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Phase evolution and cavitation erosion-corrosion behavior of FeCoCrAlNiTi$_x$ high entropy alloy coatings on 304 stainless steel by laser surface alloying

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ABSTRACT

FeCoCrAlNiTi$_x$ (x: molar ratio, $x = 0.5$, 1.0, 1.5 and 2.0) high entropy alloy coatings were prepared on 304 stainless steel by reaction synthesis of Fe with Co-Cr-Al-Ni-Ti$_x$ powder, aiming at investigating the effect of Ti elements on their phase evolution, microstructure, microhardness and cavitation erosion-corrosion behavior. Experimental results showed that the crystal structures of FeCoCrAlNiTi$_x$ high entropy alloy coatings evolved from FCC + BCC structures for $x = 0.5$ and 1.0 to FCC + BCC + Ti$_2$Ni structures for $x = 1.5$, and then to FCC + BCC + Ti$_2$Ni + ordered BCC structures for $x = 2.0$. The phase formation of FeCoCrAlNiTi$_x$ coatings was analyzed based on rules of high entropy alloys. It was found that the formation of simple solid solution was governed by the competition outcome of mixing entropy (ΔS), mixing enthalpy (ΔH), atom-size difference (δ), valence electron concentration (VEC). The microhardness of FeCoCrAlNiTi$_x$ coatings increased obviously from 615 HV to 730 HV with the addition of Ti element, which was at least 3.6 times that of 304 stainless steel substrate (170 HV). Accompanying the increase in hardness, the alloy for $x = 2.0$ exhibited the best cavitation erosion resistance among the tested samples in distilled water, but the worst in 3.5% NaCl solution, which was attributed to the fact that corrosion played an important role among the tested samples.

1. Introduction

Conventional alloys are mainly based on one or two principal elements via the addition of minor elements to improve their properties, such as Fe-, Al-, Mg-, Ni-, NiAl-, TiAl-base alloys and even for bulk amorphous [1–3]. According to the general facts of physical metallurgy, it can be predicted that using multiple major elements may form many intermetallic compounds or complex brittle phases, leading to brittleness and difficulties in processing and application [4]. This has restricted the number of alloys that can be studied and utilized. Different from the conventional alloy design concept, high entropy alloys (HEAs), which are defined as solid solution alloys having at least 5 principal elements, but no more than 13 elements, with concentrations of each principal element ranging from 5% to 35% in atomic fraction, are emerging as one of the hot research frontiers in the metallic materials field [5,6]. The concept of HEAs breaks the bottleneck stage of conventional alloys by using a variety of principal elements to prepare high property alloys. The HEAs are reported to be good candidates as structural and functional materials as they have the various combinations of high strength and hardness, good thermal stability, magnetic property or excellent resistance to corrosion, wear and oxidation, and so on [7–11]. Li et al. [7] have thoroughly investigated the FeCoNiMn$_{0.25}$Al$_{0.25}$ HEA from crystal structure to magnetic and mechanical properties. This particular study revealed that this HEA composed of FCC structure was very stable to the variations of stress and temperature, no phase transformation occurring until 1000 °C. The annealed FeCoNiMn$_{0.25}$Al$_{0.25}$ HEA had a balanced ductility and yield strength (47.1% total elongation and 331.4 MPa, respectively). Meanwhile, the FeCoNiMn$_{0.25}$Al$_{0.25}$ HEA exhibited a high Curie temperature around 800 °C and better magnetic properties than soft ferrites and comparable properties with Fe-Ni alloys, suggesting its potential applications in high temperature area, such as electric cars, aeronautics and astronautics. Lu et al. [9] have proposed the concept of eutectic high entropy alloys (EHEAs), aiming at achieving good quality industrial-scale HEAs ingots with

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good mechanical properties. They reported that $AlCoCrFeNi_{2.1}$ EHEA possessed simultaneous high strength and high ductility both at room and cryogenic temperatures. Compared to the properties at room temperatures, both the yield strength and fracture strength slightly increased at cryogenic temperatures and a quite good combination of strength and ductility was still maintained at −70 °C. Therefore, HEAs show high values and broad application prospects in science and engineering fields.

