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Corrosion performance of $Al_2CrFeCo_xCuNiTi$ high-entropy alloy coatings in acid liquids

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The $Al_2CrFeCo_xCuNiTi$ high-entropy alloy coatings were prepared by laser cladding on Q235 steel surface. The microstructure was characterized by scanning electron microscopy with spectroscopy (SEM/EDS). Electrochemical workstation was used to test the corrosion resistance of $Al_2CrFeCo_xCuNiTi$ high-entropy alloy coatings and Q235 steel in H_2SO_4 and HCl solutions. Experimental results show that the coating and its substrate are well combined. The cladding zone is mainly composed of equiaxed grains, as well as "cat foot shaped" grains and "snowflake" grains distributed in the matrix grains. Cracks appear in the coatings due to thermal stress. The corrosion resistance of $Al_2Co_xCrCuFeNiTi$ coatings is excellent in H_2SO_4 and HCl solutions, which can be attributed to three factors: the formability of Co element, passivation film formed on the alloy surface and the microstructure of the alloy. Increasing Co content can lead to an enhancement of the corrosion resistance of high-entropy alloy coatings in 0.5 mol/L HCl solution. Cyclic polarization curve shows no pitting corrosion in the 0.5 mol/L H_2SO_4 solution for the $Co_{2.0}$ high-entropy alloy coating, but slight pitting corrosion in 0.5 mol/L HCl solution for the $Co_{0.5}$ high-entropy alloy coating due to the Cl^- in the medium.

1. Introduction

High-entropy alloy is a new kind of alloy developed in recent years, showing some unique high entropy effects, such as hysteretic diffusion effect, lattice distortion effects, "cocktail" effect [1,2]. As results, a series of excellent properties can be achieved in this kind of alloys, for instance high strength and high hardness, high wear resistance, high corrosion resistance, high temperature resistance and high resistivity etc [3–7]. In particular, some high-entropy alloys were also revealed to be excellent in corrosion resistance compared with conventional alloys. For example, Li [8] studied six kinds of high-entropy alloys (CuCoCrNiFe, AlFeCuCoNiCr, $AlFeCuCoNiCrTi_{0.5}$, AlFeCoCrNi, AlFeCuNiCrV and AlFeCuCoNiCrTiV) and found, except for AlFeCuNiCrV alloy, the other five kinds of alloys exhibited excellent corrosion resistant performance, due to their higher corrosion potential than 304 stainless steel (SS), and less corrosion current density and corrosion rate than 304 SS. Our previous work [9] showed that the corrosion current density of AlCrFeNiCuTi alloy in 0.5 mol/L H_2SO_4 solution was reduced by two orders of magnitude, and the corrosion potential was more "positive", in comparison with 304 SS.

The addition of molybdenum is widely recognized for its beneficial effect on the corrosion resistance in SSs. The anodic polarization curves of the $Co_{1.5}CrFeNi_{1.5}Mo_x$ alloy in acids exhibit an active-passive transition, extensive passive region, and $\Delta E \geq 1.2$ V, which is consistent with the stability of H_2O [10,11]. The corrosion current density in the $Co_{1.5}CrFeNi_{1.5}Ti_{0.5}Mo_{0.1}$ alloy is lower than that in $Co_{1.5}CrFeNi_{1.5}Ti_{0.5}$ alloy, which may be attributed to the slightly higher Mo content [12]. In the multi-principal element composition of high-entropy alloys, it is normally noted that Cr, Ni, Co, and Ti are positive to enhance corrosion resistance in acid solutions, but Al, Cu, and Mn often display negative effect. However, the microstructure and the interaction among constituent elements might alter the intuitive prediction [13].

The corrosion resistance of high-entropy alloys is related to the composition, structure, heat treatment and preparation technologies. At present, the main method for preparing high-entropy alloys is vacuum arc furnace casting [14–19]. Other preparation methods include mechanical alloying, electrochemical, thermal spraying, magnetron sputtering, powder metallurgy, laser cladding etc. Laser

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cladding is a recently developed new method and has some advantages such as smaller heat affected zone, finer microstructure, little segregation degree. In addition, the coating and the substrate are metallurgical bonding.

In this study, $Al_2CrFeCo_xCuNiTi$ high-entropy alloy coatings were prepared on the surface of Q235 steel by laser cladding. The microstructure and corrosion properties of coatings were investigated in order to provide reference for further research and application of the alloy.

2. Experimental details

Q235 steel was used as the substrate material. Al, Cr, Fe, Ti, Co, Cu and Ni powder with high purity (greater than 99.4%) was used as cladding power. Before cladding, the Q235 steel surface was treated by grinding machine, and cleaned by acetone to remove dirt and oil. The alloy powder was mixed in a ball mill for 24 h and then precoated uniformly on Q235 steel surface with a layer thickness of 1.0 mm. Laser cladding was carried out on a laser processing machine (DL-HL-T5000B). The processing parameters were: power $P = 2500$ W, scanning speed $V = 3$ mm/s, spot diameter $D = 4$ mm. The samples used for testing corrosion performance were carried out by lap scanning in a lap rate of 35%. Argon was used as protection gas during processing. Fives high-entropy alloy coatings with different Co contents (x = 0.0, 0.5, 1.0, 1.5, 2.0 in $Al_2CrFeNiCo_xCuTi$) were prepared. For simplify, these five alloys were named as $Co_{0.0}$, $Co_{0.5}$, $Co_{1.0}$, $Co_{1.5}$, $Co_{2.0}$ alloys, respectively.

