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Effects of Different Levels of Boron on Microstructure and Hardness of CoCrFeNiAl_xCu_{0.7}Si_{0.1}B_y High-Entropy Alloy Coatings by Laser Cladding

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Abstract: High-entropy alloys (HEAs) are novel solid solution strengthening metallic materials, some of which show attractive mechanical properties. This paper aims to reveal the effect of adding small atomic boron on the interstitial solid solution strengthening ability in the laser cladded CoCrFeNiAl_xCu_{0.7}Si_{0.1}B_y (x = 0.3, x = 2.3, and $0.3 \le y \le 0.6$) HEA coatings. The results show that laser rapid solidification effectively prevents brittle boride precipitation in the designed coatings. The main phase is a simple face-centered cubic (FCC) matrix when the Al content is equal to 0.3. On the other hand, the matrix transforms to single bcc solid solution when x increases to 2.3. Increasing boron content improves the microhardness of the coatings, but leads to a high degree of segregation of Cr and Fe in the interdendritic microstructure. Furthermore, it is worth noting that CoCrFeNiAl_{0.3}Cu_{0.7}Si_{0.1}B_{0.6} coatings with an FCC matrix and a modulated structure on the nanometer scale exhibit an ultrahigh hardness of 502 HV_{0.5}.

Keywords: high entropy alloy; laser cladding; boron; solid solution strengthening

1. Introduction

It is well known that interstitial solutes can greatly improve the solution-strengthening effect of alloys and have less influence on the fracture toughness in comparison with second phase reinforcement. However, boride precipitation seems unavoidable in traditional alloys, owing to the strong binding energy between small atomic boron and metallic elements [1]. Recently, newly designed high entropy alloys (HEAs) with multi-principal elements are a breakthrough to the conventional alloying concept [2,3]. Several studies have shown that some HEAs are composed of simple solid solution phases with face-centered cubic (FCC) or body-centered cubic (BCC) crystal structure after solidification due to their high mixing entropy values. Some reported alloys—such as FeCoNiCrMn and AlCoNiFeNi₂—display attractive mechanical properties [3–5]. Therefore, it is reckoned that the solid solution strengthening effect plays a key role in the high strength, high hardness, and high wear resistance properties of the HEAs.

Nevertheless, previous studies utilized an arc melting technique to prepare bulk alloy, and reported that the complex brittle boride precipitation is inevitable after solidification in the HEAs, due to high thermodynamic enthalpy of the boride compound [1,6,7]. In comparison to the dominant arc melting synthesis technique, the laser cladding technique—which has a rapid solidification rate of 10^3 – 10^6 °C/s—has a greater ability to prepare high performance HEA coatings in engineering applications [8,9]. This is because the laser rapid solidification can enhance solute trapping and reduce the compositional segregation in solid solution matrix. This improves the solubility and decreases the precipitation tendency of compounds in the HEAs [10,11].

In this paper, we use the laser cladding technique to investigate the influences of boron content on the CoCrFeNiAl_xCu_{0.7}Si_{0.1}B_y HEA coatings. In these alloys, the FCC or BCC matrix phase can be formed when the Al content (*x*) is 0.3 and 2.3, respectively. This is supported by previous reports which suggest that increasing the Al content can trigger a FCC to BCC phase transition in HEAs [12,13]. The Boron content (*y*) was determined to be 0.15, 0.3, or 0.6. The content of Cu and Si was determined to be 70% and 10%, respectively. This is consistent with previous data showing that Cu is easily segregated during solidification and a small additional Si content benefits the cladding quality of the coating [14,15].

