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Compositive role of TiB_2 in microstructure optimization and wear-resistant improvement of selective-laser-melted $\text{TiB}_2/\text{CrCoFeNiMn}$ high-entropy composite

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ABSTRACT

The CoCrFeNiMn high-entropy alloy and $\text{TiB}_2/\text{CoCrFeNiMn}$ high-entropy composite (HEC) were manufactured by Selective laser melting. For the CoCrFeNiMn, a coarse epitaxial columnar microstructure with strong crystallographic textures was generated. While in the $\text{TiB}_2/\text{CoCrFeNiMn}$, TiB_2 particles are distributed in the significantly refined dendrites and nearly equiaxial grains, and phase transformation occurs to form σ phase. TiB_2 and σ phase construct a strong interface relationship with the matrix. $\text{TiB}_2/\text{CoCrFeNiMn}$ HEC has extremely high microhardness (329 ± 2 HV) and excellent wear resistance (coefficients of friction 0.31 ± 0.02). The wear mechanism of the HEC was studied refer to the microstructure, composition and hardness.

IMPACT STATEMENT

TiB_2 -reinforced CoCrFeNiMn-based high-entropy composite is successfully fabricated by Selective laser melting, which exhibits exceptional hardness and the best wear resistance.

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Microstructures; Mechanical
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High-entropy alloys (HEAs) [1,2], based on five or more principal elements with equal or nearly equal molar fractions, have piqued keen interest due to their unique structure [3], high specific mechanical performance [4], excellent corrosion resistance [5], wear resistance [6, 7] and thermal stability [8]. One of the base HEAs forming a stable single-phase face-centered cubic (FCC) structure is the equimolar alloy CoCrFeNiMn. However, HEAs with an FCC structure experience high wear rates because of relatively low strength and ultra flexibility [9].

Recently, in order to modify the mechanical properties of the FCC structure HEAs, ceramic reinforcement particles such as TiC [10], NbC [11], Cr_3C_2 [12] and Al_2O_3 [13] etc. have been used as in situ synthesized precipitates in HEAs, significantly enhancing the mechanical properties of HEAs. Moreover, in contrast to conventional fabrication technologies, including vacuum induction melting and casting [14], powder metallurgy [15], and mechanical alloying followed by spark plasma sintering [16], selective laser melting (SLM) [17] is one of the most progressive metal additive manufacturing

(AM) technologies. It can build three-dimensional components in an incremental layer-by-layer according to the computer-aided design model. The layer-by-layer nature of the SLM process implies some intrinsic advantages, such as complex geometry manufacturing [18], design freedom [19], ultrafast cooling [20] and high solidification rate [21]. The above advantages can manifestly hinder atomic diffusion and suppress phase transition. Furthermore, it enables a non-equilibrium microstructure characterized by fine microstructure, a supersaturated metal matrix, and high dislocation densities, which is particularly desired for enhanced solid solution strengthening and precipitation strengthening [22]. Therefore, based on the above advantages, SLM has also become the main technology for preparing high-entropy alloys with excellent mechanical properties.

TiB_2 was an excellent candidate for its high hardness, outstanding wear resistance, low density and extraordinary elastic modulus [23] in various ceramic reinforcement particles, commonly selected as strengthening phases in metallic materials [24–26]. Wang et al. [26]

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prepared TiB₂-reinforced CoCrFeNiMn high-entropy composite by laser-engineered net shaping technique (LENS), presenting good mechanical properties and tribological properties. These are closely related to the structural characteristics determined by the LENS parameters and corresponding molten pool morphology. Due to the distinction of forming methods and process parameters, the two AM technologies of SLM and LENS [27] have great differences in the molten pool morphology. Specifically, the depth-to-width ratio of the SLM molten pool is far higher than that of the LENS, which makes the difference of cooling rate between SLM and LENS process reach up to 4 orders of magnitude and is more conducive to the formation of fine crystals. Recognizing this, integrating the advantages of particle strengthening and the SLM technology to modulate the microstructure of HEA and improve the mechanical properties will be a new avenue for the development of HEA. Meanwhile, the existence form of TiB₂ particles in the matrix alloy and the generation of nano-alloying precipitates are closely related to the preparation process of SLM. There are still some uncertainties on the influencing mechanism of microstructure and mechanical properties for adding TiB₂ ceramic particles in HEAs.

Therefore, in the present work, the TiB₂ ceramic particles were in-situ fabricated in CoCrFeNiMn by SLM process. The phases and microstructure refinement of the SLM-fabricated specimens were investigated. The strengthening and wear characteristics of the HEAs composite were revealed. Moreover, this study inspires the development of HEA-based composites.

