

DOI: <https://doi.org/10.24425/amm.2022.141086>YONG-HOON CHO¹, GI-SU HAM^{1,2}, SO-YEON PARK¹,
CHOONGNYUN PAUL KIM², KEE-AHN LEE^{1*}**EFFECT OF Nb AND Mo ADDITION ON THE MICROSTRUCTURE AND WEAR BEHAVIOR OF Fe-Cr-B BASED METAMORPHIC ALLOY COATING LAYER MANUFACTURED BY PLASMA SPRAY PROCESS**

Fe-Cr-B-based metamorphic alloy coating layers were manufactured by plasma spray with a Fe-Cr-B-Mo-Nb composition (hereinafter, M+) powder. The microstructure and wear properties of the coating layers were investigated and compared with a metamorphic alloy coating layer fabricated with commercial M material. XRD analysis revealed that the M and M+ coating layers were composed of α -Fe, (Cr, Fe)₂B, and some metallic glass phases. Wear test results showed that M+ coating layers had a superior wear resistance which had 1.48 times lower wear volume than M coating layers. Observations of the worn-out surfaces and cross-sections of the coating layers showed that M+ coating layer had relatively low oxides along the particle boundaries and it suppress a delamination behavior by the oxides.

Keywords: Plasma spray; Fe-Cr-B based metamorphic alloy; Nb addition; Microstructure; Wear

1. Introduction

Fe-Cr-B-based metamorphic alloys are the materials show a metamorphic behavior which transformed crystalline to amorphous when it exposed to environments with strong kinetic and thermal energy (wear, thermal spray, etc.). These alloys have excellent wear resistance and corrosion resistance. In addition, it shows excellent mechanical properties due to the hard Cr-Fe borides distributed in the Fe-based matrix [1-6]. Fe-Cr-B metamorphic alloys are economic by using iron, which is inexpensive, as a base, and its excellent wear resistance can usefully applied for vehicles, production facilities, various machine parts, etc. [7,8].

Thermal spray is a coating process that melting a feedstock (such as powder, wire, rod, etc.) with a heat source and spray on a substrate. Thermal spray is known that it can fabricate excellent wear resistant coating layers efficiently almost no restraints of types of coating material and the size of the substrate to be coated [9]. Moreover, thermal spraying has a high cooling rate in the depositing process and apply high collision energy, allowing for the formation of partial metallic glass phases even in as-sprayed Fe-Cr-B-based metamorphic coating layers [3,9]. Therefore, there have been attempts to use the thermal spray process to manufacture Fe-Cr-B-based metamorphic alloy coating layers

and apply them to machine parts used in heavy industry (such as rollers, bearings, etc.), pipes of power plants, etc. [8].

It is necessary to improve the in-flight oxidation issue during the process to enhance the wear-resistant property of Fe-Cr-B-based coating layers manufactured using thermal spray [10-14]. However, the design of Fe-Cr-B-based metamorphic alloys was focused on the enhancement of wear resistance and corrosion resistance through the formation of reinforced phase or increased glass-forming ability, like adding Mo, Si, Cu, etc. [15-16], and there is almost no research on alloy design that considers in-flight oxidation.

Adding the Nb element in small amounts to a Fe-based alloy is known to produce grain refinement and enhance high-temperature oxidation, thermal stability, and glass-forming ability [17-21]. Therefore, adding a small amount of Nb to a Fe-Cr-B-based metamorphic alloy is expected to enhance resistance to in-flight oxidation and additionally be of assistance in the improvement of the mechanical properties of coating layers.

In the present study, Fe-Cr-B-based metamorphic alloy coating layers were manufactured by atmospheric plasma spray (APS) process utilizing a new Fe-Cr-B-based powder which small amount of Nb and Mo added and the conventional alloy (so called M) powder. After which the microstructure and abrasion characteristics of the new coating layers were examined.

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2. Experimental

New Fe-Cr-B-based metamorphic alloy (hereinafter, M+) powder which contains Fe: bal., Cr: 20 wt.%, B: 2 wt.%, C: 0.4 wt.%, Mo: 5 wt.%, and Nb 1.75 wt.%, and the commercial Armacor™ M (Liquidmetal Technologies Co.) powder, which contains Fe: bal., Cr: 44.73 wt.%, B: 6.36 wt.%, Si: 0.73 wt.%, and C: 0.13 wt.%, were employed to manufacture coating layers. Both powders were made by gas atomization process. Two initial powders were all spherical, and the average particle sizes were 31–33 μm . The M and M+ powders were deposited on AISI 316L plates using the atmospheric plasma spray (APS) process.

