Effect of In-Situ Synthesized Nitride and Oxide Precipitates on L-PBF Fe-12Cr-6Al as ATF Candidate Material

Omer Cakmak[a], Hwasung Yeom[a,b], Jung-Wook Cho[a,b*]
[a]*Division of Advanced Nuclear Engineering, Pohang University of Science and Technology (POSTECH), Pohang, 37673, Republic of Korea*
[b]*Graduate Institute of Ferrous & Eco Materials Technology, Pohang University of Science and Technology (POSTECH), Pohang, 37673, Republic of Korea*

[*]*Corresponding author: jungwook@postech.ac.kr*

***Keywords: *In-situ* synthesis, Nitride and oxide Precipitates, Laser-Powder Bed Fusion.**

1. Introduction

The advancement of industrialization and the heightened emphasis on nuclear power plant safety have imposed fresh criteria for fuel cladding possessing enhanced durability. Iron-chromium-aluminum (FeCrAl) alloys are being evaluated as prospective materials for fabricating cladding tubes in accident-tolerant fuels (ATF) to replace current zirconium (Zr) alloys. Additionally, these alloys are acknowledged for their pivotal role as essential structural materials in next-generation fission and fusion reactors due to their exceptional resistance to high-temperature creep, oxidation, and irradiation [1].

Research is underway to improve FeCrAl alloys' properties and explore cost-effective, environmentally friendly manufacturing methods. Recently, advancements have been made in developing oxide dispersion-strengthened (ODS) FeCrAl alloys to enhance their existing properties [2]. Laser Powder Bed Fusion (L-PBF) is an innovative and cost-effective additive manufacturing (AM) technique. It employs diverse shielding gases such as pure nitrogen (N_2), argon (Ar), and carbon dioxide (CO_2) [3].

New research underscores the efficiency of ultrafine ceramic precipitates such as titanium nitride (TiN) as effective sites for heterogeneous nucleation. This ceramic particle plays a crucial role in refining grain structures during solidification, presenting a cost-effective method for industrial production. Researchers highlight the favorable influence of this ceramic particle on the microstructure and mechanical properties of FeCrAl alloys. They particularly commend the interaction between titanium (Ti) and nitrogen (N), emphasizing its pivotal role in forming TiN precipitates with outstanding material characteristics [4,5].

This study investigates the *in-situ* synthesis of nitride and oxide precipitates in an N_2 reactive gas atmosphere during the L-PBF process and their impact on the Fe-12Cr-6Al microstructure, precipitate characteristics, and hardness properties.

2. Experimental Methods

The Fe-12Cr-6Al powder, acquired from MK Co. in South Korea, was produced through gas atomization, featuring a size range of 15 to 45 µm. The samples were printed using an L-PBF machine (Metalsys-250, WINFORSYS) in a nitrogen (N_2) atmosphere, with and without Ti. For both conditions, building parameters included a laser power of 250 W, a scan speed of 600 mm/s, layer thickness of 30 µm, and a hatch distance of 100 µm. The samples were printed with dimensions of 30 x 10 x 10 mm^3. The elemental compositions of the as-built samples, outlined in Table 1, were established through inductively coupled plasma-optical emission spectroscopy (ICP-OES, QSG-750, OBLF). Nitride and oxide precipitates in the as-built samples were examined for morphology, dimensions, and chemical composition via a JEOL scanning electron microscope (SEM, JSM-7900F). A dual-beam focused ion beam (FIB) milling method (Quanta 3D FEG, FEI) was employed to prepare transmission electron microscopy (TEM) lamella from the printed samples. Energy-dispersive X-ray spectroscopy (EDS) mapping was conducted using a TEM (JEM-2100F, JEOL). Vickers hardness tests were performed on the cross-sections of the specimens using the Mitutoyo/HM-220B. Each specimen underwent ten indentations, and the resulting hardness values were averaged for representation, employing a force equivalent to HV 0.5, followed by a ten-second holding time in each measurement.

Table 1. Composition of FeCrAl alloys (wt%).

Alloy	Fe	Cr	Al	Ti	O	N
Without Ti	Bal.	11.97	5.90	-	0.01	0.032
With Ti	Bal.	12.01	5.85	0.97	0.033	0.082

3. Results and discussion

3.1 SEM analysis of in-situ synthesis oxide and nitride precipitates

SEM analysis (Figure 1) was performed without Ti sample to examine the characteristics of precipitates. Examination of the SEM-EDS maps (Figure 1b) reveals in-situ formed nano precipitates of aluminum oxide (Al_2O_3). According to the Ellingham diagram [6], the standard free energy of Al_2O_3 is higher than that of Fe_2O_3 and Cr_2O_3. Consequently, oxygen (O) exhibits a greater affinity for aluminum (Al) compared to iron (Fe) and chromium (Cr).