The feedstock material here is the gas atomized CoCrFeNiMn HEA powders, which are mainly spherical or near spherical. The sizes of particles range from 21.6–67.7 μm , and the powder is only composed of the FCC phase, as shown in Figure 1(a,d). Figure 1(b,c) show the morphology of the mixed powders with a proportion of 3 wt.% TiB₂ (particle size ~ 50 nm) and 97 wt.% CoCrFeNiMn, which were mixed in a planetary ball mill for 4 h at a speed of 120 rpm. The corresponding scanning electron microscope-energy dispersive X-Ray spectroscopy (SEM-EDX) mapping of the particles is shown in Figure 1. It is indicated that the accumulated TiB₂ particles adhered to the surface of HEA powder after ball milling and the sphericity of the powder was well preserved. Cubic specimens were fabricated by a commercial SLM equipment (BLT S210) under argon atmosphere, which is equipped with a 500 W fiber laser (wavelength of 1070 nm) and 60 mm focal beam diameter. The SLM processing parameters included: laser-scan speed (v) of 800 mm/s, laser power (P) of 140 W, scan line hatch spacing (t) of 0.08 mm, layer thickness (h)

of 20 μm , and an alternate-hatching laser-scan strategy with a scan rotation of 67° between consecutive layers was employed. The X-ray diffraction spectra of the CoCrFeNiMn and CoCrFeNiMn + 3wt.%TiB₂ specimens were displayed in Figure 1(d). Compared with the FCC phase of the CoCrFeNiMn HEA powder, it is found that the main phase structure of two printed specimens does not change significantly. The CoCrFeNiMn specimen mainly consists of FCC single-phase structure, whilst the TiB₂/CoCrFeNiMn also contains weak peaks of σ phase. The illustration further reveals that the peak (111) shows a distinct blue shift, which may be attributed to the partial decomposition of TiB₂ particles during the preparation process, and the large size Ti atoms are incorporated into the matrix structure, resulting in the enlargement of matrix cell parameters.

Figure 2 presents representative microstructures and grain size of CoCrFeNiMn HEA and TiB₂/CoCrFeNiMn HEC observed from the cross-sectional plane parallel to the building direction (BD). It is obvious that the microstructures within molten pools of CoCrFeNiMn HEA consist of a coarse directional columnar architecture (Figure 2(a₂)). Moreover, a fraction of columnar grains even continuously span multiple molten pools presenting an epitaxial growth trend, and the growth direction of the overwhelming majority of columnar grains between the adjacent layers moderately alters and tends to be perpendicular to the molten pool boundary (Figure 2(a₁,a₃)). This phenomenon is mainly due to the exact composition of metal powder and solidified alloy matrix, which makes them have better wettability. As a result, the nucleation potential barrier is minimal. When the molten metal temperature is slightly lower than the equilibrium temperature, nucleation is preferentially performed on the base metal. More independent new nucleation is prevented. Meanwhile, the larger vertical temperature gradient determined by the building strategy promotes the full growth of columnar crystals.

Unlike the former isotropic coarse grains of printed HEA in the absence of TiB₂, the microstructure of printed TiB₂/CoCrFeNiMn is remarkably refined and anisotropic. The refined dendritic grains are located inside the molten pool, and on the contrary, many equiaxed grains accumulate at the boundary, as shown in Figure 2(b₁,b₂). The statistical measurement of dendrite arm spacing shows that average primary and secondary dendrite arm spacing are about 1.04 and 0.33 μm , respectively (Figure S1). Some white regions are distributed along grain boundaries (Figure 2(b₃) and (b₆)). Meanwhile, the corresponding EDX elemental mapping images reveal that the TiB₂ nanoparticles are distributed uniformly in the interiors and at the boundaries of grains,