For phase analysis and microstructural observation, X-ray diffraction (XRD, Rigaku Ultima IV, Cu $K\alpha$, scan step size: 0.05° , scan rate: 2°min^{-1}), field-emission scanning electron microscope/energy-dispersive X-ray spectroscopy (FE-SEM/EDS, Tescan MIRA 3, Oxford Instruments X-max 50) analysis were implemented. Samples for microstructural observation were polished to 1 μm using SiC paper and diamond suspension. Porosity value and fraction of oxide were measured by using image analyzer (Image-pro plus).

To obtain the mechanical property of the coating layers, micro-Vickers hardness test was conducted using Mitutoyo HM-200 equipment, and the test condition were load: 300 gf, loading time: 10 sec. To evaluate wear properties of the M and M+ coating layers, pin-on-disk wear test was performed. The metamorphic alloy coated disc was used as wear specimen with the counterpart pin of silicon nitride. The wear test was conducted by using R&B RB-102PD with the test condition of sliding speed: 0.05 m/s, sliding distance: 400 m, and vertical load: 5 kgf. After the wear test, worn-out surface and its cross-section were observed using FE-SEM to check wear behavior.

3. Results and discussion

Fig. 1 shows low-magnification SEM images (Fig. 1(a–b)) and XRD analysis results (Fig. 1(c)) of the cross-sections of the M and M+ coating layers. The thickness of the manufactured coating layers were M: 278.0 μm , M+: 388.3 μm . The porosity of the coating layers were measured to be M: 1.56%,

M+: 3.84%. The XRD analysis revealed that both of coating layers have α -Fe phases and $(\text{Cr, Fe})_2\text{B}$ phases, and some halo patterns were detected near the α -Fe peak located at 2θ (theta) 40 – 50° . The APS process uses plasma over approx. $10,000^\circ\text{C}$ as a heat source, which means that Cr-Fe borides may degraded as the powder melts. Boride decomposition supplies Cr and B elements (which enhance glass-forming ability) to the matrix, facilitating formation of metallic glass in the coating process. In other words, the halo patterns found in the M and M+ coating layers are expected to be the results of metallic glass formation.

Fig. 2 shows the results of high-magnification observation of the cross-sections of the M and M+ coating layers. The two coating layers were composed of mostly splats, with a few unmelted powders. Fe-Cr oxides (yellow arrows) and a small number of pores (orange arrows) were found at the particle boundaries. The fraction of Fe-Cr oxide was found to be M: 2.48%, M+: 1.50%, that is M+ coating layer was less oxidized than M. The oxides in the particle boundaries inside the coating layer are considered to have arisen from in-flight oxidation that occurs during the process. Moreover, APS process not only uses ultra-high temperature heat source but has relatively slower particle flight velocities compared to other thermal spray processes, increasing exposure to heat sources and causing in-flight oxidation. In this situation, the oxidation behavior is influenced by the characteristics of the powders. In the case of Fe-Cr-based alloys, it has been reported that a small amount of Nb facilitates the formation of passive film and enhances the high-temperature oxidation characteristics [17–18]. Considering this, we can understand that M+ powder with Nb added had enhanced oxidation resistance properties, ultimately reducing the amount of in-flight oxidation of the M+ coating layer.

The average hardness values of M and M+ coating layers were obtained as $662.7 \pm 66.3 \text{ Hv}$ (M) and $726.0 \pm 92.2 \text{ Hv}$ (M+), respectively. According to Szulc et al. [10], in-flight oxidation reduces the adhesion strength between particles and reduces the hardness. In other words, M+ coating layer can be considered to have higher particle adhesion strength and hardness because of repression of in-flight oxidation.

