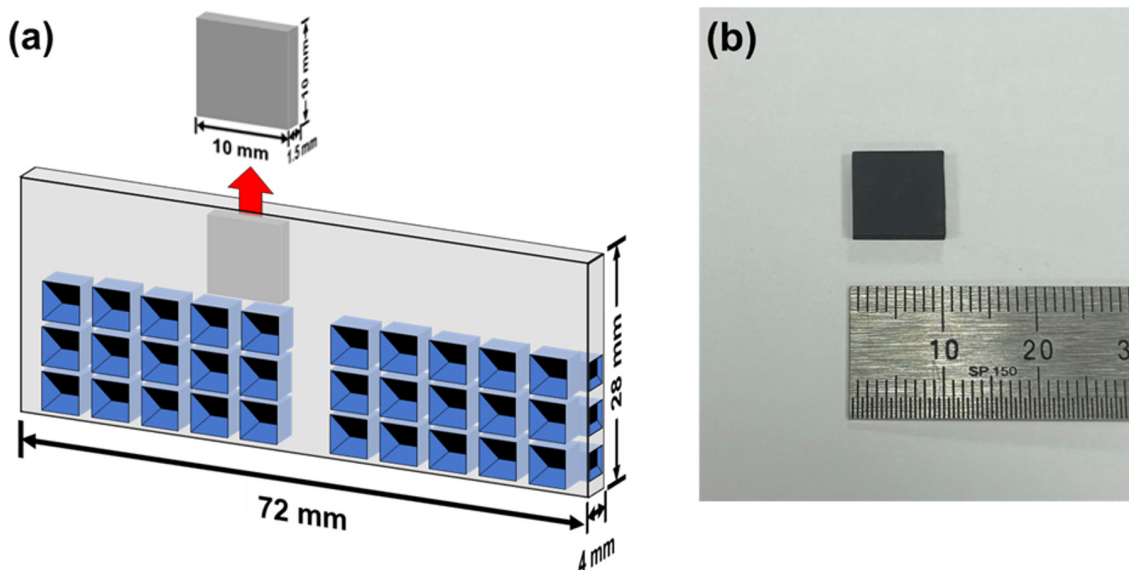


Fig. 4. (a) Schematic diagram of specimen extraction for thermal conductivity measurements from a sample, and (b) a photograph of a specimen.

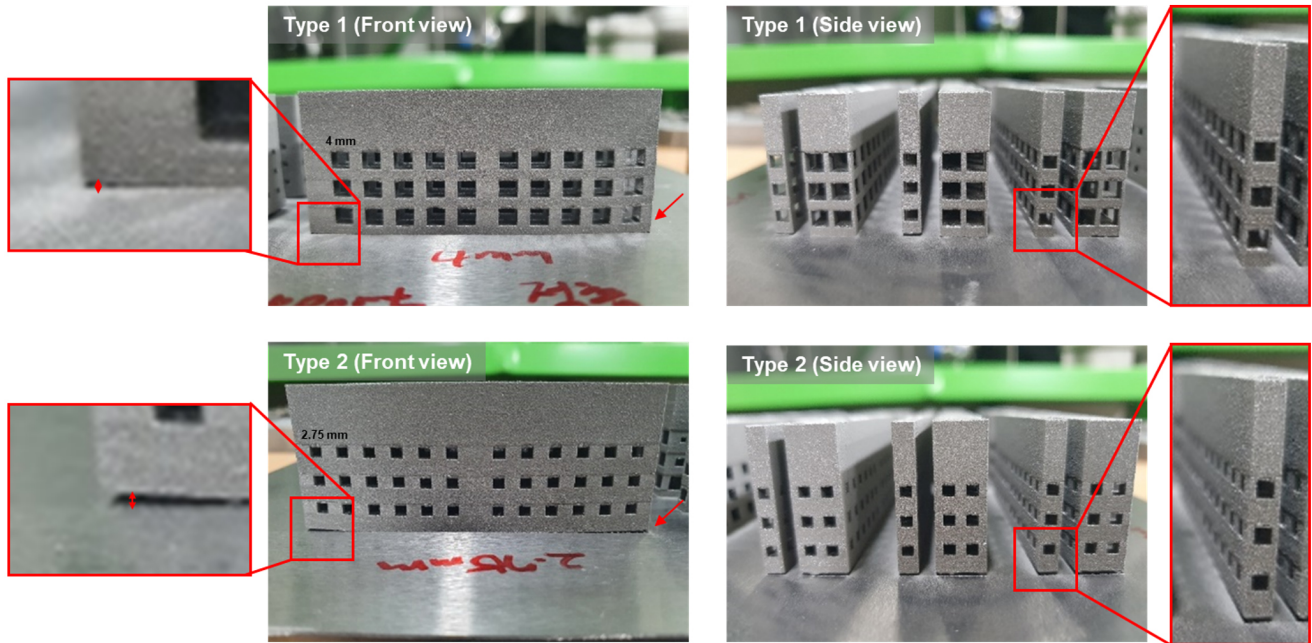


Fig. 5. Optical photographs of the double-cantilever-structured samples manufactured by LPBF.

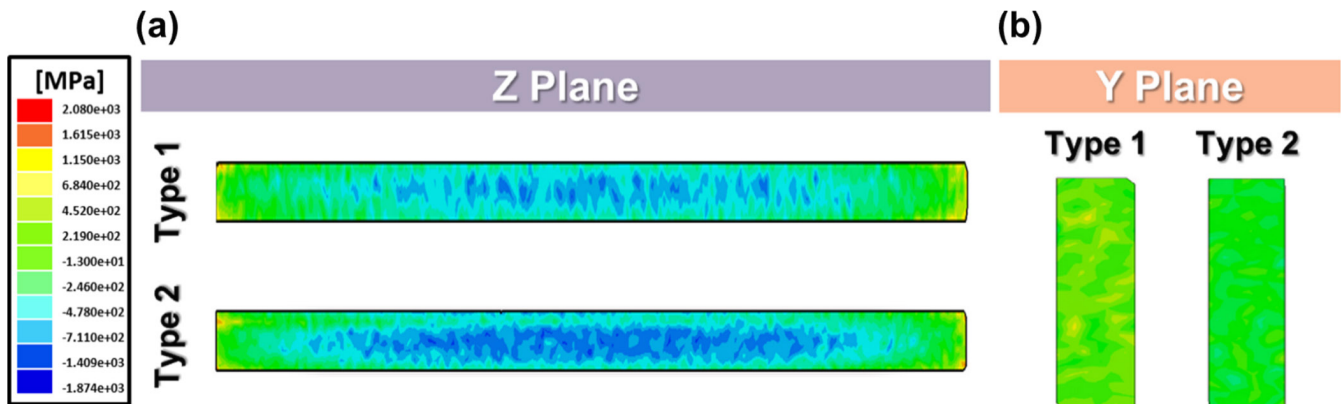


Fig. 6. Residual stress distribution measured using the contour method on the (a) Z and (b) Y planes of the type 1 and 2 samples.

과를 나타낸 것으로, 조형체의 길이방향(X축) 끝하단부에서 기판으로부터 들려 올려지는 형태인 *Warping* 현상이 관찰되었다. 일반적으로, 서포트 홀의 크기가 작을수록 기판과의 접촉 면적이 증가하여 더욱 견고한 구조의 적층 결과가 예상되나, 본 실험 결과는 예측과 상반된 경향을 보였다. 실제 적층 결과에서는 Type 1 시편 대비 서포트 홀 크기가 작은 Type 2 시편에서 더 극심한 *Warping* 현상이 나타나는 것을 확인할 수 있었다.