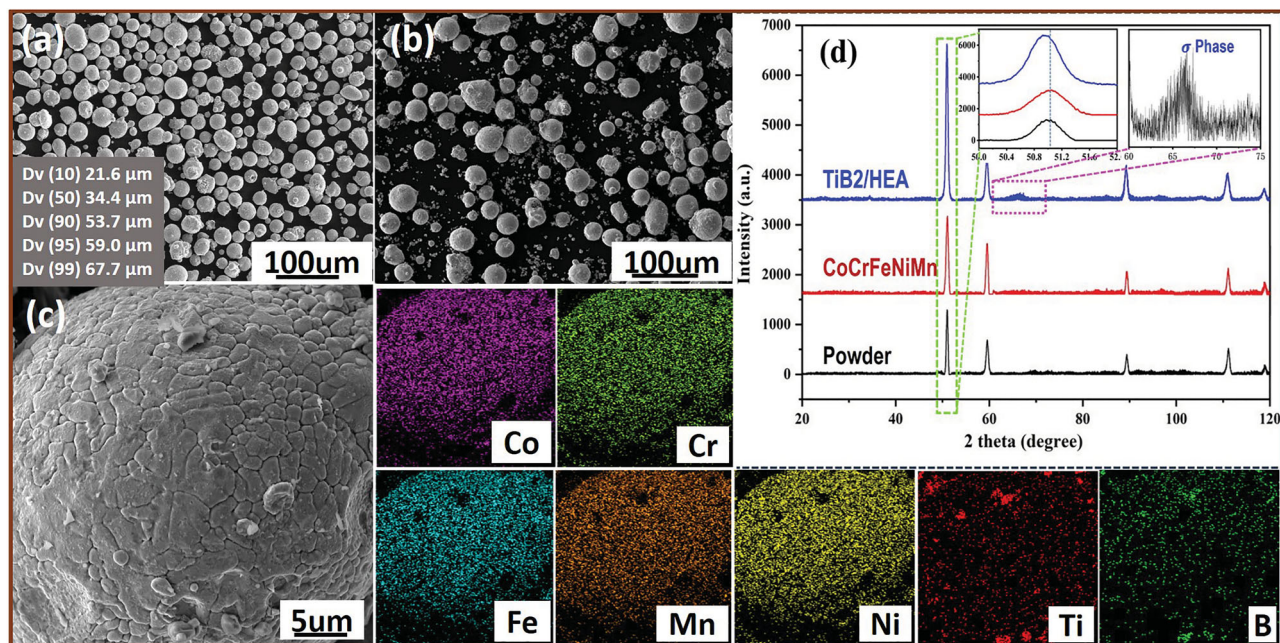


Figure 1. (a) SEM micrograph of CoCrFeNiMn HEA powder, (b, c) micrographs of TiB₂_p/CoCrFeNiMn powder and corresponding EDX maps, (d) comparison of XRD patterns of CoCrFeNiMn HEA powder and as-built CoCrFeNiMn HEA and TiB₂_p/CoCrFeNiMn HEC specimens, and the illustrations correspond to the amplification of FCC (111) diffraction peak and the amplification of sigma (σ) phase diffraction peak.

and no evident cluster phenomenon is found. Significantly, Co, Fe and Ni-depletion and Cr-segregation occurred at the grain boundary, which can be represented by the mechanisms of Bernard Marangoni driven instability [28, 29] and the particle accumulated structure formation [30], elements with a high melting point are more likely to form the segregation for SLM. Thus, Element Cr with a most high melting point in the constituent elements of the experimental HEAs is more likely to form the segregation for SLM [31, 32].

What is more, the inverse pole figures (IPFs) and IPF plots of specimens confirmed a firm texture along the SLM direction (BD) of the as-built CoCrFeNiMn HEA, as shown in Figure 2(a₄, a₅). It is evident that the FCC grains of as-built CoCrFeNiMn HEA present a preferred growth orientation of $\langle 001 \rangle$ along BD, synchronously forming elongated grains and more vigorous texture intensity. Whereas the crystallographic orientations of grains in an as-built TiB₂_p/CoCrFeNiMn show distinct anisotropy in the absence of strong texture intensity (Figure 2(b₄) and (b₅)). Meanwhile, the grain size distributions of the HEA and HEC specimens were statistically analyzed and correspondingly with the average grain sizes of about 20.74 μm vs. 6.83 μm (Figure 2(a₄, b₄)).

It also suggests that, compared to unmodified powders and under the same SLM conditions, the critical value of undercooling required to induce equiaxed and refined grain growth during laser-induced melt solidification in

a molten pool is reduced. The main reason is the presence of high-density low-energy barriers and heterogeneous TiB₂ nucleation sites before the solidification front. Furthermore, the heat source with high energy density during the process of SLM will cause strong Marangoni convection [28, 29, 33] in the molten pool. This dynamic behavior facilitates the dispersion distribution of particles in the molten pool and improves the wettability between particles and HEA melt. And beyond that, some TiB₂ particles distributed in the HEA matrix, acting as an effective growth restrictor, simultaneously play the opposite role of FCC grain growth because of Zener pinning effect [34] exerted by ceramic nanoparticles TiB₂ with high melting point and thermal stability. Then, the synchronous products of enhancing the heterogeneous nucleation potency and growth restriction contribute to formatting desirable, refined, uniform equiaxed HEA grains.