2. Materials and Methods

The nominal chemical composition of the powder mixture with the mole ratio of CoCrFeNiAl_xCu_{0.7}Si_{0.1}B_y was obtained by the mechanical mixing of metal powders (at least 99 wt.% purity) of Co, Cr, Fe, Ni, Al, and Cu. Si and B were added using ferrosilicon (77 wt.% Si) and ferroboron (18 wt.% B) powders. The particle size of the powders was in the range of 50–120 μ m. Then, the mixed powders were preplaced onto the surface of Q235 steel substrate (C: 0.17, Mn: 0.08, Si: 0.37, S: 0.039, P: 0.036, Fe: balance in mass percentage) to form a powder bed with a thickness of 1.7–2.0 mm. A 5 kW TJ-HLT5000-type continuous-wave CO₂-laser system with a directly focused laser beam (Unity Laser, Wuhan, China) was used for laser cladding. By the relative movement between the laser beam and substrate, the preplaced powder was melted and produced a single-track rapidly solidified coating strongly bonded with the substrate. High-purity argon gas was used as shielding gas through the coaxial nozzle to prevent oxidation. The laser cladding parameters were given as follows: 2.0 kW laser power, 4.5 mm beam diameter, and 400 mm·min⁻¹ scanning speed. The thickness of the coating after laser cladding was about 1.2–1.5 mm. In the following for simplicity, the component series of CoCrFeNiAl_{0.3}Cu_{0.7}Si_{0.1}B_y and CoCrFeNiAl_{2.3}Cu_{0.7}Si_{0.1}B_y are donated as Al_{0.3}B_y and Al_{2.3}B_y, respectively.

The phase structure and microstructure of the coatings were characterized using a Rigaku smartlab X-ray diffractometer (XRD) (Rigaku, Tokyo, Japan) with Cu-K α radiation operating at 40 kV and 30 mA, and a JSM-6490 scanning electron microscope (SEM) (JEOL, Tokyo, Japan). The component distribution was analyzed by an energy dispersive spectrometer (EDS) equipped with SEM (EDAX, Mahwah, NJ, USA). It is noted that the light element boron cannot be accurately calibrated by EDS. Therefore, it is omitted in the EDS calibration results to avoid the error of other elements. The microhardness was measured in a Vickers hardness tester with a load of 4.9 N and loading time of 30 s. The average value was calculated based on ten measurements made on each coating.

3. Results and Analysis

3.1. Phases

Figure 1a,b show the XRD patterns of the CoCrFeNiAl_xCu_{0.7}Si_{0.1}B_y coatings. It was found that all the prepared HEA coatings are mainly composed of single solid solution phase, while other complex precipitated phases may exist with very low content and cannot be detected by XRD—a desirable result. The main phase is a simple FCC matrix in the series of $Al_{0.3}B_y$ component, while the matrix transforms to a BCC solid solution in the series of $Al_{2.3}B_y$ component. The present results suggest that laser rapid solidification can play an effective role in preventing the precipitation of undesired brittle boride in HEA coatings. Thus, the small atomic boron of interstitial size can be expected to mainly dissolve in the solid solution structure, leading to a supersaturated solid solute strengthening effect in the coatings. A closer look at the XRD diffraction peaks reveals that the peak position shifted to the left with increasing boron addition, and this clearly indicates that the increase of boron content leads to a larger lattice parameter and lattice distortion. Meanwhile, it could also be found that the deviation tendency is higher in the $Al_{0.3}B_y$ component than that in the $Al_{2.3}B_y$ component; this may be attributed to the higher space occupied by octahedral interstice in the FCC lattice compared to the BCC lattice.



Figure 1. XRD patterns of the CoCrFeNiAl_xCu_{0.7}Si_{0.1}B_y high entropy alloy (HEA) coatings: (a) Al_{0.3}B_y component series; (b) Al_{2.3}B_y component series. BCC: body-centered cubic; FCC: face-centered cubic.

3.2. Microstructure

Figure 2 shows the influence of increased boron content on the cross-sectional microstructure at the central region in the series of the $Al_{0.3}B_y$ component. In Figure 2a,b, it can be seen that the $Al_{0.3}B_{0.15}$ coating has a typical dendritic microstructure with obvious growth of secondary arms. The coating was identified to consist of a simple FCC phase. Its dendritic morphology can be attributed to solute segregation, which causes different etching velocities in the two regions during sample preparation. The dendritic and interdendritic regions are marked as DR and ID, respectively. In Figure 2c,d, the $Al_{0.3}B_{0.3}$ coating has a similar dendritic microstructure with refined grain size and greater interdendritic area content.

