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Characterization and properties of CuZrAlTiNi high entropy alloy coating obtained by mechanical alloying and vacuum hot pressing sintering

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ABSTRACT

CuZrAlTiNi High entropy alloy (HEA) coating was synthesized on T10 substrate using mechanical alloying (MA) and vacuum hot pressing sintering (VHPS) technique. The MA results show that the final product of as-milled powders is amorphous phase. The obtained coating sintered at 950 °C is compact and about 0.9 mm in thickness. It is composed of a couple of face-centered cubic (FCC), one body-centered cubic (BCC) solid solutions and $AlNi_2Zr$ phase. The interface strength between coating and substrate is 355.5 MPa measured by three point bending test. Compared with T10 substrate, the corrosion resistance of CuZrAlTiNi HEA coating is enhanced greatly in the seawater solution, which is indicated by the higher corrosion potential, wider passivation region, and secondary passivation. The average microhardness of the coating reaches 943 $HV_{0.2}$, and is about 3.5 times higher than the substrate, which is mainly ascribed to the uniformly dispersed nano-size precipitates, phase boundary strengthening and solid solution strengthening. Moreover, the wear resistance of the coating is slightly improved in comparison with the substrate.

1. Introduction

Recently, high entropy alloys (HEAs) as novel materials have attracted increasing attentions due to their unique properties [1,2], such as high strength, superior corrosion resistance, high fatigue and wear resistance [3,4]. Escaping from the design concept of traditional alloys, it is simplified to design HEA compositions that are usually composed of five or more elements with equiatomic or near-equiatomic concentration, which renders the high entropy effect and sluggish diffusion effect [5]. Generally, face-centered cubic (FCC) or body-centered cubic (BCC) solid solutions as the main phases were formed for HEAs [2]. Moreover, some HEAs tend to form nanoprecipitates [6] or amorphous phase [7]. Thus, HEAs are pioneering alloys and have broad application prospects in science and engineering fields.

Additionally, in view of unique properties of HEAs, they can be used for preparing high speed cutting tools, various moulds, refractory skeletons and turbine blades. But it is worth mentioning that the preparation methods of HEAs are mainly concentrated in casting process, which can cause the formation of defects, such as shrinkage holes, dispersed shrinkages and pores, due to thermal expansion and contraction [8–10]. However, the HEA coating is a good way to improve the surface properties of substrate alloys [8,11], and the preparation methods of coatings are mainly plasma transferred arc cladding [11,12], laser cladding [13–15], reactive magnetron sputtering [16] and electrospark process [17]. Cheng et al. have revealed that CoCrCuFeNiNb HEA coating prepared by plasma transferred arc cladding process displayed excellent wear and corrosion resistance compared to Q235 steel substrate [11]. The AlFeCoCrNi HEA coating synthesized by laser cladding process showed better corrosion resistance than aluminum substrate in the NaCl solution [13]. The TiVCrAlSi HEA coatings deposited on Ti-6Al-4V alloy by laser cladding had a remarkable improvement of the oxidation resistance at 800 °C [18]. Thus, the coating could extend the application of HEAs in engineering material field.

However, there are limited reports about the vacuum hot pressing sintering (VHPS), which makes the raw material powders molding and sintering at the same space and time. What's more, mechanical alloying (MA) is a simple, rapid and repetitive solid state processing route to prepare alloy powders. There are some reports that HEAs or amorphous HEAs were synthesized by MA process [19,20]. Thus, it is meaningful that MA and VHPS are combined to synthesize bulk HEA samples.

In this study, CuZrAlTiNi equiatomic alloy powders were synthesized by MA technique. It needs to be noted that these five prin-

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cipal elements have been commonly selected to fabricate amorphous alloys [21,22]. Then, the as-milled HEA powders were chosen to prepare the coating on T10 steel substrate by VHPS furnace. Microstructures and properties including microhardness, wear and corrosion resistance of coating have been investigated.

2. Experimental

The Cu, Zr, Al, Ti and Ni element powders with equiatomic compositions were used as starting materials. All raw metal powders came from Jia Ming Platinum Industry Non-Ferrous Metals Ltd. of Beijing, China. Besides, they all had irregular morphologies with particle size of ~70 μm and purity of >99.5 wt%. The HEA powders were prepared by MA in a planetary ball mill (KE-2L) using stainless steel vials and balls at an Ar atmosphere. The diameters of balls used were 10, 6 and 3 mm, and the mass ratio of these three kinds of balls was 1:1:1. The ball-to-powder weight ratio was 15:1 and the rotation speed was 350 rpm (revolutions per minute).

The T10 steel substrate was processed into cylindrical block with 20 mm in diameter and 5 mm in thickness. Surface of the substrate was ground with 400, 1000 and 2000-grit SiC abrasive papers in turn, followed by polished to mirror using the polishing machine. Then the substrate was cleaned by the distilled water and alcohol in supersonic cleaner orderly, further dried in air. The processed T10 substrate was put into graphite mould, and then the as-milled CuZrAlTiNi powders were superposed to the mirror side of substrate directly. Finally, the upstream head is put on the alloy powders. The graphite mould equipped with sample was put into VHPS furnace (ZT-70-20Y). The thickness of coating obtained was more than 1 mm. The operating vacuum level of the VHPS furnace is 3×10^{-3} Pa. Moreover, the schematic diagrams of the VHPS furnace and graphite mould were shown in Fig. 1. Hot pressing process was conducted to 950 °C at a heating rate of 5 °C/min, under a pressure of 30 MPa with 30 min holding time.