Fig. 6은 Contour 법을 활용하여 조형체의 Z Plane 및 Y Plane 영역에서 측정된 잔류응력 분포 결과를 나타낸 것이다. Fig. 6(a)를 통해, 시편의 중앙부에는 압축 잔류응력이, 가장자리에는 인장 잔류응력이 분포하는 전형적인 LPBF 공정의 응력 분포 양상을 확인할

수 있다[29]. 또한, 서포트 형상에 따른 영향을 비교해보면 서포트 홀 크기가 작은 Type 2 시편에서 Type 1 시편 대비 더 큰 인장 및 압축 잔류응력이 나타나는 경향을 보였다. Fig. 6(b)는 Y Plane에서의 잔류응력 분포를 나타낸 것으로, 두 Type 시편들 간의 유의미한 차이는 나타나지 않았다. 전체적으로 시편 내 위치에 따른 잔류응력 값의 편차가 크지 않았으며, 서포트 형상에 따른 잔류응력 영향도 미미한 것으로 분석되었다. 이러한 결과는 조형체의 길이 방향(X 방향)으로는 *Warping* 현상이 발생하는 반면, 두께 방향(Y 방향)으로는 형상 뒤틀림이 거의 나타나지 않는 경향과 일치한다. 또한, 서포트 홀 크기가 작아질수록 기판과의 접촉 면적 증가로 인해 열이 보다 빠르게 기판으로 전달되어 냉각 속도가 증가하고, 이에

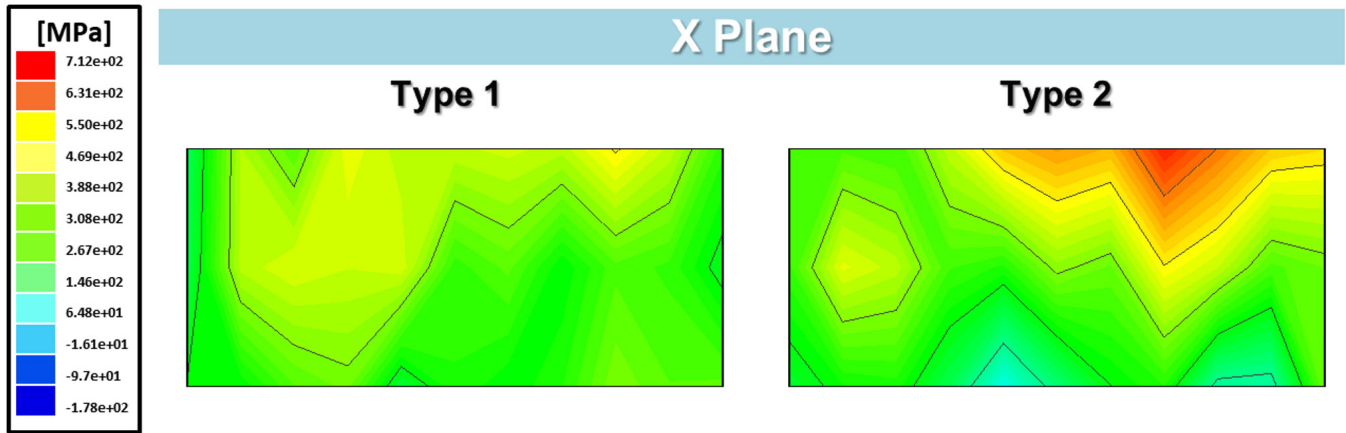


Fig. 7. Results of X-ray diffraction for the X-plane of the samples of types 1 and 2.

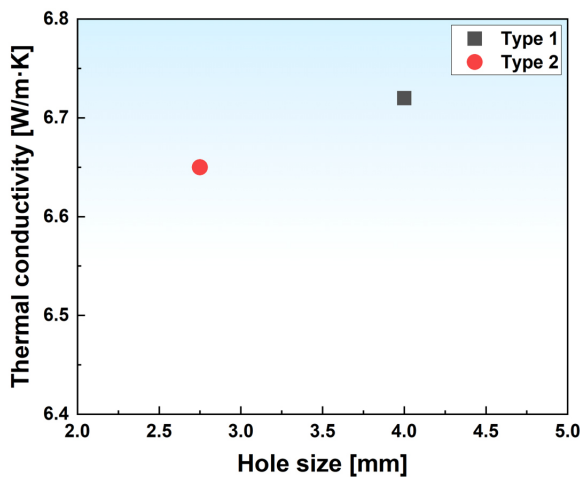


Fig. 8. Results of thermal conductivity measurements of types 1 and 2.

따라 국부적으로 더 높은 잔류응력이 축적되는 경향을 보이는 것으로 유추할 수 있다.

Fig. 7은 적층 제조된 Ti-6Al-4V 합금 조형체의 X Plane에 대해 XRD 법을 활용하여 측정된 잔류응력 분포를 시각화한 결과이다. 해당 결과에서는 시편의 하단부에는 전반적으로 압축 잔류응력이 분포하고 상단부에는 인장 잔류응력이 분포하는 경향을 보여준다. 특히, Type 1 시편 대비 Type 2 시편에서 압축 잔류응력과 인장 잔류응력의 대비가 더욱 극심하며, 이는 Fig. 6의 분석 결과와 대응된다. 이러한 압축/인장 잔류응력 분포는 조형체의 길이 방향 끝단에서 관찰되는 Warping 현상과 밀접하게 연관되어 있다. 한편, 본 연구에 적용된 XRD 법은 표면 근처의 잔류응력을 정밀하게 측정하는데 적합하지만, 적층 부품 내부에서 두께 방향으로 존재할 수 있는 잔류응력 구배를 고려하기에는 한계가 있다. 따라서 본 연

구에서는 서로 다른 서포트 구조에 따른 상대적인 잔류응력 분포 경향 비교에 초점을 맞추었으며, 향후 연구에서는 부품 전체의 3차원 잔류응력 분포를 보다 정량적으로 분석할 예정이다[16, 31, 33].

Fig. 8은 열전도도 측정 결과이다. Type 1 시편은 6.72 W/m·K, Type 2 시편은 6.65 W/m·K 으로 소폭의 차이를 보였으며, 서포트 홀 크기가 작은 Type 2 시편에서 더 낮은 열전도도를 나타내는 경향을 확인할 수 있었다. Type 2 시편에서는 공정 도중 축적된 높은 잔류응력으로 인해 고밀도의 전위 구조가 형성되어 결정 격자 내 열전달 경로를 방해함으로써 열전도도를 저하시키는 것으로 해석된다. 따라서, 서포트 형상이 기판과의 면적을 증가시켜 열전달 경로를 확장시키는 구조라 하더라도, 그로 인해 발생하는 높은 잔류응력 및 전위 밀도와 같은 미세조직적 요인이 열전도도 저하를 유발할 수 있음을 본 결과는 실험적으로 뒷받침하고 있다[37, 38].

Fig. 9은 LPBF 공정 중 잔류응력 형성 메커니즘을 개략적으로 나타낸 모식도이다. LPBF 공정에서는 고에너지 레이저가 금속 분말을 국부적으로 용융시키며 용융풀(melt pool)을 형성하고, 해당 용융풀 내부의 용융잠열(latent heat)이 방사형으로 빠르게 빠져나간다[17, 39]. 이 과정에서 조형체 상·하부 간의 급격한 온도 구배가 형성되어 잔류 열응력이 축적된다. 레이저가 조사되는 영역에서는 급격한 국부 가열로 인해 열팽창 변형이 발생하지만, 주변 소재가 이를 구속하면서 내부에는 압축응력이, 표면 근처에는 상대적으로 인장 응력이 유도된다. 이후 용융풀이 응고되고 냉각이 진행됨에 따라, 응고된 재료는 수축하려 하지만 하부층이나 기판에 의해 수축이 제한되어, 표면에는 인장 응력이, 하부에는 압축 응력이 잔류하게 된다[40]. 이처럼 인장/압축 응력이 반복적인 열사이클을 통해 누적되면서, 부품 내에 높은 수준의 잔류응력이 축적되고, 이는 최종적으로 Warping이나 Distortion과 같은 치수 정밀도 저하 등의 문제로 이어질 수 있다.