To identify the nanoscale crystal structure of the precipitates and the presence of the TiB₂ particles within the matrix, a high-angle annular dark field (HAADF)-STEM image and the corresponding EDX elemental mapping results were employed. Figure 3 shows the HAADF-STEM images and elemental mappings of the TiB₂_p/CoCrFeNiMn sample. It is obvious that abundant large white precipitates and spherical granular precipitates are dispersed in the matrix, as shown in Figure 3(a₁). EDX mapping results indicated that these

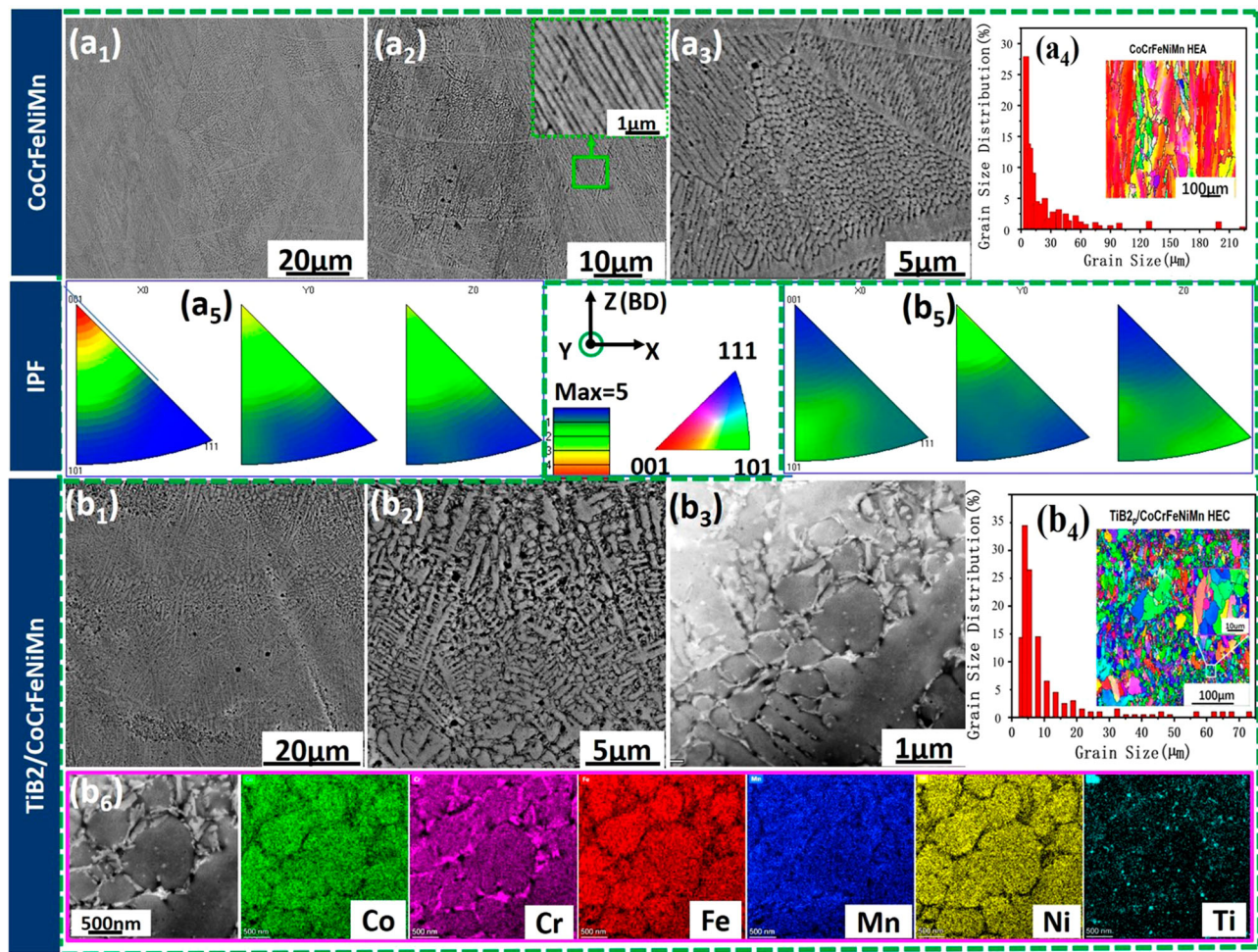


Figure 2. Microstructure BSE images of SLMed CoCrFeNiMn HEA (a_1 - a_3) and $\text{TiB}_{2p}/\text{CoCrFeNiMn}$ composite (b_1 - b_3) in vertical direction (parallel to the BD), EBSD orientation maps and grain size distribution of CoCrFeNiMn HEA (a_4) and $\text{TiB}_{2p}/\text{CoCrFeNiMn}$ composite (b_4), (a_5) and (b_5) IPF maps of CoCrFeNiMn HEA and $\text{TiB}_{2p}/\text{CoCrFeNiMn}$ composite, (b_6) a closer view of the grain boundaries and the corresponding EDX maps of coherent elements, Inset in each figure is in a higher magnification and the reference axis for the IPF map is the Z direction (i.e. build direction).