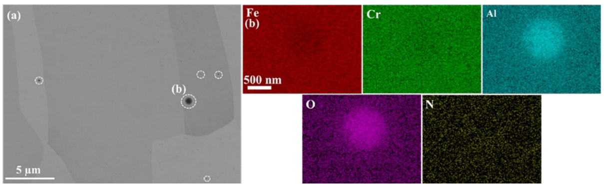


Fig.1. (a) Backscattered electron images and (b) EDS maps results for without Ti as-built sample.

The sample matrix with titanium (Ti) addition showcases the presence of in-situ formed titanium nitride (TiN), as shown in Figure 2. The TiN precipitates exhibits a rectangular morphology. Compared to Fe, Cr, and Al Ti's nitriding efficiency is higher, likely due to its optical and thermal properties [7].

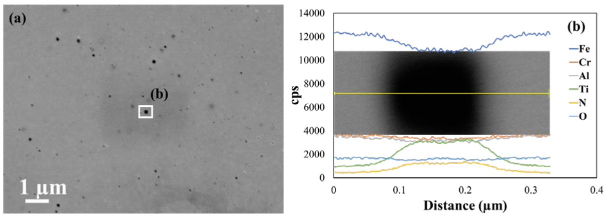


Fig.2. (a) Backscattered electron images and (b) EDS maps results for with Ti as-built sample.

A comparison between samples printed with Ti and those without Ti indicates visible differences in their microstructure (Figure 3 a,b), even when using the same build strategies and process parameters. The analysis investigates the effect of adding Ti on grain structure characteristics, such as orientation, morphology, and size. Significant differences are observed in the orientation maps: the sample without Ti shows a columnar grain structure, while the sample with Ti exhibits an equiaxial grain structure. Additionally, introducing Ti significantly decreases mean grain size from 58 µm to 9 µm (Figure 3. e, f). Adding Ti into ferritic alloys has shown a considerable impact on the resulting material's microstructure during the solidification process [4].

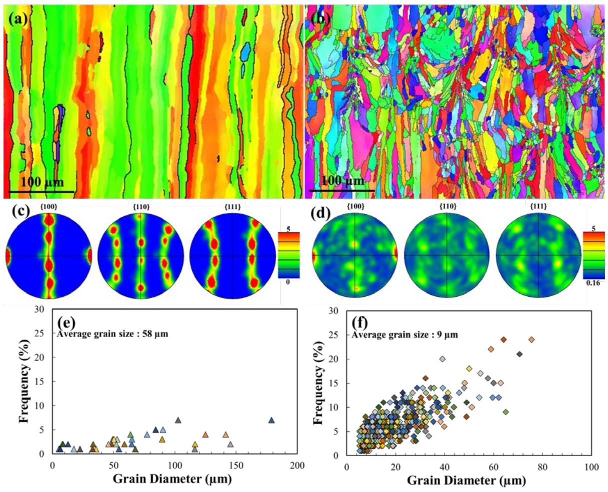
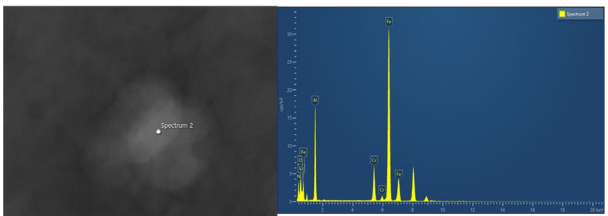


Fig.3. Scan direction IPF-X maps, pole figures and grain size distribution analysis results of as build samples; (a, c, e) without Ti and (b, d, f) with Ti.

3.2 TEM analysis of in-situ synthesis oxide and nitride precipitates

In Figure 4a, a bright-field scanning transmission electron microscopy (BF-STEM) image of the sample without Ti displays the formation of a complex AlN-O precipitate, confirmed by EDS-point ID (Figure 4b). The rapid cooling during the solidification process in L-PBF can hinder the diffusion of aluminum (Al), nitrogen (N), and oxygen (O), which dissolve in the molten pool at high temperatures. Consequently, irregular precipitates of the AlN-O complex might be formed [6].



Elements	Fe	Cr	Al	N	O
Spectrum-2 (Wt%)	4.3	1.1	29.7	22.4	42.5

Fig.4. (a) BF-STEM image and corresponding (b) EDS-point ID validate the in-situ synthesis of the AlN-O precipitate for the as-printed sample without Ti.

The analysis of the as-built samples with Ti addition showed that the nano-precipitates had a core-shell structure. The shell was enriched with Ti and N, while the core was enriched with Al and O (Figure 5).

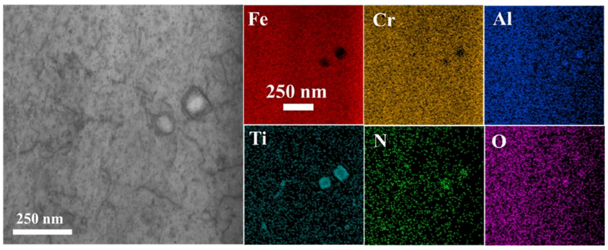


Fig.5. BF-STEM image of the as-printed sample with Ti and corresponding EDS maps verifies the in-situ synthesis of Al_2O_3@TiN.