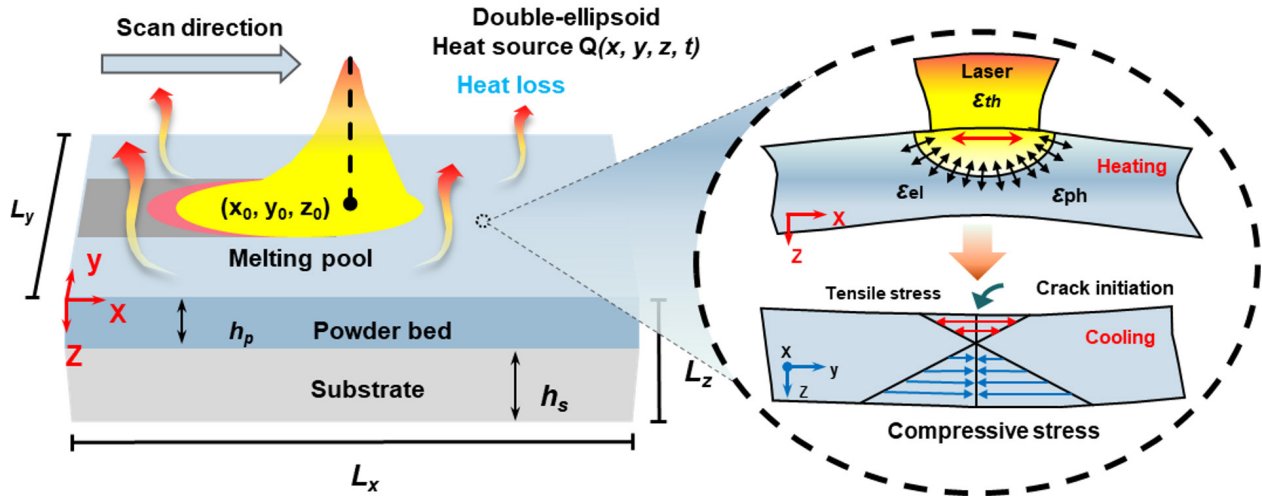


Fig. 9. Schematic illustration of Thermo-mechanical behavior during the laser powder bed fusion process.

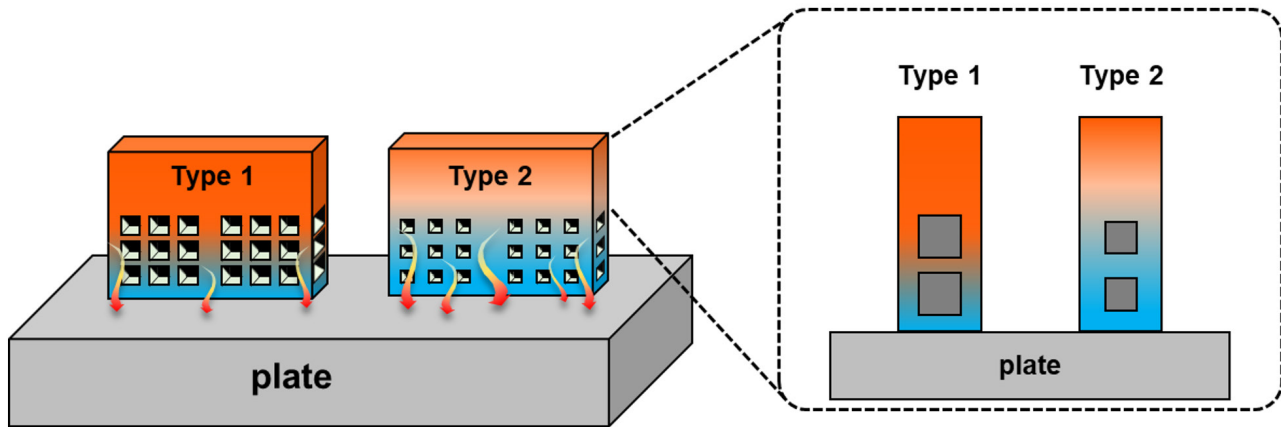


Fig. 10. A schematic of thermal transport according to the support structure design.

Fig. 10은 서포트 형상에 따른 열 전달 및 냉각 속도 차이를 설명한 모식도로, 서포트 구조가 잔류응력 형성에 미치는 영향을 시각적으로 나타낸 것이다. 서포트 구조의 형상은 조형체의 냉각 속도와 이에 따른 잔류응력 축적에 직접적인 영향을 미친다. LPBF 공정 도중 조형체에는 반복적인 레이저 조사가 이루어진다. 즉, 한 분말 층에서 레이저가 하나의 pass를 따라 조사된 후, 핫칭 간격만큼 떨어진 인접 구간에서 다시 한번 레이저가 조사됨에 따라 기존에 응고된 영역은 일부 재용융이 일어나거나 지속적으로 열 영향을 받게 된다. LPBF로 제조되는 조형체는 공정 도중 지속적인 입열이 가해지게 되고, 선행문헌에서는 해당 양상이 In-situ annealing 및 In-situ tempering 환경에 놓이는 것으로 묘사된다[41-43]. Park et al. [43]은 같은 LPBF 공정조건으로 제조된 서로 다른 두께를 지닌 Ti-6Al-4V 조형체의 미세조직과 기계적 물성을 분석하였으며, 두꺼운 두께의 시편일수록 LPBF 공정 도중 레이저에 노출되는 횟

수가 더 많아짐에 따라 잔류 전위밀도가 감소됨을 분석한 바 있다. 또한, 잔류 열응력은 LPBF 공정 도중 조형체 내부의 온도구배가 높을수록 극심해짐에 따라, 기판의 온도를 높여 조형체 내부 온도구배와 냉각속도를 감소시켜 잔류 열응력을 감소시키는 연구가 다수 이루어진 바 있다[16, 20, 44-46].

Fig. 10과 같이 Type 1 시편은 서포트 홀의 크기가 Type 2 시편 대비 상대적으로 큼에 따라 조형체 내부에서 기판으로의 열흐름이 원활하지 않으며, 이는 조형체 내부 온도구배 및 냉각속도를 감소시켜 잔류응력을 완화시킬 수 있다. 즉, 공정 도중 축적된 열이 Type 1 시편 대비 높은 냉각속도로 빠져나가는 Type 2 시편에서 더욱 극심한 잔류 열응력이 발생하게 되며, 해당 양상은 조형체가 적층 도중 레이저 노출에 의한 입열이 반복될수록 더욱 뚜렷해진다. 이로 인해 Type 2 시편은 Type 1 시편 대비 시편 끝단부와 중앙부의 잔류응력 차이가 더욱 극심하게 되며 이는 Type 2 시편의

극심한 Warping 현상을 야기하게 된다(Fig. 3).

본 연구 결과, 서포트 구조의 형상은 LPBF 공정에서 부품 내 열 전달 및 냉각 특성에 영향을 미치는 중요한 변수이며, 서포트 설계를 통해 냉각 속도를 제어함으로써 잔류응력을 완화하고 형상 안정성을 확보하는 전략이 필요함을 시사하고 있다. 다만, 본 연구는 서포트 구조에 따른 열전달 특성을 기반으로 잔류응력 형성 경향을 고찰하였으나, 열전달 과정에서 발생하는 열응력 및 이에 따른 변형 거동을 함께 고려하지는 않았다. 보다 정밀한 해석을 위해 향후 연구에서는 유한요소해석(FEM) 기반 in-situ 실험을 통해, 열응력 및 변형 거동을 정량적으로 검증하고 보다 체계적인 분석을 수행할 예정이다[16].