white precipitates were composed of Cr, followed by Fe, Mn, Co, O and Ni, which were less but the Ni element is missing in some precipitates. Some studies [35–37] also concluded that SLM-built CoCrFeNiMn HEAs had nano-sized Cr-enriched σ phase within the matrix. Based on these literatures, the TEM image and corresponding selected area electron diffraction (SAED) analyses were conducted to identify the nano-sized white precipitates, as shown in Figure 3(a_2), (b_1) and (b_2). The SAED analyses revealed that the precipitates exhibited a tetragonal σ phase crystal structure with an average size of about 85.13 nm (Figure S2) and random growth direction. Furthermore, the high-resolution lattice interfaces relationships and corresponding fast Fourier transformation (FFT) analyses from the interfacial region indicated by the purple color were also deduced, as shown in Figure 3(c_1 - c_3). It is obvious that the tetragonal sigma (σ) phase and primary FCC matrix display the orientation

relationship $[011]_{\text{FCC}}//[1-10]_{\sigma}$ and prove that the σ phase and FCC matrix have a coherent relationship. From the SAED patterns and FFT analyses, it was confirmed that some precipitates were coherent with the matrix, and others were parallel to a certain crystal plane of the crystal. All of them showed a strong interface relationship, which has a strengthening effect on the mechanical properties of the $\text{TiB}_{2p}/\text{CoCrFeNiMn}$ HEC.

In addition, the EDX mapping results indicated that these spherical granular precipitates were the Ti-enriched phases. Figure 3(d_1 - d_3) show the HR-TEM analysis with corresponding FFT for the spherical granular precipitate/matrix interface marked with yellow, which exhibit the orientation relationship of $[011]_{\text{FCC}}//[010]_{\text{TiB}_2}$ between the FCC matrix and TiB_2 particle. Thus, it can be reasonably speculated that the particles were TiB_2 and had a coherent relationship with FCC matrix. On the other hand, the EDX mapping in