The EDS results (Table 1) show that the segregation becomes worse with increasing boron content in the coatings. Cr and Fe intend to be enriched in the interdendrite, while dendritic regions are rich in Co, Ni, Cu, and Al. Calculating the mixing enthalpies of atomic pairs between the boron and other alloying elements, the values between B–Fe, B–Co, B–Ni, B–Cr, and B–Cu are -37, -34, -32, -45, and $1.76 \text{ kJ} \cdot \text{mol}^{-1}$, respectively [16]. Low mixing enthalpies suggests stronger binding energy of the atomic pairs. B–Cr and B–Fe should be segregated at the interdendritic areas during the solidification, as they have the lowest mixing enthalpies. Therefore, the component segregation of Cr and Fe is more serious in the $Al_{0.3}B_{0.3}$ coating than that in the $Al_{0.3}B_{0.15}$ coating. Moreover, it was found that boron can play an effective role in improving the clad quality of the coatings, which is evidenced by the decreased porosity defects compared with Figure 2a,c. According to welding metallurgical theory, boron additives can act as strong deoxidizing agents and slagging elements in the laser melted pool, and hence cause the reduction of residual gas formed during solidification.

In Figure 2e, an egg-like core–shell structure—denoted as CS—is clearly observed in the $Al_{0.3}B_{0.6}$ coating. The EDS information indicates that the component in the matrix (MT) is enriched with Co, Fe, Al, and Ni, while the core–shell region has high content of Cu and Cr. Similar core–shell structure was observed in our previously prepared laser cladded nano- Y_2O_3 enhanced AlCoCrCuFeNiSi_{0.5} coating [8]. This is attributed to the liquid phase separation caused by the positive enthalpy of mixing between Cu and other alloying elements. EDS results here also indicate high content of Cu (41.32 at.%) in the CS area, considering the positive enthalpy of mixing value of $1.76 \text{ kJ} \cdot \text{mol}^{-1}$ between the Cu and B atomic pair. It is believed that the CS structure is still formed due to the liquid phase separation. Meanwhile, it is considered that the phases in the CS region may not be a single BCC solid solution, as the component in it is quite different than that of the matrix. Some other phases might exist in low levels, but cannot be detected by XRD analysis. In Figure 2f (the magnified image of the matrix), it can be seen that the microstructure transforms to a modulated basket-weave morphology at the nano-meter scale.

Figure 2. The dendritic (DR) and interdendritic (ID) microstructure in the $Al_{0.3}B_y$ HEA coatings: (**a**,**b**) $Al_{0.3}B_{0.15}$ coating; (**c**,**d**) $Al_{0.3}B_{0.3}$ coating; (**e**,**f**) core–shell (CS) and the magnified matrix (MT) microstructure in the $Al_{0.3}B_{0.6}$ coating.

Component	Regions	Со	Cr	Fe	Ni	Al	Cu	Si
FCC Matrix	Nominal	19.61	19.61	19.61	19.61	5.88	13.72	1.96
Al _{0.3} B _{0.15}	DR	23.45	15.64	16.34	21.34	7.54	13.45	2.24
	ID	19.54	23.34	19.98	20.19	3.65	11.32	1.98
Al _{0.3} B _{0.3}	DR	21.98	13.26	15.91	22.64	7.76	14.78	2.67
	ID	17.74	26.56	22.87	17.35	3.56	10.39	1.53
Al _{0.3} B _{0.6}	MT	26.87	13.87	19.87	23.45	9.56	3.82	2.56
	CS	12.04	19.24	11.43	12.85	2.89	41.32	0.23
BCC Matrix	Nominal	14.08	14.08	14.08	14.08	32.41	9.86	1.41
Al _{2.3} B _{0.15}	DR	14.57	12.09	15.24	13.65	34.09	9.04	1.32
	ID	6.71	26.06	18.72	10.34	29.93	6.86	1.38
Al _{2.3} B _{0.3}	DR	15.18	10.44	19.08	15.48	28.41	10.14	1.27
	ID	6.48	43.44	13.11	12.89	17.40	5.46	1.24
Al _{2.3} B _{0.6}	DR	16.54	5.91	20.01	11.31	39.79	4.95	1.49
	ID	5.42	51.71	3.66	26.84	7.28	3.11	1.98

Table 1. Energy dispersive spectrometry (EDS) results of the elemental distribution in the HEA coatings (boron too small to be detected), at.%.