Previous studies have shown that the microstructure and mechanical properties of FeCoCrAlCuNi high entropy alloy system have been widely investigated [12], while the rules of phase formation and cavitation erosion resistance have been rarely studied. Ma et al. [13] have explored the feasibility of using the CALPHAD method to investigate the phase stability of HEAs. However, most multicomponent systems are not fully covered by the available CALPHAD databases. Instead, current CALPHAD simulations of multicomponent systems are mainly based on binary, ternary systems. Until now, the existing formation rules of simple solid solutions are all based on conventional alloys having one or two principal elements. As the constituent phases formed in multicomponents systems usually decides the mechanical properties of HEAs to a significant degree, why and how simple solid solutions formed in HEAs needs much more clarification [14]. On the other hand, most of HEAs are usually synthesized by arc melting technology or casting methods [15–17] and only a limited number of studies have focused on their usage in surface modification [18]. To the best knowledge of the authors, a combination of bulk and surface properties may not coexist in a single material, or if they do, the cost may be high [19]. Furthermore, cavitation erosion resistance, like corrosion resistance and wear resistance, is a surface phenomenon and mainly determined by the surface properties of a material rather than by the bulk properties [20]. Cavitation erosion is mainly caused by the localized cyclic impact of fluid against a surface during the collapse of cavities. When cavitation occurs in corrosive media, the synergistic effect between the mechanical and electrochemical processes plays an important role in contributing to the total mass loss [21]. Therefore, it is necessary to select more resistant material or applying a protective coating against cavitation erosion and corrosion. Laser surface modification of stainless steel using various elements (Co, Ni, Mn, C, Cr, Mo and Si) and alloys or compounds (AlSiFe, NiCoCrB and Si_3N_4) was reported in a number of studies by Kwok et al. [22]. The highest increase in cavitation erosion resistance could reach 12 folds. In comparison, laser surface melting of 316L stainless steel could only bring about minimal increase in cavitation erosion resistance (20%). In general, the degree of improvement achieved by laser surface alloying (LSA) is higher than that in laser transformation hardening and laser surface melting. Kwok et al. [22] have reported that the resistance of laser surface-alloyed stainless steel using NiCrSiB was improved by factors of 7.7. Zhang et al. [23] have found that the FeCoNiCrCu coating exhibited a wider passive region and higher corrosion resistance compared to the NiCrSiB coating. However, the total content of Ni, Cr and Co in the FeCoNiCrCu coating was only about 60% that of the NiCrSiB coating. Therefore, the HEA coating prepared by laser surface alloying has lower cost in preparation and shows great potentials for use in cavitation erosion and corrosion environment.

In the present study, FeCoCrAlNi alloy system which has been commonly investigated was selected as the matrix alloy, and Ti with various content was added. Compared with AlCoCrCuFeNi system, Cu was removed as it would lead to serious segregation and deteriorate corrosion resistance [24]. The mixture was laser processed to form $FeCoCrAlNiTi_x$ HEA coatings, in which Fe was introduced into the coatings because of partial melting of the 304 stainless steel substrate. The phase evolution, microstructure, mechanical properties and cavitation erosion resistance in distilled water and 3.5% NaCl solution of $FeCoCrAlNiTi_x$ HEA coatings with the variation of x from 0 to 2.0 were investigated and discussed. The current study aims at (a) exploring phase evolution mechanisms of the HEA coatings during laser processing and (b) exploring damage mechanisms during cavitation erosion in distilled water and 3.5% NaCl solution, and optimizing the Ti content of $FeCoCrAlNiTi_x$ HEA coatings on 304 stainless steel by reaction synthesis of Fe with Co-Cr-Al-Ni-Ti_x powder system.

2. Materials and experimental details

2.1. Materials and specimen preparation

As-received 304 stainless steel in the form of plate with dimensions of 40 mm × 20 mm × 10 mm was used as the substrate material, with nominal composition in wt %: 0.08 C; 19 Cr; 11 Ni; 1.0 Si; 2.0 Mn; 0.03 S; 0.035 P and balance Fe. Co-Cr-Al-Ni-Ti_x (x: molar ratio, $x = 0.5, 1, 1.5, 2.0$) powder system of purity 99.9% and particle size ~ 45–100 μm was used as the LSA material. The detailed process of the substrate and powder was reported in our former work [25]. Fabrication of surface HEA coatings on 304 stainless steel was performed using a DL-HL-T5000B type continuous-wave CO_2 laser, in which Fe was introduced into the coatings because of partial melting of the substrate. Within a range of optimisation runs, the optimized process parameters were obtained as shown in Table 1, under which good quality $FeCoCrAlNiTi_x$ (x: molar ratio, $x = 0.5, 1.0$, 1.5 and 2.0, denoted as Ti05, Ti10, Ti15 and Ti20 alloys, respectively) HEA coatings of moderate dilution could be achieved.

2.2. Metallographic and microstructural analysis

After the LSA process, cross-section of HEA coating transverse to the laser tracks was prepared by the usual metallographic techniques and then sectioned, polished and etched with acidic ferric chloride solution (5 g $FeCl_3$, 50 mL HCl and 100 mL H_2O). The constituent phases of HEAs were determined using the X-ray diffraction (XRD, Rigaku, D/max2500Pc) at a scanning speed of 2° min^{-1}, ranging from 20° to 100°. The radiation source used in XRD was Cu K_α ($\lambda = 1.5406$ Å) with nickel filter generating at a voltage of 30 kV and a current of 15 mA. The cross-sectional microstructure and chemical composition of the samples were investigated using scanning-electron microscope (SEM, Hitachi, S-3400N), equipped with an energy-dispersive spectrometer (EDS). The microhardness of the polished surface of the samples was measured by a Vickers hardness tester (HV, Huayin, HVS-1000) with a load of 2 N and a duration time of 10 s. A minimum of seven measurements were performed for each position aiming at determining the average microhardness value.

2.3. Characterization of the coating

Cavitation erosion tests were carried out using untrasonic-induced cavitation facility (HN-500M) resonating at 20 kHz with peak to peak vibratory amplitude of 60 μm, with conforming to ASTM Standard G32-92 [26]. Distilled water and 3.5% NaCl solution, prepared with reagent grade NaCl and distilled water, were used as the test media. The test media were maintained at a constant temperature of 23 ± 2 °C by a circulatory cooling system. All the samples for the cavitation erosion tests were polished to a uniform surface roughness with 2.5 μm diamond paste, and then cleaned, degreased, dried and weighed using an electronic balance with an accuracy of 0.01 mg before and after each subsequent cavitation erosion test. Cavitation erosion tests were carried out for time periods of up to 20 h. The samples were held stationary below the