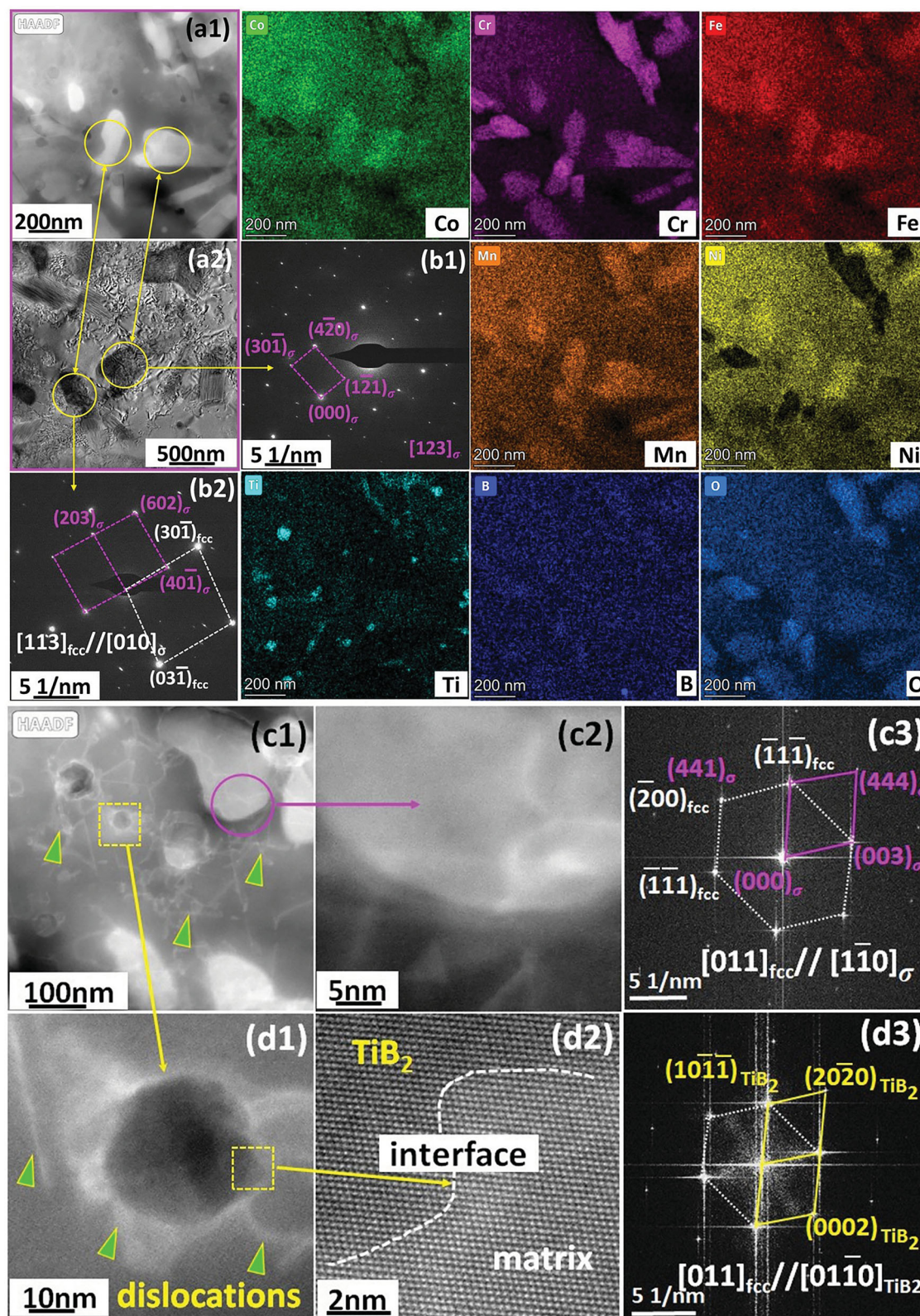


Figure 3. TEM analysis of Cr-enriched σ phases and TiB_2 particle for the $\text{TiB}_2\text{p}/\text{CoCrFeNiMn}$ HEC, (a₁) HAADF-STEM image and corresponding EDX elemental mappings, (a₂) (b₁) and (b₂) TEM image and corresponding SAED patterns, (c₁) HAADF-STEM image containing Cr-enriched σ phases and TiB_2 particle, (c₂, c₃) high resolution lattice image and the corresponding FFT patterns of Cr-enriched σ phases, (d₁-d₃) high resolution lattice image, interface image between TiB_2 particle and matrix, and the corresponding FFT patterns.

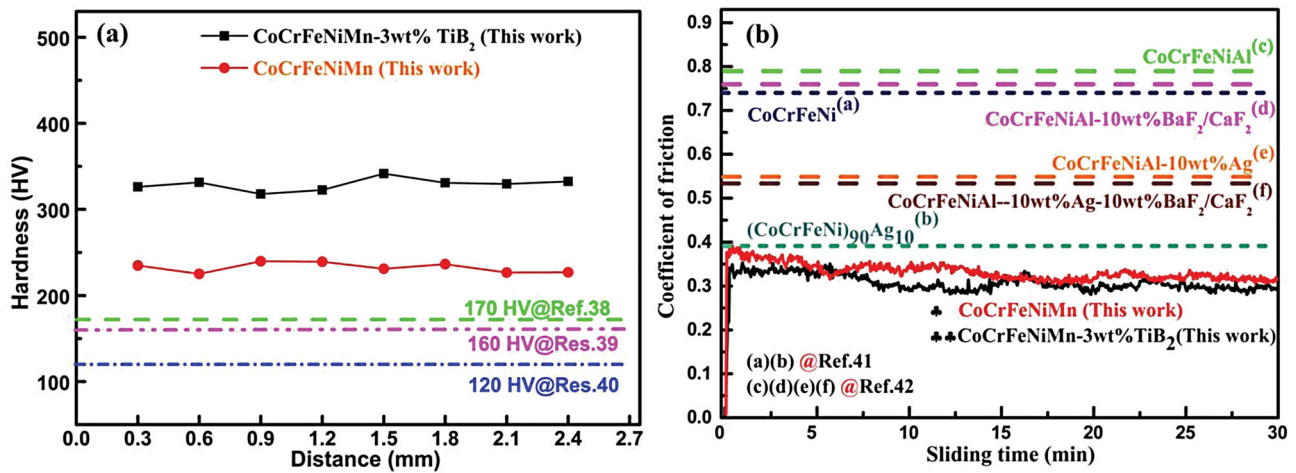


Figure 4. (a) Microhardness distributions along depth direction in the cross-section of SLMed CoCrFeNiMn HEA and TiB₂p/CoCrFeNiMn HEC and other coatings by arc melting [38–40], (b) COFs for SLMed CoCrFeNiMn HEA, TiB₂p/CoCrFeNiMn HEC and similar HEAs prepared by other traditional methods [41,42] sliding against Al₂O₃.

Figure 3 also shows that several in-situ oxides are produced as a precipitate affecting the microstructure of SLM-built TiB₂p/CoCrFeNiMn HEC. This has also been confirmed by SLM-built CoCrFeNiMn HEAs experiments.