The grinding and polishing of sintered coating surface were the same with T10 substrate except that the types of SiC abrasive papers used were 180, 1000 and 2000-grit in turn. The final thickness of coating after surface grinding was about 0.9 mm. As-prepared aqua regia was dropped on the surface of coating, then after 3 s time, the surface of coating was cleaned with flowing water and washed in distilled water, then dried in air. The cross-sectional sample was prepared by precision cutting machine with diamond tools.

Microstructures of the as-milled powders and coating were examined by X-ray diffraction (XRD, Rigaku D8 Advance) using Cu Kα radiation (λ = 0.15406 nm). The thermodynamic parameters of as-milled powders were determined by a differential scanning calorimetry (DSC, TGA/DSC 1, Mettler-Toledo) at a heating rate of 20 K/min under the continuous flow of purified argon. Morphologies of the as-milled powders and coating were observed using a field emission scanning electron microscope (FESEM, QUANTA FEG 250, FEI), and the chemical compositions were determined by energy dispersive spectroscopy (EDS).

Microhardness was made on the cross-sectional CuZrAlTiNi coating by a Microscopy/Vickers hardness tester (HV-1000), with a loaded of 200 g and a duration time of 15 s. The HV measurements were repeated for ten times, finally obtained the average values and error bars. The interface strength between coating and substrate was measured by three point bending test using universal testing machine (CMT5105, Shenzhen). Corrosion behaviors of the CuZrAlTiNi coating and T10 substrate were carried by electrochemical polarization measurements using a potentiost at (CHI 660E, Chenhua, Shanghai) in the seawater solution. Electrochemical analysis was conducted in a three-electrode cell using a platinum counter electrode and an Ag/AgCl reference electrode, and the scanning rate was 0.003 V/s. Wear resistances of coating and substrate were tested by tribometer (MMG-10) at room temperature, using GCr15 steel as grinding material which was gone through heat treatment. The loading force and rotate speed were 30 N and 200 r/min, respectively, and the holding time is 1200 s.

3. Results and discussion

The CuZrAlTiNi HEA powders after 200 h of MA time consisted of complete amorphpus phase [23]. The onset crystallization temperature (T_x) and melt temperature (T_m) of as-milled powders were obtained by DSC curves [23], and the corresponding values are tabulated in Table 1. The as-milled CuZrAlTiNi amorphous HEA powders are particle-like as well as uniform in size, and average sizes of the particles are about 35 μm, as shown in Fig. 2. From the above results, CuZrAlTiNi equiatomic alloy powders after MA process are amorphous phase rather than solid solutions or intermetallic compounds. Generally, mixing enthalpy ($\triangle H_{mix}$) and atomic difference (δ) [2] play a favorable role on the phase evolution of HEAs, and the related values of CuZrAlTiNi are calculated and listed in Table 1. As can be seen, the values of $\triangle H_{mix}$

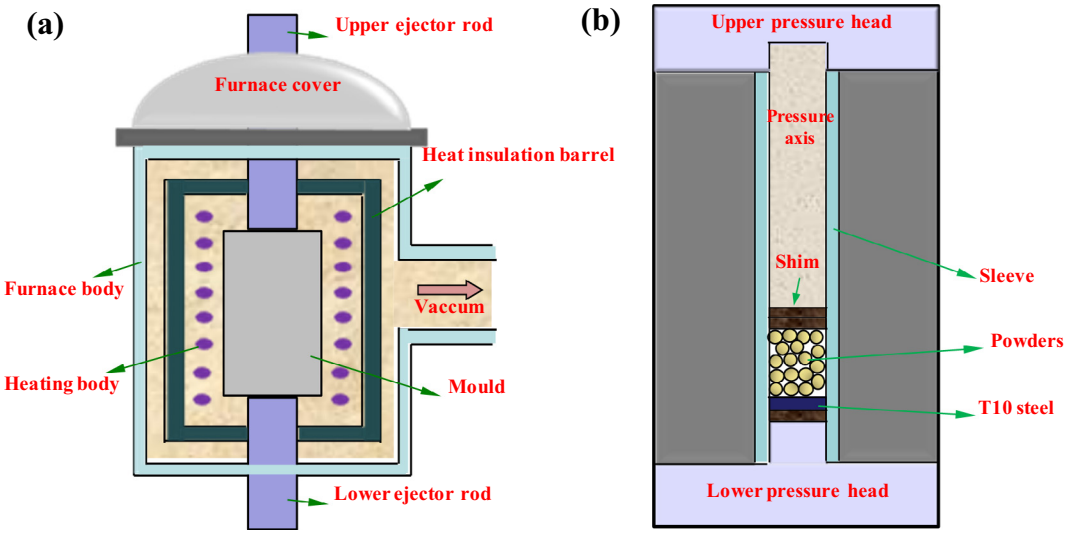

Fig. 1. The schematic diagrams of the hot pressing setup (a) and mould (b).