3.3 Effect of various nitride precipitates on Hardness Properties

The yield strength of FeCrAl alloys fabricated by additive manufacturing, similar to the composition in this study, typically ranges around 349 MPa [8], while Micro-Hardness values may vary between 240 and 266 depending on the printing parameters [6]. The hardness test results for the as-built samples with and without Ti are shown in Fig.6. The sample with Ti (303 ± 8) exhibited a higher hardness, with an increase of around 50 HV compared to the sample without Ti (253 ± 4). This study demonstrates that adding Ti results in the formation of different types and shapes of nanoprecipitates, which have a favorable impact on the material's hardness properties by reducing the grain size.

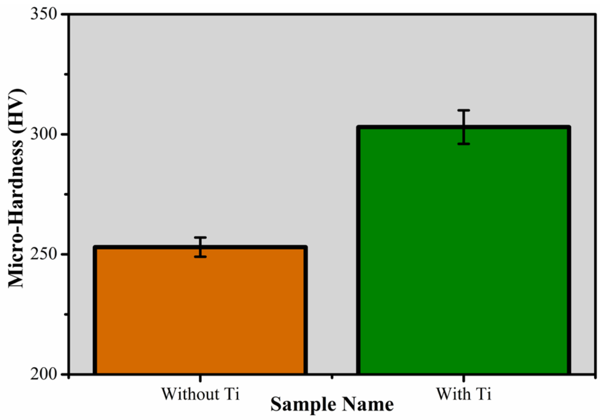


Fig.6. Microhardness values of as-built samples, both without Ti and with Ti, tested at room temperature.

4. Conclusion

This study aimed to evaluate the in-situ synthesis of various nitride and oxide precipitates in an N_2 reactive gas atmosphere during Laser Powder Bed Fusion and their impact on the properties of Fe-12Cr-6Al alloy. Al_2O_3 and AlN-O nanoprecipitates were synthesized *in-situ* under the N_2 atmosphere in the Fe-12Cr-6Al matrix. However, the addition of Ti resulted in the formation of different nano precipitates, including TiN and Al_2O_3@TiN. The sample without Ti exhibited a columnar grain structure, while the with Ti sample demonstrated an equiaxial grain structure. The as-built sample with Ti demonstrated a higher hardness, with an increase of approximately 50 HV compared to the sample without Ti.

REFERENCES

[1] C. P. Massey *et al.*, "Microstructure Dependent Burst Behavior of Oxide Dispersion – Strengthened FeCrAl Cladding," *Mater. Des.*, p. 112307, 2023, doi: 10.1016/j.matdes.2023.112307.

[2] K. Sakamoto *et al.*, "Development of accident tolerant FeCrAl-ODS fuel cladding for BWRs in Japan," *J. Nucl. Mater.*, vol. 557, p. 153276, 2021, doi: 10.1016/j.jnucmat.2021.153276.

[3] M. P. Haines, N. J. Peter, S. S. Babu, and E. A. Jägle, "In-situ synthesis of oxides by reactive process atmospheres during L-PBF of stainless steel," *Addit. Manuf.*, vol. 33, no. January, p. 101178, 2020, doi: 10.1016/j.addma.2020.101178.

[4] A. Durga *et al.*, "Grain refinement in additively manufactured ferritic stainless steel by in situ inoculation using pre-alloyed powder," *Scr. Mater.*, vol. 194, p. 113690, 2021, doi: 10.1016/j.scriptamat.2020.113690.

[5] T. Huang, D. Naumenko, P. Song, J. Lu, and W. J. Quadakkers, "Effect of Titanium Addition on Alumina Growth Mechanism on Yttria-Containing FeCrAl-Base Alloy," *Oxid. Met.*, vol. 90, no. 5–6, pp. 671–690, 2018, doi: 10.1007/s11085-018-9861-6.

[6] O. Cakmak, S. Lee, S. Gyu, D. Eo, H. Yeom, and J. W. Cho, "In-situ synthesis of nitrides and oxides through controlling reactive gas atmosphere during laser-powder bed fusion of Fe-12Cr-6Al," *Mater. Des.*, vol. 240, no. October 2023, p. 112862, 2024, doi: 10.1016/j.matdes.2024.112862.

[7] S. Desmoulins-Krawiec *et al.*, "Synthesis of nanostructured materials in supercritical ammonia: Nitrides, metals and oxides," *J. Mater. Chem.*, vol. 14, no. 2, pp. 228–232, 2004, doi: 10.1039/b310806f.

[8] W. J. Lv *et al.*, "Effects of TiC nanoparticle additions on microstructure and mechanical properties of FeCrAl alloys prepared by directed energy deposition," *J. Nucl. Mater.*, vol. 554, 2021, doi: 10.1016/j.jnucmat.2021.153094.