4. Conclusion

본 연구에서는 LPBF 공정으로 적층 제조된 Ti-6Al-4V 합금 조형체의 서포트 형상에 따른 잔류응력 분포를 정량적으로 분석하였다. 잔류응력 측정은 Contour 법과 XRD 법을 활용하여 수행하였으며, 그 결과 Z Plane에서는 시편의 중앙부에 압축 응력이, 가장 자리에는 인장 응력이 분포하는 전형적인 LPBF 공정의 응력 형상 분포가 관찰되었다. X Plane에서는 조형체 상단부에는 인장 잔류응력이 인가되고 하단 중앙부에는 압축 잔류응력이 집중되는 경향을 확인하였고, 이는 조형체의 길이 방향(X축)을 따라 Warping 현상이 발생하고 두께 방향(Y축)에서는 상대적으로 형상 변형이 작게 나타나는 결과와 일치한다. 서포트 형상에 따른 영향도 명확히 나타났다. Type 1 시편은 서포트 홀 크기가 커 기판과의 접촉 면적이 상대적으로 작고, 열전달이 제한됨에 따라 냉각 속도가 낮아지는 경향을 보였다. 이에 따라 온도 구배가 완화되어 상대적으로 낮은 수준의 잔류응력이 축적되었다. 반면, Type 2 시편은 서포트 홀 크기가 작아 기판과의 열적 접촉이 증가하고, 열이 빠르게 방출되어 급속 냉각이 유도되었다. 이로 인해 더 큰 온도 구배가 형성되며 인장 및 압축 잔류응력이 크게 축적되었고, 이러한 차이는 실제 조형체의 형상 변형에도 영향을 미쳐 Type 2 시편에서 보다 심한 Warping 현상이 관찰되었다. 이는 시편 내 위치 별 응력 차이와 직접적으로 연관됨을 확인할 수 있었다. 본 연구는 서포트 구조의 형상이 조형체 내부의 열전달 거동과 잔류응력 형성 메커니즘에 영향을 미치는 것을 실험적으로 입증하였으며, LPBF 공정에서의 서포트 설계가 기계적 신뢰성과 형상 정밀도 확보를 위한 중요한 요소임을 제시하였다. 향후에는 본 연구 결과를 기반으로 열·기계적 시뮬레이션 및 최적 설계 기법을 접목하여, 복잡 형상 및 중·대형 부품의 응력 완화와 품질 향상을 위한 공정 제어 전략으로 확장될 수 있다. 아울러, 실제 제조 현장에서의 다양한 형상 조건 및 공정 제약 요소를 고려한 설계 전략 수립이 필요하며, 본 연구는 이러한 설

계기법의 기초 자료로 활용될 수 있을 것으로 기대된다.

Funding

This work was supported by Principal R&D Project (PNKA 590) of the Korean Institute of Materials Science (KIMS). This work was also supported by the projects (RS-2024-00431717, RS-2025-02308933, and RS-2025-02317513) through the Ministry of Trade, Industry, and Energy.

Conflict of Interest

Jae Wung Bae and Jeong Min Park serve as an editor of the Science editing, but have no role in the decision to publish this article. Except for that, no potential conflict of interest relevant to this article was reported.

Data Availability Statement

Data will be made available on request.

Author Information and Contribution

Seungyeon Lee : Master's student; Writing – original draft, Investigation, Data curation, Formal analysis, Visualization. Haeum Park: PhD candidate; investigation, conceptualization. Min Jae Baek: PhD candidate; investigation, Formal analysis. Dong Jun Lee: Principal researcher; resources. Jae Wung Bae: Assistant professor; supervision. Ji-Hun Yu: Principal researcher; Validation, Resources, Project administration, Funding acquisition. Jeong Min Park: Senior researcher, Adjunct Professor; supervision, writing–review & editing, Methodology, Validation, Investigation, Formal analysis, Conceptualization.

Acknowledgments

None.

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Al-Mg 상호 고용 특성과 소결 제어를 통한 AlTiCrVMg 초경량 고엔트로피 합금의 제조 및 합금화 거동

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Fabrication and Alloying Behavior of Ultra-Lightweight AlTiCrVMg High-Entropy Alloy via Al-Mg Mutual Solubility and Sintering Control

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High-entropy alloys (HEAs) incorporating low-melting-point elements (Mg and Al) and high-melting-point elements (Ti, Cr, and V) were fabricated via mechanical alloying and spark plasma sintering. Sintering temperatures were varied to investigate phase behavior and microstructural evolution. X-ray diffraction was used to identify phase structures, scanning electron microscopy to analyze microstructures, X-ray fluorescence to determine elemental composition, and a gas pycnometer to measure density. Micro-Vickers hardness testing was conducted to evaluate mechanical properties. Mechanical-alloyed HEAs exhibited a body-centered cubic (BCC) phase and lamellar structures with element-enriched regions. Sintering introduced additional BCC and Laves phases, while higher temperatures promoted Mg liquid-phase sintering, increasing density and hardness. This study highlights the effects of sintering on HEAs containing elements with differing melting points to optimize their properties.

Keywords: powder metallurgy; high-entropy alloys; ultra-lightweight; mutual solubility; sintering

Received: February 23, 2025

Revised: April 8, 2025

Accepted: April 11, 2025

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1. Introduction

고엔트로피 합금(high entropy alloys, HEAs)은 서로 다른 다섯 가지 이상의 원소가 혼합되어 BCC (body-centered cubic), FCC (face-centered cubic), HCP (hexagonal close-packed) 등의 simple solution phase를 형성하는 특성을 갖는다. 이러한 합금은 구성 원소의 조성과 조합에 따라 다양한 물성을 발현할 수 있다는 점에서 큰 관심을 받고 있다[1-3]. 특히, BCC 구조를 가지는 고엔트

로피 합금은 FCC 기반의 고엔트로피 합금과 비교하여 뛰어난 강도와 경도를 제공하는 것으로 보고되고 있다[4].

최근에는 구조용 소재의 경량화에 대한 요구가 증가하면서, Al, Mg, Ti 등의 경량 원소를 포함한 경량 고엔트로피 합금(light-weight high entropy alloys, LWHEAs)에 대한 연구가 주목받고 있다[5, 6]. LWHEAs에 포함되는 경량 원소들은 일반적으로 최외각 전자 수(valence electron concentration, VEC)가 낮아, Guo의 VEC 법칙에 따라 높은 강도와 경도를 갖는 BCC 구조를 형성하는 경향이 있으며[7-9], 경량 고엔트로피 합금에서 활용될 수 있는 주요 경량 원소로는 Li, Be, Mg, Al, Sc, Ti 등이 있다. 그러나 Li, Be, Sc은 높은 화학적 반응성과 독성 문제로 인해 구조용 합금으로 적

<https://doi.org/10.4150/jpm.2025.00059>

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합하지 않으므로, Mg, Al, Ti를 첨가한 LWHEAs가 주로 연구되고 있다[10]. 특히, Mg는 1.7 g/cm^3 의 밀도를 지닌 가장 가벼운 구조용 금속 원소로서 HEAs의 경량화를 효과적으로 달성할 원소로 주목받고 있다. 그러나 기존 연구들은 주로 합금화가 쉬운 Al, Ti를 기반으로 소량의 저용점 원소를 첨가한 주조 공정에 국한되어 있으며, 낮은 용점과 높은 포화 증기압, 다른 금속 원소와 쉽게 금속간 화합물(intermetallic compounds, IMCs)을 형성하는 Mg는 기존의 주조 공정으로 LWHEAs의 고용체 형성이 원활하지 않고, 제조가 어렵다는 한계가 있다[11, 12].

본 연구에서는 이러한 문제를 해결하고자, 기계적 합금화(mechanical alloying)를 활용하여 Mg를 포함하는 LWHEAs를 제조함으로써 초경량화를 달성하고자 한다. LWHEAs의 구성 원소로는 경량화를 위하여 Mg와 Ti, V를, 구조 안정화를 위하여 3주기 전이 원소 중 가장 경량 특성을 보이는 Cr을 선정하였으며, Mg와 다른 고용점 원소 간의 고용 증가를 위하여 Al을 추가 원소로 선정하였다. 기계적 합금화는 상온에서 물리적 에너지로 합금화를 수행하여 원소 간 용점 차이 및 증기압에서 상대적으로 자유로운 효과적인 방법으로, 용점 차이가 큰 원소로 이루어진 LWHEAs 제조 시 주조 공정이 가지는 한계를 보완할 수 있다. 그러므로, Mg 기반 초경량 고엔트로피 합금(ultra-lightweight high-entropy alloys, ULWHEAs)를 제조하고, 합금화 과정의 미세조직적 거동을 연구함으로써 향후 항공우주, 에너지 산업 등의 분야에서 필요로 하는 초경량 고강도 구조 소재 개발에 기여하고자 한다.