Figure 3 shows the cross-sectional microstructure in the series of the $Al_{2.3}B_y$ component. In Figure 3a,b, the microstructure of the $Al_{2.3}B_{0.15}$ coating is mainly composed of equiaxed grains. There is no obvious growth of secondary arms due to segregation. The EDS results in Table 1 confirm uniformly distributed alloying element in the coating, indicating that the boron atom is expected mainly to remain in the BCC solid solution matrix. From Figure 3c–f and EDS results in Table 1, it can be seen that the increasing boron content leads to increasing component segregation and coarsened growth of the interdendritic region. The component segregation tendency is similar to that of the $Al_{0.3}B_y$ coatings. The elements Cr and Fe tend to be enriched in the interdendrites, while other elements are enriched in the dendrites.



Figure 3. The dendritic (DR) and interdendritic (ID) microstructure in the Al_{2.3}B_y HEA coatings: (**a**,**b**) Al_{2.3}B_{0.15} coating; (**c**,**d**) Al_{2.3}B_{0.3} coating; (**e**,**f**) Al_{2.3}B_{0.6} coating.

3.3. Hardness Performance

Figure 4 shows the influence of increasing boron content on the hardness in the central area of the HEA coatings. In the series of the $Al_{2.3}B_y$ coatings, the hardness increases from 694 to 756 HV_{0.5} with increasing boron content. In the series of the $Al_{0.3}B_y$ coatings, the hardness is 312 and 342 HV_{0.5} in the $Al_{0.3}B_{0.15}$ and $Al_{0.3}B_{0.3}$ coatings, respectively. The latter is about 10% higher than the former. Moreover, it was found that the hardness in the matrix of the $Al_{0.3}B_{0.6}$ coating greatly increases and reaches approximately 502 HV_{0.5}. This is significantly higher than the hardness reported by a number of previous studies [8,14]. These papers have reported that the HEAs with a FCC matrix generally have good plasticity and low hardness (mostly between 200 to 400 HV).



Figure 4. The average microhardness in the center of the $Al_x B_y$ HEA coatings.

4. Discussion

It is well known that the solid solution strengthening effect of interstitial atoms should be higher than that of a substitutional solute. This is because the interstitial atom can produce a lattice asymmetric distortion, and the substitutional solute is spherically symmetric in crystal lattice distortions. However, most studies have found that brittle boride precipitation is unavoidable by arc melting preparation, and it is difficult to obtain high boron solubility in the boron-containing HEAs [1–3]. The results of this paper prove that laser rapid solidification can play an effective role in preventing the precipitation of the boride phase in HEA coatings.

According to the disorder trapping model during rapid solidification of intermetallic compounds [17], the formation of an ordered structure in the intermetallic compound requires the short-range diffusion of atoms. If the growth interface mobility is sufficiently rapid and approaches the speed of atomic diffusion in the intermetallic crystal lattice, disorder trapping can occur and lead to the formation of a disordered solid solution phase. Therefore, it is considered that the kinetic effect introduced by high solidification rate or undercooling plays a key role in enhancing the growth of the disordered solid solution phase and preventing the growth of boride precipitation in the HEAs. In laser-cladded coatings, only the strong bonding energy between B–Cr and B–Fe atomic pairs can induce component segregation in the interdendritic areas. Boron may accompany Cr and Fe atoms and segregate in the ID region, but partial solute trapping still occurs and prevents the growth of boride precipitation.

As for the $Al_{0.3}B_{0.6}$ coating, HEAs with a simple FCC matrix are rarely reported to have such high hardness. The hardness in the $Al_{0.3}B_{0.6}$ coating is more than 50% higher than the hardness in the $Al_{0.3}B_{0.15}$ and $Al_{0.3}B_{0.3}$ coatings. This can be attributed to the formation of the nanometer-modulated structure. As the coating mainly has a simple FCC phase, the two phases composed of the modulated structure should have similar crystal lattice with slightly different lattice constant. Future studies should be carried out on the formation mechanism of the core–shell structure and the nanometer-modulated structure in the $Al_{0.3}B_{0.6}$ coating.

5. Conclusions

- The laser rapid solidification can effectively prevent the precipitation of the boride phase in the boron-containing HEA coatings.
- Increased additional content of the small atomic boron element can lead to an interstitial solid solution strengthening effect and improve the hardness in HEA coatings.
- Increased additional content of boron leads to a high degree of segregation of Cr and Fe in the interdendritic microstructure.
- The CoCrFeNiAl_{0.3}Cu_{0.7}Si_{0.1}B_{0.6} coating with a simple FCC matrix has ultrahigh hardness of 502 HV_{0.5}.

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