The microstructures of $Al_2CrFeNiCo_xCuTi$ high-entropy alloy coatings were investigated by optical microscope (OM, GX71) and field emission scanning electron microscope (SEM, JSM-6700F). Before observation, samples were sanded, polished and then treated by aqua regia. The chemical composition of studied area was analyzed by energy dispersive spectrometry (EDS). The potentiodynamic polarization curve and cyclic polarization curve of the studied coatings and substrate in 0.5 mol/L H_2SO_4 solution and 0.5 mol/L HCl solution were investigated by an electrochemical workstation (CHI660 D) at room temperature. Three-electrode system was used, in which the saturated calomel electrode is a reference electrode, auxiliary electrode is a platinum electrode and laser alloying specimens is a working electrode. The potential scan range of polarization curve was −1.0−1.2 V in 0.5 mol/L H_2SO_4 solution and −0.8−0.6 V in 0.5 mol/L HCl solution, respectively. The potential scan range of cyclic polarization curve was −1.0−1.2 V in 0.5 mol/L H_2SO_4 solution and −0.5−0.0 V in 0.5 mol/L HCl solution, respectively. The scanning rate was 1 mV/s.

3. Results and discussion

3.1. Microstructure

Fig. 1(a) is a SEM micrograph, showing the typical microstructure of $Al_2CrFeCo_{0.5}CuNiTi$ high-entropy alloy coating. It can be seen that the cladding coating was ball-lacking shaped, consisting of cladding zone (CZ), bounding zone (BZ) and heat affected zone

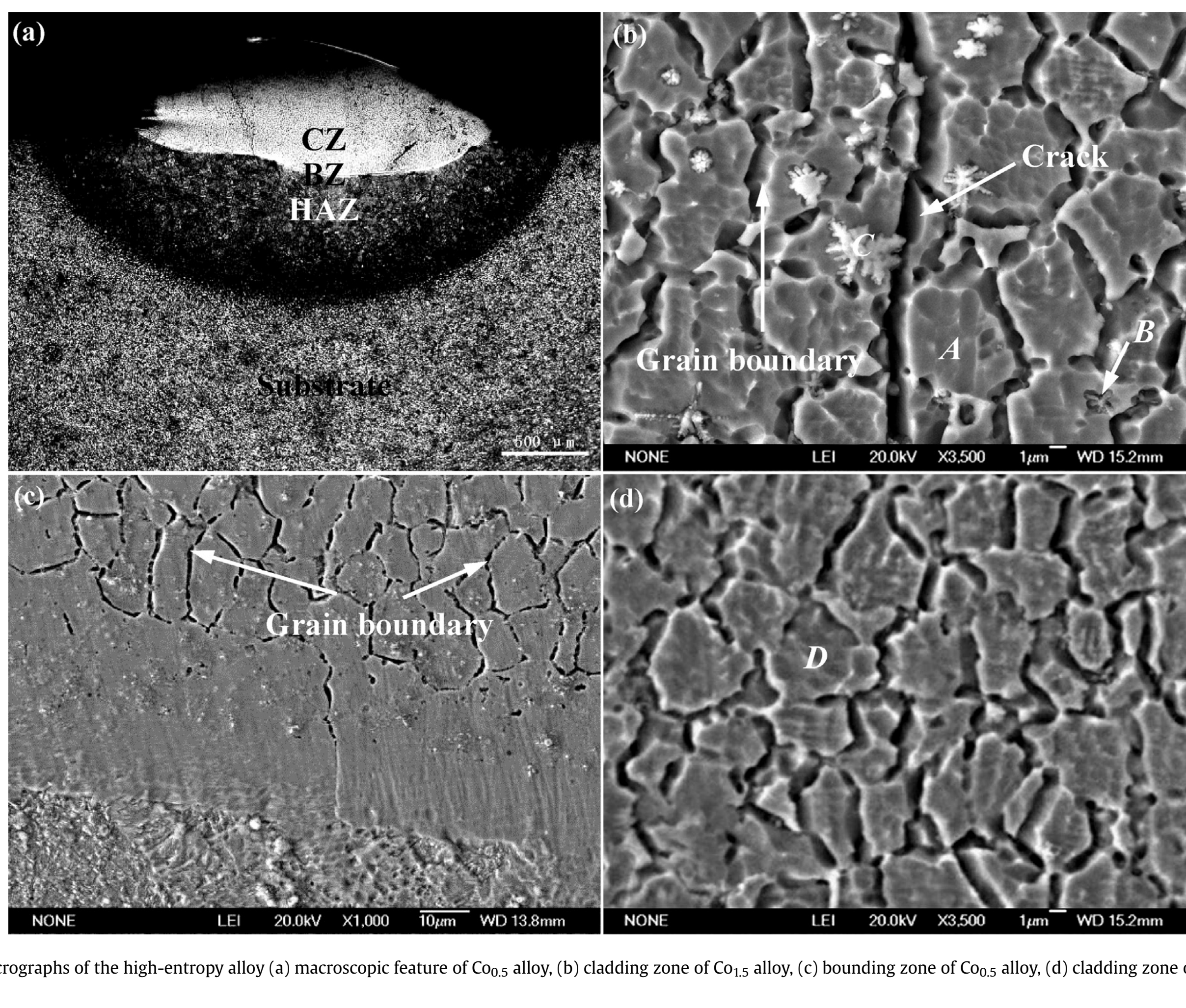

Fig. 1. Micrographs of the high-entropy alloy (a) macroscopic feature of $Co_{0.5}$ alloy, (b) cladding zone of $Co_{1.5}$ alloy, (c) bounding zone of $Co_{0.5}$ alloy, (d) cladding zone of $Co_{2.0}$ alloy.