2. Experimental

본 연구에서는 큰 용점 차이를 갖는 원소들을 효과적으로 합금화하기 위하여 기계적 합금화를 이용하여 ULWHEAs 제조하였다. ULWHEAs 분말은 고에너지 볼 밀링(high energy ball milling, HEBM, PM-400MA, Retsch, German)을 이용하여 제조하였다. 밀링 공정에는, SUS304 재질의 jar와 ball을 사용하였으며, 300rpm, BPR 10:1의 조건에서 60시간 동안 밀링을 진행하였다. 이후 방전 플라즈마 소결(spark plasma sintering, SPS, sps-212Lx, Dr. Sinter LAB Jr., Japan)을 이용하여 분말의 치밀화를 진행하였다. 소결 과정은 Ar 분위기에서 30MPa의 하중 하에 8분 동안 수행하였다. 소결 온도는 400°C 에서 800°C 까지 100°C 간격으로 설정하여 소결 온도에 따른 ULWHEAs의 상 거동 및 합금화 거동을 관찰하고자 하였다.

기계적 합금화 및 방전 플라즈마 소결 이후 제조된 ULWHEAs의 미세조직은 X-선 회절 분석(X-ray diffraction analysis, XRD, $\lambda = 1.5418 \text{ \AA}$, D8 Advance, Bruker, USA), 전계 방사형 주사전자 현미경(field-emission scanning electron microscope, FE-SEM, JSM 7500F, JEOL, Japan)-에너지 분산 분광기(energy-dispersive X-ray spectroscopy, EDS, INCA x-act, Oxford, UK)을 이용하여 분석하였다. 또한 X선 형광분석기(X-ray fluorescence, XRF, ZSX Primus, Rigaku, Japan)를 통해 고온 소결 조건에서 저용점 원소의 비율 변화를 확인하였다. 소결 온도에 따른 ULWHEAs의 물성으로는 gas pycnometer(AccuPyc II 1345, micromeritics, USA)로 밀도를, 마이크로 비커스 경도계(micro-Vickers hardness tester, HM-200, Mitutoyo, Japan)로 경도를 측정하였으며, 이를 상용 합금과 비교하였다.

3. Results and Discussion

본 연구에서는 열역학적 계산을 통하여 $\text{AlTiCrV}_{0.5}\text{Mg}_{0.5}$ ULWHEAs를 설계하였으며, 설계에 사용한 열역학적 변수는 아래의 Table 1과 같다. 각 열역학적 변수를 계산한 결과, 대부분의 변수가 고용체 형성 기준을 만족하는 것을 확인할 수 있다. 다만, 원자 반경 차이를 나타내는 변수인 δ 와 각 원소 간의 전기음성도 차이를 나타내는 $\Delta\chi_{\text{Allen}}$ 이 다소 높은 값을 보인다. 이러한 결과는 원소 간의 고용도를 제한시켜 편석 및 특정 원소간 화합물이 발생할 가능성을 시사한다[13].

본 연구 재료의 XRD 분석의 결과는 Fig. 1과 같다. Fig. 1(a)를 보면, 밀링 이후 제조된 ULWHEAs 분말의 경우 BCC main phase와 더불어 Cr, Ti, V의 rich peak을 확인할 수 있다. 이를 소결 온도에 변화를 주어 치밀화를 진행한 결과, 400°C 의 소결에서는 여전히 rich phase가 남아있는 형태를 보였으나, 소결 온도가 증가함에 따라 점차 고용점 원소의 rich phase가 사라지고 새로운 BCC phase와 laves phase가 형성된 것이 확인되었다. 또한 main phase의 peak이 집중적으로 발생한 40° 에서 46° 까지의 구간을 확대한 결과는 Fig. 1(b)에 나타내었다. 이를 보면 밀링 이후 소결 온도 증가에 따라 고용체 phase인 BCC phase와 특정 원소들의 rich phase의 peak이 증가하다가 700°C 를 기점으로 새로운 고용체 phase인 BCC phase와 laves phase의 peak이 나타나는 것을 확인할 수 있다. 이를 통해 밀링 직후에는 매우 낮았던 결정성이 소결이 진행됨에 따라 증가하여 peak의 intensity가 증가하였으며, 700°C

Table 1. Thermodynamic parameter calculation results of $\text{AlTiCrV}_{0.5}\text{Mg}_{0.5}$

Parameter	ΔS_{mix}	ΔH_{mix}	Ω	δ	VEC	$\Delta\chi_{\text{Allen}}$
$\text{AlTiCrV}_{0.5}\text{Mg}_{0.5}$	12.97 J/molK	-7.56 kJ/mol	2.83	7.20%	4.13	13.30%

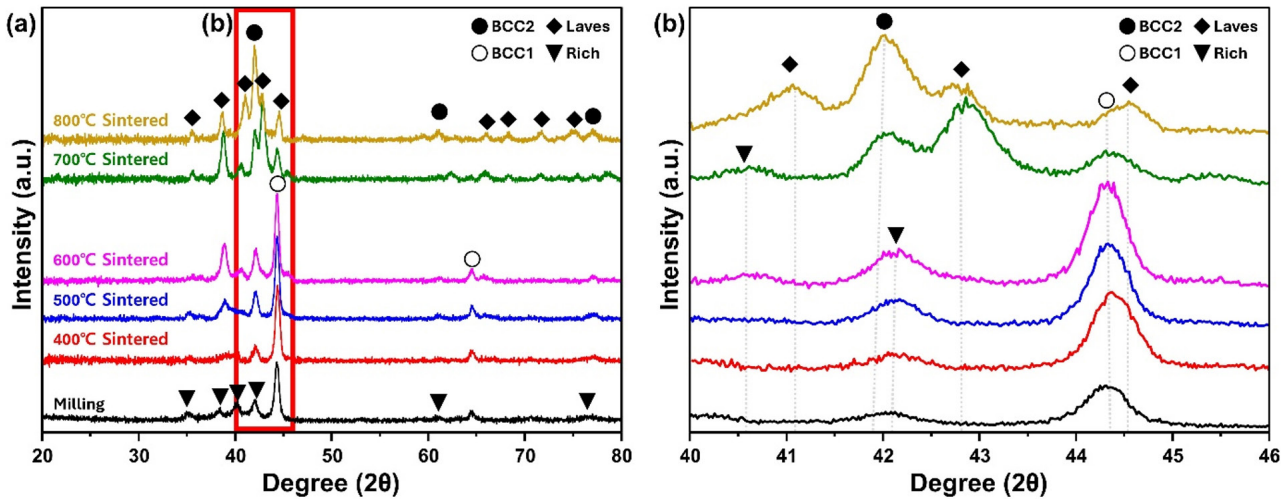


Fig. 1. X-ray diffraction patterns of AlTiCrV_{0.5}Mg_{0.5} for (a) and magnified (b).

°C 이후에는 특정 고용점 원소들의 추가 고용이 발생하여 기존의 rich phase가 사라지고 새로운 BCC phase와 laves phase가 형성되었다고 판단하였다.

ULWHEAs의 형성 및 치밀화 과정에서 성분 원소 중 Al과 Mg의 rich phase가 관찰되지 않은 이유는 두 원소의 용점과 상호 고용도로 설명할 수 있다. ULWHEAs의 성분 원소들의 용점을 살펴보면, Mg은 649°C, Al은 660°C, Ti은 1660°C, Cr은 1857°C, V은 1902°C이다. 용점이 낮은 원소는 자가 결합력이 비교적 약하여 낮은 온도에서도 자가 결합을 끊을 충분한 열에너지를 전달받는다[14]. 따라서 비교적 낮은 용점의 Al, Mg이 낮은 소결 온도에서도 다른 고용점 원소들보다 높은 이동도를 갖는다고 판단하였다.