Fig. 3 shows the coefficient of friction (Fig. 3(a)) and wear volumes (Fig. 3(b)) of the two coating layers as measured by the wear test. First, the average coefficient of friction values of M

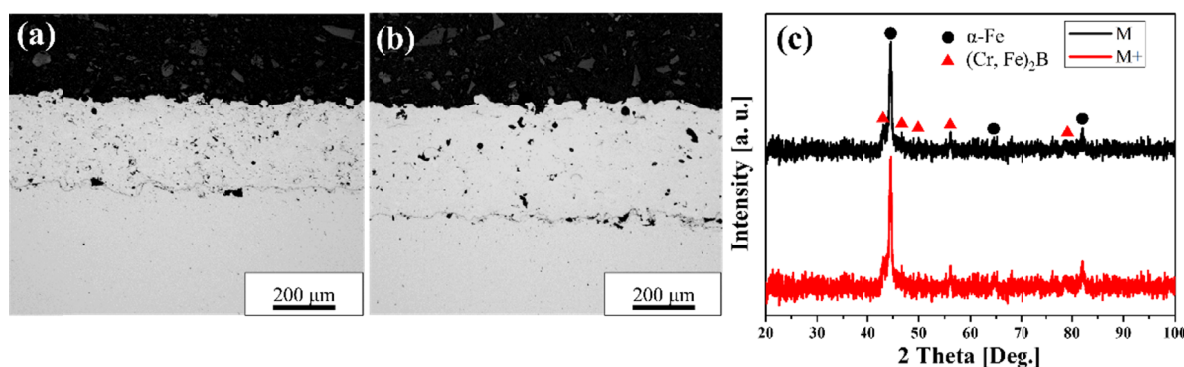


Fig. 1. Macroscopic microstructures of APS Fe-Cr-B based metamorphic alloy coating layers of (a) M, (b) M+, and (c) XRD analysis results of coating layers

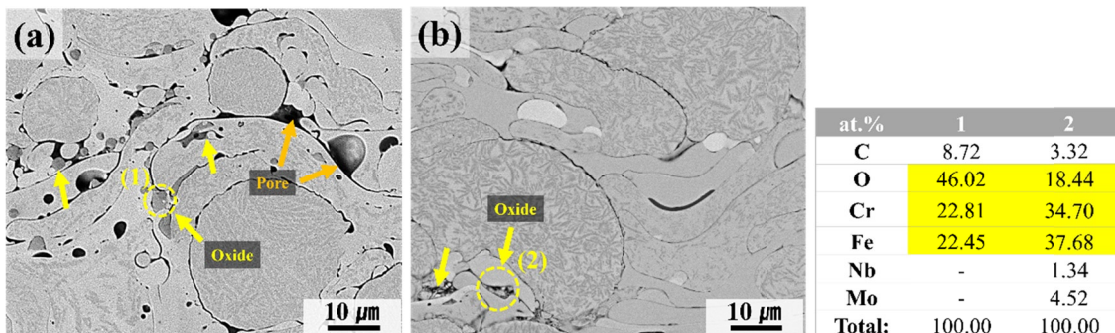


Fig. 2. Microstructures of APS Fe-Cr-B based metamorphic alloy coating layers: (a) M, and (b) M+

and M+ coating layers were M: 0.30, M+: 0.26. The curves of the coefficient of friction revealed that it became constant with increasing wear distance. Wear volumes were measured as M: 0.46 mm³, M+: 0.31 mm³. In other words, M+ coating layer had approx. 1.48 times less wear volume than M (high wear resistance). In addition, the M+ coating layer in this study had

about 2.18 times higher wear resistance than the APS Fe-based metallic glass coating layer (wear volume: 0.676 mm³) reported in our previous research [22].

Fig. 4 shows surface and cross-sectional observation results of worn-out surfaces at the M and M+ coating layers. A macroscopic inspection of the surface of the wear tracks showed that

