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Microstructure and properties of $Al_2CrFeCoCuTiNi_x$ high-entropy alloys prepared by laser cladding

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ABSTRACT

The $Al_2CrFeCoCuTiNi_x$ high-entropy alloys were prepared by laser cladding. Using metallurgical microscope, scanning electron microscopy with spectroscopy (SEM/EDS), X-ray diffraction, micro/Vickers hardness tester, electrochemical workstation and tribometer to test the structure and hardness, corrosion resistance and wear resistance of $Al_2CrFeCoCuTiNi_x$ high-entropy alloys. The result shows that, $Al_2CrFeCoCuTiNi_x$ high-entropy alloys samples consist of the cladding zone, bounding zone and heat affected zone. The bounding between cladding layer and the substrate of a good combination; the cladding zone is composed mainly of axis crystal, nanocrystalline and fine white crystals. The $Al_2CrFeCoCuTiNi_x$ high-entropy alloys coating phase structure simple (FCC and BCC structure) due to high-entropy effect. The surface microhardness of $Al_2CrFeCoCuTiNi_x$ high-entropy alloys samples up to 1102 HV, about 4 times as the substrate, and the hardness increases with increasing Ni content. $Al_2CrFeCoCuTiNi_x$ high-entropy alloys coating has good corrosion resistance in 1 mol/L NaOH solution and 3.5% NaCl solution. With the increase of Ni content, the corrosion resistance first increases and then decreases. The relative wear resistance of $Al_2CrFeCoCuTiNi_x$ high-entropy alloys coating shows a first increased and then decreased trend with the increase of Ni content. Both the hardness and ductility are affected by wear resistance. The coating can play a good protective role on substrate Q235 steel.

1. Introduction

China Taiwan scholar Jien-wei Yeh breakthrough the traditional concept and put forward a new alloy design conception in 1995 [1–3]. The research found that high-entropy alloys have high entropy values and atomic difficult diffusion, easily obtain high thermal stability of the solid solution phase and nanostructures, even amorphous structure. The performance is superior to the conventional alloys. Multi-master element high-entropy alloys is a new alloy world, which has high academic value and great potential for industrial development [4–10].

The mainly process of preparation high-entropy alloys in previously research is the casting method [14–21], the cast product has performance deficiencies (due to thermal expansion and contraction caused by the voids, porosity, etc.), and the process is relatively complex, and high-entropy alloy material microstructure and performance are difficult to control. In this study, the $Al_2CrFeCoCuTiNi_x$ high-entropy alloys were prepared by laser cladding. Laser cladding have the following advantages [11–13]: (1) high energy density, fast heating speed, and small thermal effect on substrate; (2) the low dilution is limited by control the laser input energy, thereby to maintain the excellent properties of the original cladding material; (3) can obtain a fully dense metallurgically bonded layer between the coating and the substrate; (4) due to the rapid heating and cooling process, the laser cladding layers uniform, dense, less microscopic defects.

In this paper, we studied the microstructure and properties of $Al_2CrFeCoCuTiNi_x$ high-entropy alloys, and expect to provide a reference for its further study and application of the alloys.

2. Experimental materials and methods

Choose Q235 steel as the substrate material, the steel has some good properties, but its hardness, wear resistance, corrosion resistance are not ideal. Al, Cr, Fe, Ti, Co, Cu and Ni powder with high purity (greater than 99.5%) as cladding materials.

The matrix was treated by grinding machine, and then uses the cleaning acetone to remove surface dirt and oil. Mixing the alloy powder in a ball mill for 24 h and prevent oxidation, and then mix thoroughly with an organic solvent, pre-coated uniformly on Q235 steel surface, the power thickness is 0.8 mm. Laser cladding was carried out by the laser processing machine (DL-HL-T5000B). The processing parameters were: power P = 2500 W, spot diameter D = 4 mm, the scanning speed for V = 3 mm/s, use argon as the protection gas. With the different Ni content (x in $Al_2CrFeCoCuTiNi_x$ is a molar content, the values are 0.0, 0.5, 1.0, 1.5, 2.0, respectively, following represent five alloys with $Ni_{0.0}$, $Ni_{0.5}$, $Ni_{1.0}$, $Ni_{1.5}$, $Ni_{2.0}$) in the alloys.

$Al_2CrFeCoCuTiNi_x$ high-entropy alloys morphology and microstructures were investigated by metallographic microscope (OM, GX71) and field emission scanning electron microscope (SEM, JSM-6700F). Chemical compositions of different

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micro-area were analyzed by SEM energy dispersive spectrometry (EDS). The high-entropy alloys coating phase composition were identified using an X-ray diffractometer (XRD-7000) with Cu target, voltage 40 kV, current 40 mA, the scan range from 30° to 90°, and the scanning speed is 4 °/min. High-entropy alloys samples hardness were determined using a Microscopy/Vickers hardness tester (TUKON2100), with a loaded of 20 g and a duration time of 10 s, measured seven sets of data, take the average as the final outcome. High-entropy alloys coating and substrate potentiodynamic polarization curves in 1 mol/L NaOH solution and 3.5% NaCl solution were investigated by an electrochemical workstation (CHI660 D) at room temperature, using three-electrode system: the saturated calomel electrode as reference electrode, auxiliary electrode was a platinum electrode, laser cladding specimens as working electrode, the potential scan range in 1 mol/L NaOH solution and 3.5% NaCl solution of −1.0 to 0.0 V and –0.8 to 1.0 V respectively, the scanning rate of 1 mV/s. Use of tribometer to test high-entropy alloys coating relative wear resistance.