또한 Al과 Mg의 rich phase가 관찰되지 않은 현상에는 Al과 Mg의 상호 고용도(mutual solubility)가 영향을 미쳤을 것으로 예상하였다. 두 원소의 상호 고용도는 Hume-Rothery 법칙[15]에 따라 원자 반경 및 전기음성도, 원자가전자 수와 같은 요인에 영향을 받는다. Al과 Mg의 경우에는 원자가 전자의 수는 비슷하나 원자 반경 및 전기음성도의 차이가 다소 커서 일반적으로 상온에서 상호 고용도가 그리 높지 않으며, 주로 금속간 화합물을 형성한다. 하지만 본 연구에서 사용한 방법인 기계적합금화는 이를 억제하고 과포화 고용체를 형성하는 특징을 갖는다[16]. 그 결과 가장 원소의 이동도가 활발한 두 원소가 고용체를 원만히 발생시킨 것으로 판단하였다. 이후 소결 온도 증가에 따른 rich phase 소멸의 순서는 각 원소의 용점 및 Al, Mg과의 상호 고용도의 영향에 의한 것으로 예상하였다.

각 조건에서의 ULWHEAs의 미세조직은 Fig. 2와 같이 관찰된다. 밀링 직후에는 크기가 매우 다양한 phase가 혼합된 multi-phase 구조가 확인되며, 소결 온도가 증가함에 따라 dark gray

phase가 main phase가 되어 white phase, bright gray phase 등의 크기 및 비율이 감소하는 경향을 보인다.

이를 토대로, 소결 온도가 증가함에 따라 불규칙한 원소의 분포를 보이던 ULWHEAs의 미세조직이 점차 균일화되고 phase의 종류가 감소한다고 판단하였다. 또한 고용체 상으로 확인되는 위치의 경우, Al과 Mg만이 주로 고용체를 형성하는 밀링 직후, 400°C, 500°C, 600°C 소결 조건에서는 하나의 상으로 이루어진 것을, 700°C 이후의 소결 조건에서는 2가지의 상이 수십~수백 nm의 크기로 혼합되어 있는 형태가 관찰되었다. 이 결과와 앞선 Fig. 1를 통해, 600°C 이하의 소결 조건에서는 Al과 Mg이 BCC 고용체를 형성하며, 700°C 이상의 소결 조건에서는 고용점 원소의 추가 고용으로 새로운 BCC phase와 laves phase가 형성되었다고 판단하였다. 이때 700°C와 800°C의 소결에서는 기공이 발생하기 시작하며, 이러한 소결 온도 조건 변화에 따른 미세조직의 변화를 더 자세히 분석하기 위하여 여러 조건 중 미세조직에서 큰 변화를 보이는 조건에서 EDS 분석을 진행하였다. 미세조직에서 눈에 띄는 변화가 관찰되는 밀링 직후 분말과 400°C, 600°C, 800°C 온도에서 각각 소결한 소결체의 SEM과 EDS 분석 결과는 Fig. 3과 같다.

밀링 직후에는 앞선 XRD 결과와 마찬가지로, Al과 Mg이 함께 위치하며, 그 외의 고용점 원소인 Ti, Cr, V은 일정 구역에 편석되어 있음이 확인된다. 400°C 소결의 경우에도 밀링 직후와 비슷한 경향을 보이며, 600°C 소결에서는 Ti과 Cr이 편석을 이루는 경향이 감소하고 Al과 함께 고용된 형태가 확인된다. 또한 가장 높은 용점의 V은 여전히 일부 구역에 편석을 이루고 있으며, Mg의 경우 Al과 함께 고용되어 있으나, 일부 편석 경향을 보인다. 800°C 소결에서는 V도 비교적 고용 경향이 증가하였으며, 반대로 Mg은 편석의 경향이 강해져, SEM 분석에서 기공으로 관찰되는 곳에 위치하

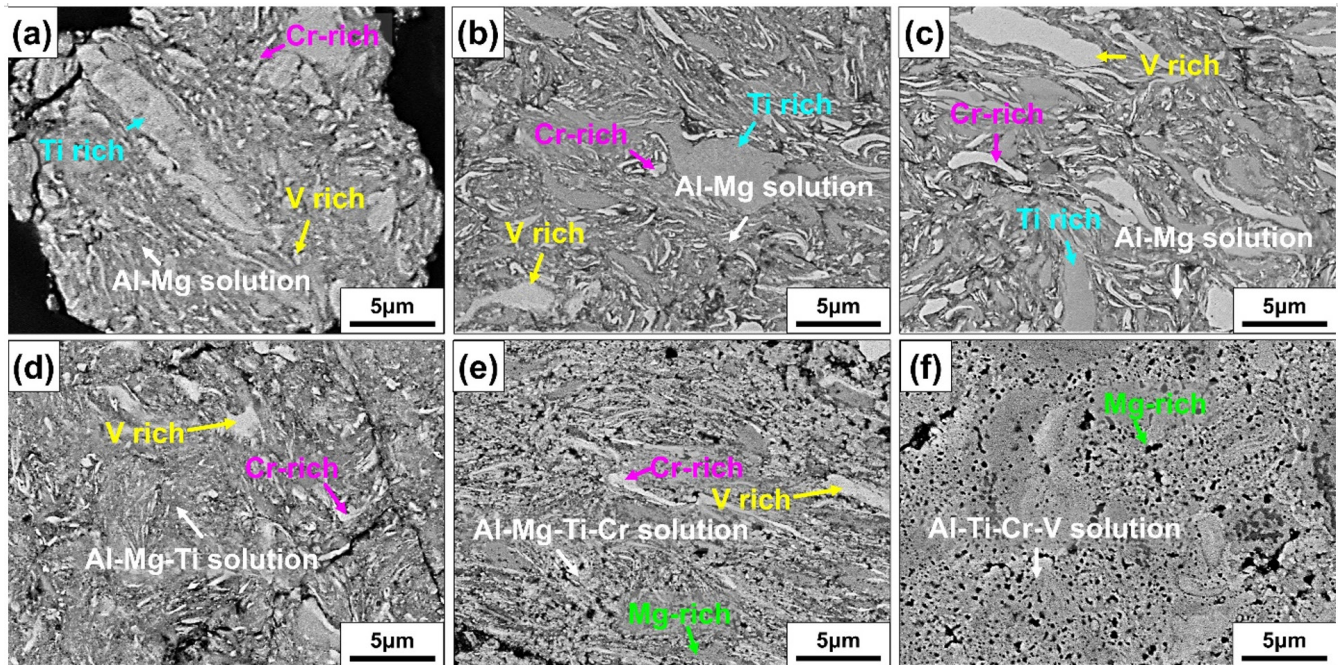


Fig. 2. Scanning electron microscopy with backscattered electrons image of $\text{AlTiCrV}_{0.5}\text{Mg}_{0.5}$ with different conditions: (a) as-milled powder, sintered at (b) 400°C, (c) 500°C, (d) 600°C, (e) 700°C, and (f) 800°C, respectively.

는 것이 확인된다.