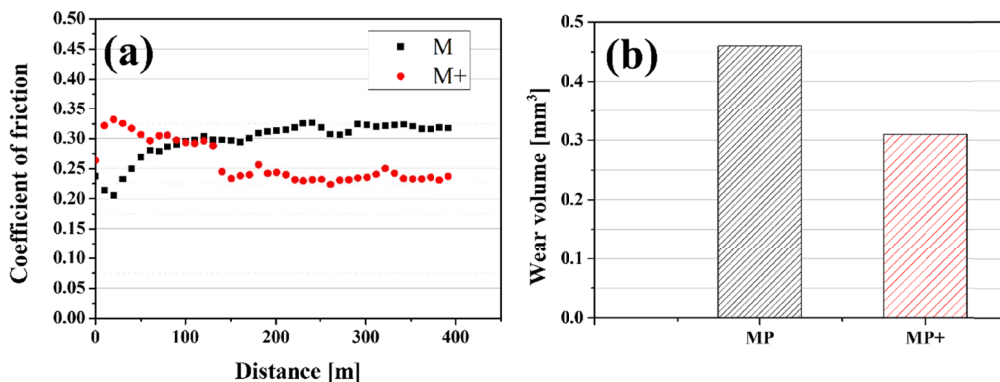


Fig. 3. (a) Coefficient values of friction and (b) wear volumes of APS Fe-Cr-B based metamorphic alloy coating layers

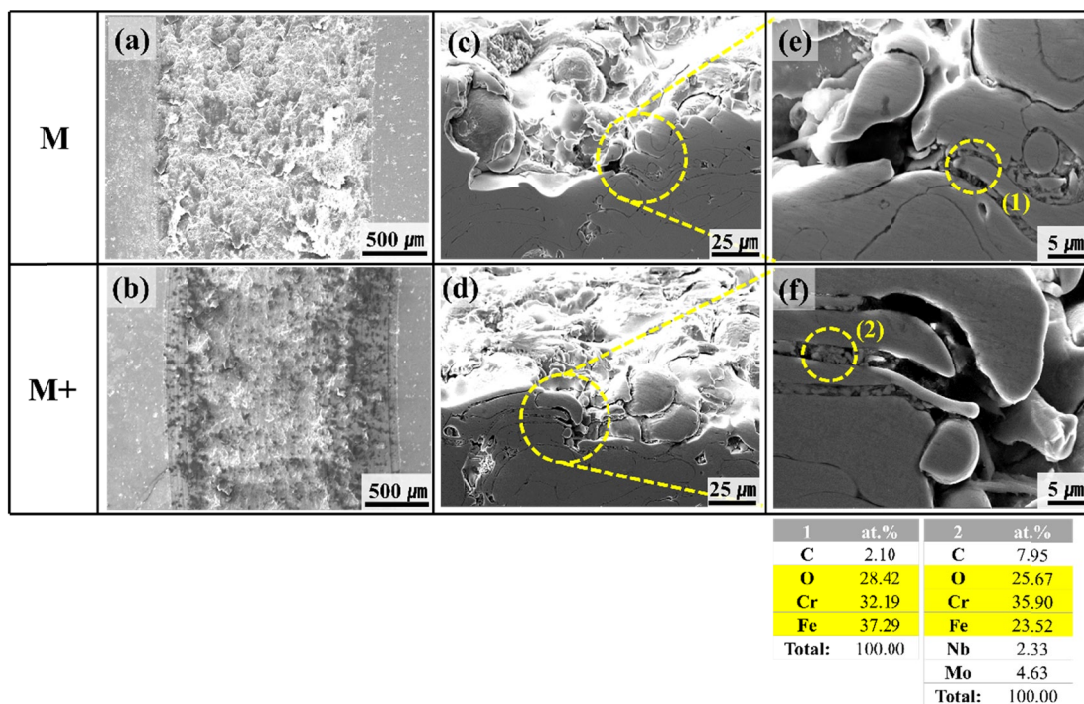


Fig. 4. SEM images of (a-b) worn out surface, (c-d) cross-section region and (e-f) particle boundaries at the worn-out surface

the M+ coating layer worn-out surface (Fig. 4(a)) had smoother surface with some abrasive wear and less delamination behavior than M. On the other hand, the worn-out surface of the M (Fig. 4(b)) was rough due to delamination and adhesive wear behavior. The cross-section of the worn-out surface (Fig. 4(c), (d)) showed that cracks were formed along the particle boundaries. The closed-up images of the particle boundaries (Fig. 4(e), (f)) revealed that the cracks were initiated with a fracture of Fe-Cr oxides that exist in the particle boundaries. Therefore, it is considered as the addition of Nb is effective on improving wear properties of Fe-Cr-B-based metamorphic alloys by controlling in-flight oxidation which causes cracks and delamination.