3. Results and discussion

3.1. Microstructure and XRD analysis

Fig. 1 shows the $Ni_{1.5}$ high-entropy alloy microstructure. Fig. 2 for TEM image of the cladding zone. Fig. 1(a) for macroscopic feature of metallographic microscope. As can be seen, the geometry of laser cladding shows a circular-arc shape. Cladding layer of $Ni_{1.5}$ high-entropy alloys consists of cladding zone (magnification shows in Fig. 1(b)), bounding zone (magnification shows in Fig. 1(c)) and heat affected zone (magnification shows in Fig. 1(c)). The cladding zone microstructure is relatively simple, mainly composed of equiaxed grains and small nanocrystals distribute on the equiaxed grains, the more types of elements make the alloys solidification structure prone to supersaturated and larger lattice distortion, the atoms diffusion process becomes very difficult, so nanocrystals appears. The cladding zone scattered distributed white small microstructure (magnification shows in Fig. 1(d)). Bounding zone is the transition portion between the cladding powder and the substrate, from Fig. 1(c) we can see that the cladding layer and the substrate with good combination. There are more nanocrystallines near the bounding zone. Heat affected zone is the area where substrate close to the bounding zone, by the rapid laser heating and rapid cooling effect in this portion, a change also occurs to the microstructure. The results of spectrum analysis of A area in Fig. 1(b), B area Fig. 1(c) and C area in Fig. 1(d) are listed in Table 1.

EDS analysis shows that, elements amount of A and B area were approximately equal. Fe content higher than the theoretical content, this is because in the rapid heating of the high-energy laser beam, the surface of the substrate steel Q235 melt with a small thin layer and then solidification together with the cladding powder, Fe content was increased, but marginally, confirm the truth of dilution rate is appropriate. Al element content lower than the theoretical content, this is because the low melting point of Al element, in the role of a high energy laser beam, and Al power will be part burning and evaporation, which is the reason why the molar ratio of the Al element is 2 times of other elements. Cu elements are close to the theoretical content, and the phenomenon of segregation in the intergranular doesn't appear as reported by other researchers. Ti content is significantly more than the theoretical content in area C. This indicated that there exists segregation in the alloy.

The XRD results displayed in Fig. 3. According to the Gibbs phase fraction, the n types of elements alloy, the equilibrium phases number $p = n + 1$, the non-equilibrium solidification phase number $p > n + 1$, due to the high-entropy effect, the microstructure of $Al_2CrFeCoCuTiNi_x$ alloys formed simple face-centered cubic (FCC) and body-centered cubic (BCC) phase and does not tend to form a brittle intermetallic compound, and the number of the phase is far less than eight. Seven elements alloy, its mixing entropy $\Delta Sm = R\ln(n) = R\ln 7 = 1.95R$, R is the gas constant, the value is 8.314 J/mol K, n is the number of elements. $Al_2CrFeCoCuTiNi_x$ seven elements alloys mixing entropy is higher, greater than the entropy change of formation into intermetallic compounds, the emergence of the brittle intermetallic compound is suppressed, and to promote mixing between elements, and the formation of simple face-centered cubic (FCC) and body-centered cubic (BCC) structure [22,23].

3.2. Microhardness

The hardness distribution curves of of $Al_2CrFeCoCuTiNi_x$ high-entropy alloys sample is showed in Fig. 4. The hardness

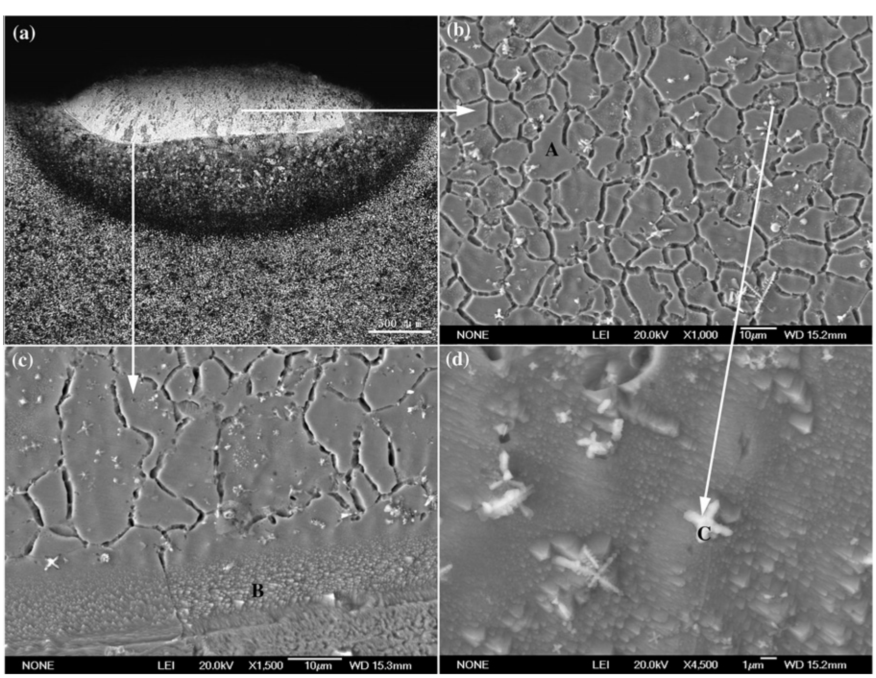

Fig. 1. Microstructure morphologies of the $Ni_{1.5}$ high-entropy alloy (a) macroscopic feature, (b) cladding zone, (c) bounding zone and (d) high magnification feature of cladding zone.