이러한 원소의 고용 경향 변화는 각 원소 간의 상호 고용율에 따른 결과로 해석할 수 있다. 일반적으로 대부분의 원소는 공정 온도가 증가함에 따라 많은 열에너지가 공급되어 자가 결합을 끊고 서로 고용되는 경향을 보인다[14]. 이러한 경향은 앞서 확인한 Ti, Cr, V의 고용 경향 변화를 통해 확인할 수 있다. 반대로 Mg의 경우에는 소결 온도가 증가함에 따라 오히려 감소하는 경향을 보였는데, 이는 용점 외의 다른 원소와의 상호 고용율에 의한 결과로 설명할 수 있다. 기계적 합금화에 의해 초기 분말에서는 Mg은 Al과 충분히 고용되어 있다. Mg은 성분 원소 중에서는 Al과 가장 높은 상호 고용 경향을 보이며, Ti, Cr, V과는 원자 반지름 및 전기 음성도 등의 열역학적 변수간 차이가 커서 상호 고용이 아닌 상분리가 유리한 경향을 보인다[17]. 이와는 달리 Al은 Ti, Cr, V과 비교적 우수한 상호 고용율을 갖는다. 이에 따라, 소결 온도 상승에 따른 Ti, Cr, V의 고용 증가 시 반대로 Mg은 편석 경향이 강해지며, Mg 편석은 용점보다 높은 온도 조건에서 액상 소결(liquid phase sintering, LPS)을 발생시킨 것으로 예상된다. 액상 소결이 발생하는 경우, 액상에 의한 입자간 접촉 증가로 고상 확산이 활발해지며, 용해 및 재 침전 현상이 발생하여 특정 금속간 화합물의 형성이 가속화될 수 있다[17, 18]. 또한 그 과정에서 shrinkage 등의 현상이 발생할 수 있으며, 이러한 shrinkage 현상은 Fig. 3(d)에서 확실히 관찰된다. 따라서 고온 소결에서 원소의 분포가 급격하게 변화한 데에

는 액상 소결이 영향을 끼친 것으로 판단된다. 액상 소결에 의한 원소의 분포 변화를 확인하고자, Fig. 3에서 확인한 바와 같이 Mg의 편석 경향이 강해진 700°C, 800°C 조건에서 XRF 분석을 진행하였다. 700°C와 800°C에서 각각 소결한 고엔트로피 합금의 XRF 결과는 Table 2와 같다.

설계와 각 조건에서의 원소 비율을 비교해보았을 때 Al과 Mg은 설계보다 낮은 비율을, Ti, Cr, V은 설계보다 높은 비율을 나타낸다. 특히 Mg의 경우 설계와 그 차이가 매우 큰 것을 확인할 수 있는데, 이 결과를 통해 Mg의 액상 소결 및 일부 소실이 발생했음을 확인할 수 있다. 또한 XRF 분석 결과에서는 LWHEAs의 성분 원소 외에도 Fe 등의 금속 원소가 함께 검출되었는데, 이는 milling 공정 중 SUS304 jar와 ball에 의해 발생한 contamination으로 확인하였다. 하지만 검출된 Fe의 비율은 0.1 at.% 이하로 매우 미소하기 때문에 전체 LWHEAs의 물성에는 큰 영향을 미치지 않을 것으로 판단하였다.

ULWHEAs의 소결 조건에 따른 밀도와 경도는 Fig. 4와 같다. 소결 온도 증가에 따라, 밀도는 전체적으로 증가하는 경향을 보이거나 일부 구역에서는 감소하며, 경도는 전체적으로 상승하는 경향이 확인된다. 일반적으로, 소결에서는 소결 온도 증가 시 재료의 소결성이 증가하여 같은 분말 재료라도 밀도, 경도 모두 증가하는 경향을 보인다[19–21]. 본 연구의 ULWHEAs는 경도에 대해서는 이러한 소결성 증가에 의한 경향을 따르지만, 밀도의 경우에는 그렇지

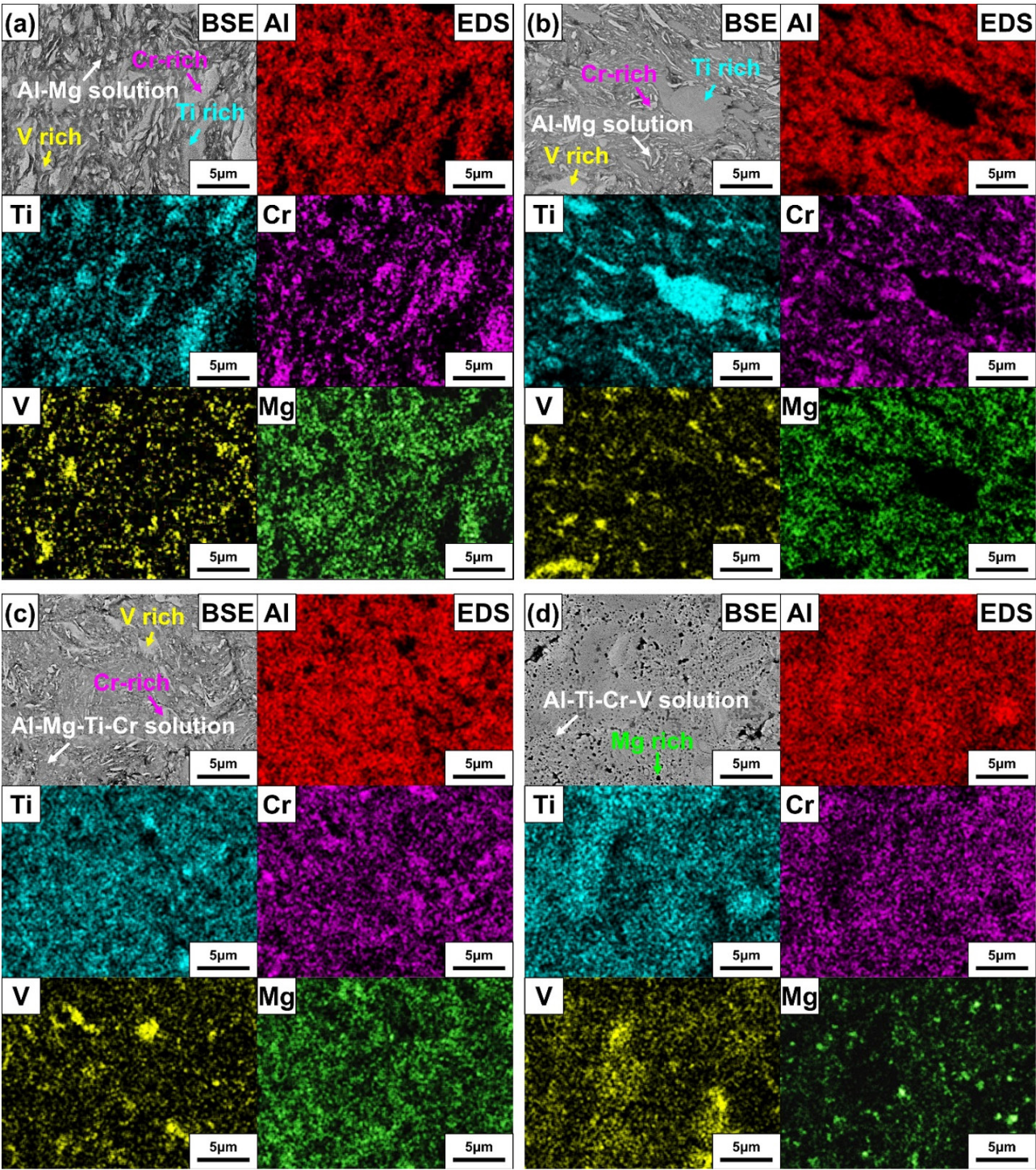


Fig. 3. Scanning electron microscopy images showing the microstructure and energy-dispersive X-ray spectroscopy result of AlTiCrV_{0.5}Mg_{0.5} with different conditions: (a) as-milled powder, sintered at (b) 400°C, (c) 600°C, and (d) 800°C, respectively.

Table 2. X-ray fluorescence results of AlTiCrV_{0.5}Mg_{0.5} sintered at 700°C and 800°C

Elements(at.%)	Al	Ti	Cr	V	Mg
700°C	23.9	24.9	30.5	12.8	7.8
800°C	24.4	26.0	31.2	13.1	5.3

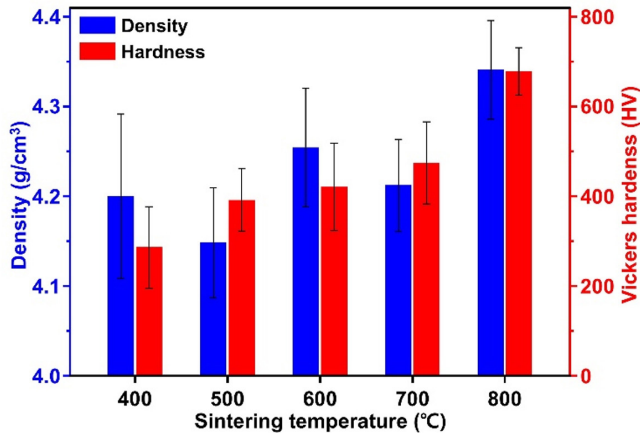


Fig. 4. Density and Vickers hardness values of AlTiCrV_{0.5}Mg_{0.5} with different sintering temperatures.