4. Conclusions

This study investigated the microstructure and wear behaviors of APS Fe-Cr-B-based metamorphic alloy coating layers with addition of Nb and Mo, and compared the results with those of a commercial M. M+ coating layer had less oxides in the particle boundaries than the M. Wear test results showed that the M+ coating layer had superior wear resistance than the M. The worn-out surface of the coating layers shows that wear loss was accelerated by the delamination along the particle boundary, where oxides are usually located. In other words, in-flight oxidation is an important factor that decides the wear property of a Fe-Cr-B coating layer, and the addition of Nb increases in-flight oxidation resistance and enhances the adhesive strength of the new M+ coating layers, resulting in reducing delamination during wear and leading to excellent wear resistance.

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REFERENCES

- [1] K. Lee, D.H. Nam, S. Lee, C.P. Kim, *Mater. Sci. Eng. A* **428**, 124-134 (2006).
- [2] H.W. Jin, Y.M. Rhyim, C.G. Park, M.C. Kim, *Met. Mater.* **3**, 60-64 (1997).
- [3] A.A. Sorour. *Microstructure and Tribology of Fe-Cr-B-Based Alloys*. PhD thesis, McGill University, Montreal, Quebec H3A 0G4, April. 2014.
- [4] K.A. Lee, Y.C. Kim, J.H. Kim, C.S. Lee, J. Namkung, M.C. Kim, *Mater. Sci. Eng. A* **449-451**, 181-184 (2007).
- [5] D.M. Scruggs, USA Patent No. 4725512 (1988).
- [6] Y.A. Joo, Y.K. Kim, T.-S. Yoon, K.A. Lee, *Met. Mater. Int.* **24**, 371-379 (2018).
- [7] J. Gou, P. Lu, Y. Wang, S. Liu, Z. Zou, *Appl. Surf. Sci.* **360**, 849-857 (2016).
- [8] Samsung Heavy Industries, Volvo Group Korea, Korea Patent No. 1019930030183 (1993).
- [9] J.R. Davis, *Handbook of thermal spray technology*, ASM international, Ohio (2004).
- [10] M. Szulc, S. Kirner, G. Forster, J. Schein, *J. Therm. Spray. Tech.* **29**, 932-946 (2020).
- [11] H. Choi, S. Lee, B. Kim, H. Jo, C. Lee, *J. Mater. Sci.* **40**, 6121-6126 (2005).
- [12] H. Xiong, L.L. Zheng, L. Li, A. Vaidya, *Int. J. Heat Mass Transf.* **48**, 5121-5133 (2005).
- [13] K. Volenik, F. Hanousek, P. Chraska, J. Ilavsky, K. Neufuss, *Mater. Sci. Eng. A* **272**, 199-206 (1999).
- [14] M. P. Planche, B. Normand, H. Liao, G. Rannou, C. Coddet, *Surf. Coat. Technol.* **157**, 247-256 (2002).
- [15] J. Ju, C. Yang, S. Ma, M. Kang, K. Wang, J. Li, H. Fu, J. Wang, *Corros. Sci.* **170**, 108620 (2020).
- [16] J. Y. Law, V. Franco, R. V. Ramanujan, *Appl. Phys. Lett.* **98**, 192503 (2011).
- [17] T. Zhao, J. Zhang, L. Teng, Y. Yang, *Trans. Indian. Inst. Met.* **74**, 301-312 (2021).
- [18] S.-Y. Huang, W.-T. Tsai, Y.-T. Pan, J.-C. Kuo, H.-W. Chen, D.-Y. Lin, *Metals* **9**, 975 (2019).
- [19] H. Hu, G. Xu, L. Wang, Z. Xue, Y. Zhang, G. Liu, *Mater. Des.* **84**, 95-99 (2015).
- [20] S. Sharma, C. Suryanarayana, *Scr. Mater.* **58**, 508-511 (2008).
- [21] L. Ma, L. Wang, T. Zhang, A. Inoue, *Mater. Res. Bull.* **34**, 915-920 (1999).
- [22] G.-S. Ham, K.-W. Kim, G.-S. Cho, C.P. Kim, K.-A. Lee, *Mater. Des.* **195**, 109043 (2020).