The microhardness of the CoCrFeNiMn and TiB₂p/CoCrFeNiMn samples are shown in Figure 4(a). It can be seen that the TiB₂p/CoCrFeNiMn has an average microhardness of 329 ± 2 HV, which is larger than the microhardness 233 ± 5 HV of the CoCrFeNiMn HEA. For comparison, the HEAs with an identical chemical composition of Co, Cr, Fe Ni and Mn produced by arc melting and identified in Figure 4(a) with different color dash lines all show weaker microhardness of 170, 160, and 120 HV [38–40], respectively. This high microhardness of the SLM-built TiB₂p/CoCrFeNiMn HEC system is attributed to the rapid solidification and cooling rate of SLM processing, which results in the reduction of dendrite spacing and the enrichment of solute atoms in the FCC matrix, as shown in Figure S1. Furthermore, the hardness of the TiB₂ particle within the grains is up to 1200 HV, much larger than that of the FCC matrix, and meanwhile σ phase and oxides yielded a significant alloy hardening. Considering the combined effect of the above factors, the microhardness of the TiB₂p/CoCrFeNiMn HEC was also quantitatively estimated (Detailed calculations in the supplementary materials), and the calculated microhardness is about 294.09 HV which is close to the actual measured value (329 ± 2 HV). Consequently, these factors synergistically facilitate the improvement of the hardness.

The dry-sliding coefficients of friction (COF) from the printed CoCrFeNiMn HEA and TiB₂p/CoCrFeNiMn HEC sliding against Al₂O₃ vary with the sliding

time, as shown in Figure 4(b). The COF of printed TiB₂p/CoCrFeNiMn is 0.31 ± 0.02 , which is lower than that of printed CoCrFeNiMn HEA (0.33 ± 0.05). Additionally, some other data of COF results on the spark-plasma-sintered and atmospheric-plasma-sprayed HEAs consisting of Co, Cr, Fe and Ni are also marked by dash lines of different colors [42,42] in Figure 4(b). Therefore, this indicates that the SLM-printed TiB₂p/CoCrFeNiMn HEC in this study has the best wear resistance.

Figure 5 shows 3D surfaces and SEM morphologies of the worn tracks of two specimens after sliding against Al₂O₃. It can be seen from Figure 5 (a) and (d) that the average wear volumes are 14×10^2 mm³ and 9.8×10^2 mm³ for the CoCrFeNiMn and TiB₂p/CoCrFeNiMn. Correspondingly, the maximum depths of the two specimens are about 83.61 μ m and 73.83 μ m, respectively. Meanwhile, the wear rate of TiB₂p/CoCrFeNiMn is 5.806×10^{-5} mm³/Nm, which is about 29.998% lower than that of CoCrFeNiMn (8.294×10^{-5} mm³/Nm). It is found that adhesive wear and abrasive wear play a leading role together, evidenced by large numbers of intense plastic deformation, delamination and plow-furrows on the surface of the two specimens, as shown in Figure 5(b,c,e,f).

In the case of TiB₂-free HEA, there are a considerable accumulation of wear debris, severe plastic-deformation and slight grooves on the surface, showing that the severe adhesive wear and abrasive wear had happened. The reason arises from the weaker hardness of HEA relative to the micro-cutting during wear process. The EDX results of the red wear scar areas A, B and C in Figure 5(c) are displayed in Table 1. In addition to the nearly equal atomic ratio of metal elements corresponding approximately to