않음을 알 수 있다. 두 물성 변화의 차이는 소결 중 발생한 Mg의 특이점을 통하여 설명하고자 한다.

먼저 가장 저온 조건인 400°C에서는 낮은 소결성으로 재료에 많은 내부 기공이 존재하여, gas를 사용하는 pycnometer의 측정 결과에 많은 오차가 나타난 것으로 판단하였다. 500°C, 600°C에서는 소결성의 증가로 인한 내부 기공의 감소로 비교적 안정적인 밀도의 측정이 이루어졌으며, 소결성이 증가함에 따라 밀도도 증가하는 일반적인 경향을 나타내는 것이 확인된다. 700°C에서는 다시 밀도가 감소하는 경향을 보이는데, 이 지점은 고용점 원소들의 고용이 증가하고 Mg의 편석 경향이 강해지는 시작점으로, Mg의 액상 소결로 인한 기공 형성으로 인해 밀도가 감소하는 경향을 보인 것으로 추측하였다. 800°C에서는 그 값이 이론적 설계보다도 증가한 결과를 보이는데, 이는 Mg의 소실이 본격적으로 발생하여, 저밀도 원소 비율 감소에 따른 단위 질량의 증가와 소결성의 증가에 의한 결과로 판단하였다.

경도 시험의 결과로 보아, ULWHEAs의 소결성은 400°C와 500°C 사이에서 크게 증가하였으며, Mg에 의한 액상 소결 효과 및 소결성 증가의 상승효과로 800°C에서 큰 경도 상승이 발생한 것으로 판단하였다. 소결 온도 증가에 따른 경도의 변화는 밀도와는 달리 꾸준히 증가하는 경향을 보였다. 이는 Mg의 소실에 의한 영향이 주를 이루었던 밀도 거동과는 다르게, 소결 온도 증가에 따른 소결성이 주요 거동 원인으로 작용하였기 때문으로 판단하였다. 그 결과, 소결성이 전반적으로 좋지 않은 저온에서부터 온도가 증가함에 따라 작은 차이라도 꾸준히 증가하는 결과를 나타낸 것으로 판단하였다. 본 연구에서 측정된 ULWHEAs의 밀도와 경도를 바탕으로 상용 재료와의 material selection chart를 Fig. 5와 같이 나타내었다.

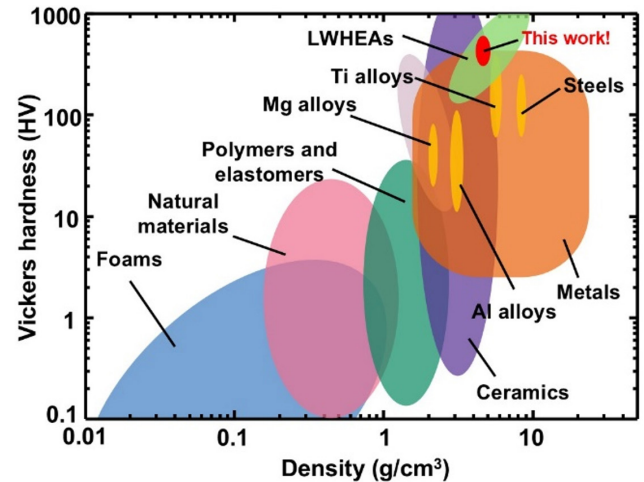


Fig. 5. Material selection chart (density vs. hardness) [22].

본 연구의 ULWHEAs는 저밀도 합금인 Ti alloy보다도 낮은 밀도를 보이며, 일반 합금들에 비해 매우 우수한 경도를 나타냄을 확인할 수 있다. 이는 일부 세라믹보다도 높은 값으로, 다른 ULWHEAs와 비교하였을 때에도 좌상향에 위치하는 것을 확인할 수 있다. 따라서 본 연구의 재료인 ULWHEAs는 기존의 상용 합금 재료들과 비교하여 저밀도, 고경도 등의 우수한 특성을 보여 그 활용도가 기대된다고 판단하였다.

4. Conclusions

본 연구는 기계적 합금화를 이용하여 금속간화합물 형성을 억제함과 동시에 저용점 경량원소 Mg와 고용점 경량원소 Ti를 첨가한 AlTiCrV_{0.5}Mg_{0.5} ULWHEAs의 제조를 성공적으로 달성하였다. 또한, 소결 온도에 따른 합금화 거동과 기계적 물성을 밀도와 비교하여 체계적으로 분석하였다. 본 연구에서는 다음과 같은 주요 결론을 얻을 수 있었다.

- (1) HEBM을 통해 제조된 ULWHEA powders는 BCC phase와 Ti, Cr, V계 rich-phase가 공존하며, SPS 후 소결 온도가 증가함에 따라 mutual solubility가 향상되어 BCC phase와 Laves phase가 나타난다.
- (2) 500°C 이하 소결 온도에서 Mg는 고용점 원소와 상분리가 발생하며, 이는 온도로 인한 확산 에너지 부족의 결과로 rich-phase를 형성한다.
- (3) 600°C 이상 소결 온도에서 Mg는 액상 소결 효과를 통해 원소 확산을 촉진시키며, ULWHEAs의 밀도와 경도를 동시에 증가시킨다.
- (4) 본 연구에서 제조한 ULWHEAs는 3가지 경량 원소(Al, Mg,

Ti)를 동시에 첨가하여 상용 소재보다 낮은 밀도와 동시에 우수한 경도를 가질 뿐만 아니라, 기존 연구된 LWHEAs와 비교하여 우수한 밀도 대비 경도를 보인다.

결과적으로, 본 연구에서는 초경량화를 달성하기 위해 저융점 및 고융점 경량원소가 포함된 ULWHEAs를 MA를 통해 제조하였으며, 소결 조건에 따른 합금화 거동 및 기계적 물성을 이해하였다. 이를 기반으로 융점 차이가 큰 원소를 포함하는 ULWHEAs의 제조 및 물성 향상 연구의 마중물이 되고자 한다.

Funding

This work was supported by a National Research Foundation of Korea (NRF) grant funded by the Korean government (MSIT) (2021R1A2C1005478).

Conflict of Interest

The authors declare no competing financial interests or personal relationships.

Data Availability Statement

The original contributions presented in the study are included in the article, further inquiries can be directed to the corresponding authors.

Author Information and Contribution

송은효: 석사과정 학생; Conceptualization, Methodology, Investigation, Visualization, Writing –original draft

이한성: 박사후 연구원; Conceptualization, Validation, Supervision, Visualization, Writing – review & editing

안병민: 교수; Supervision, Writing – review & editing, Reviewing & editing – review contribution, Funding acquisition, Resources

Acknowledgments

This work was supported by the National Research Foundation of Korea (NRF) grant funded by the Korean government (MSIT) (2021R1A2C1005478).

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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 objectively 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

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1. Introduction
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Acknowledgement (This is author's option.)

References

List of Table and Figure captions

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- [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.
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- [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.

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

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

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성 명	소 속	성 명	소 속	성 명	소 속
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김휘준	한국생산기술연구원	유지훈	한국재료연구원	한유동	한국재료연구원
김희수	월드인텍션	윤덕용	KAIST	현승균	인하대학교
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류성수	한국세라믹기술원	윤중열	한국재료연구원	홍순형	KAIST
류시완	(주)풍산홀딩스	윤탈식	대신강업(주)	홍현선	성신여자대학교
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