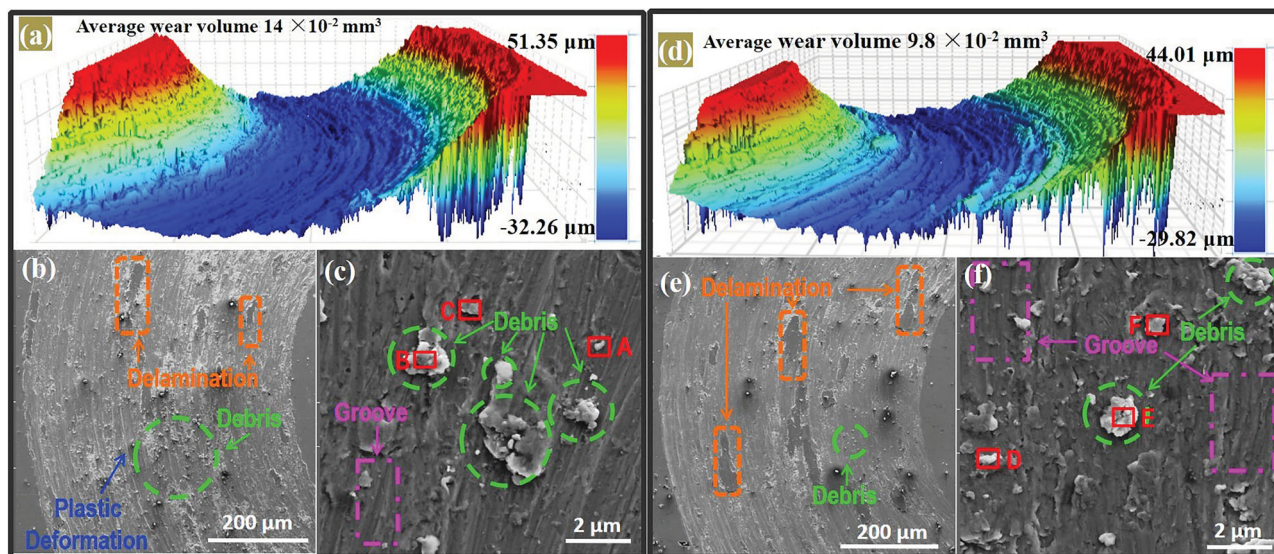


Figure 5. 3D worn morphologies and SEM images of worn surface for two specimens after sliding against Al_2O_3 , (a-c) CoCrFeNiMn HEA, (d-f) $\text{TiB}_2\text{p}/\text{CoCrFeNiMn}$ HEC.

Table 1. EDS analysis results of the red rectangle marked area on the worn surface in Figure 5(c,f) (at %).

Materials	Area in wear surfaces	Chemical composition (at%)							
		Ni	Co	Fe	Cr	Mn	Ti	O	B
HEA	A	22.23	17.30	19.89	18.08	15.46	–	8.59	–
	B	18.80	17.77	15.83	15.40	13.66	–	18.86	–
	C	22.23	21.94	19.05	19.22	15.79	–	1.76	–
$\text{TiB}_2\text{p}/\text{HEA}$	D	18.25	15.83	16.48	15.79	14.04	1.33	18.28	–
	E	15.34	14.25	13.72	13.30	12.89	1.07	29.43	–
	F	20.08	17.35	17.77	15.40	14.69	1.19	13.51	–

the elemental proportions of the matrix, it is particularly noteworthy that high oxygen levels were found in local worn surface. Thus, it suggests that oxidative wear also occurs in the wear process.

As for the introduction of TiB_2 nano-particles, the worn surface exhibits visible grooves accompanied by a reduction in the amount of debris, as seen in Figure 5(e,f), confirming slight material removal during the friction test. The better wear resistance is attributed to the following contributions. Wear performance in materials composed of coarse grains correlates closely with their bulk hardness. According to Archard's law [43,44], the wear resistance of $\text{TiB}_2\text{p}/\text{CoCrFeNiMn}$ is positively related to the hardness. The high hardness of $\text{TiB}_2\text{p}/\text{CoCrFeNiMn}$ -based on the comprehensiveness of multiple reinforcement mechanisms is far higher than the shear force and then conducive to enhancing wear resistance. Besides, the introduction of TiB_2 particles acts as a pinning effect, increasing the resistance to dislocation motion (Figure 3(e,h)) and inhibiting plastic deformation [45,46]. Meanwhile, particles TiB_2 is gradually exposed to the worn surface during the repetitive sliding through Ti

content in EDX results (Table 1), leading to the appearance of projecting reinforcements and playing a load-bearing role. The protruding TiB_2 particulates arouse a decrease in the total contact area and adhesion between friction pairs, accompanied by a reduction in the friction force and wear loss. In addition, the high oxygen content (Table 1) is also observed in the local region (red area D, E and F in Figure 5(f)), which means that oxidative wear behavior still exists on the surface of $\text{TiB}_2\text{p}/\text{CoCrFeNiMn}$ HEC.

In this study, two kinds of CoCrFeNiMn HEA and $\text{TiB}_2\text{p}/\text{CoCrFeNiMn}$ HEC were printed by SLM-assisted AM. The TiB_2 reinforcements achieved a uniform distribution in the HEA matrix, which presents distinct anisotropy and ultrafine grain as less than $6.83\text{ }\mu\text{m}$ in the average grain size, compared with the coarse grains with a preferred growth orientation of $\langle 001 \rangle$ along BD of printed CoCrFeNiMn HEA. The average microhardness of $\text{TiB}_2\text{p}/\text{CoCrFeNiMn}$ composite achieved up to $329 \pm 2\text{ HV}$. It attested that a significant increase in strength was obtained for the SLM-printed $\text{TiB}_2\text{p}/\text{CoCrFeNiMn}$ composite. The printed

TiB₂/CoCrFeNiMn composite exhibited good sliding-wear resistance. The COF also reached a relatively low 0.31 ± 0.02 . In addition, it can be determined that the synergistic effect of abrasive wear, oxidation wear and TiB₂ ceramic particles imparted superior wear resistance to the TiB₂/CoCrFeNiMn composite.

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Disclosure statement

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