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Characterization of Al0.5FeCu0.7NiCoCr high-entropy alloy coating on aluminum alloy by laser cladding

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ABSTRACT

Al0.5FeCu0.7NiCoCr high-entropy alloy (HEA) coatings were synthesized on aluminum by laser cladding, aiming at enhancing surface properties. Samples were characterized by using scanning electron microscopy with spectroscopy (SEM/EDS), X-ray diffraction, laser induced breakdown spectroscopy (LIBS), microhardness. The results showed that the HEA coatings exhibited good metallurgical bonding to the matrix by using optimized laser processing parameters. The HEA coatings were composed of fcc + bcc phases. All the composed elements can be noted in mapping through the calibration of the plasma, and the plasma of the collected Al confirmed that come from substrate dilution. The intensity change of Al-II reflected the depth variety of the cladding layer. The microstructure of clad layer was consisted of dendrite. The microhardness of HEA layer reached $750HV_{0.2}$ that was about 8 times larger than that of the substrate.

1. Introduction

Aluminum and its alloys have been widely used in the fields of aircraft, household, transportation and military, because of its high intensity, excellent lightweight, high forming quality, and good thermal conductivity [1,2]. However, the low hardness, easy oxidation, poor corrosion and wear resistance limit its wide application. Moreover, it is not feasible to enhance their mechanical properties via conventional solid-state heat treatments and phase transformations, because they have not allotropic transformations [3]. Laser cladding is one of the important surface modification techniques in today's industry due to its several advantages such as high velocity of heating and cooling, low dilution, small heat affected zone and allows the precise adaptation of surface properties [4]. Laser cladding on aluminum and its alloys have been widely investigated. The materials systems that have been studied, including: molybdenum [3], tungsten [2], Ni-Ti-C [5], MMC [6], Ti-Al-Fe-B [7], WC-Co-NiCr [8], TiB2-TiC-Al [9]. However, these researches were only aimed at improving wear or corrosion resistance through coating materials.

The concept of high-entropy alloy (HEA) was presented by Taiwan scholar Yeh and his colleague that break through the traditional alloy design framework, which was on the base of one or two major alloy element [10–12]. With the effects of the lattice distortion, sluggish diffusion, cocktail effect, and high mixing entropy, the HEA easily form simple solid-solution phases and nanostructures during solidification, rather than intermetallic or other complicated phases [13–15]. Owing to these characterizations, the HEAs usually possess several properties, such as high hardness, super corrosion resistance and better wearing resistance [16–19]. Previous HEAs studies focus on arc melting and casting, while the size and costs of HEAs restricted its usage. So high entropy alloys also considered attractive coating materials for enhancing surface behavior. With high temperature and rapid cooling rate during laser processing, the HEA phase was easy to be synthesized, leading to the enthusiasm of study HEA coatings by laser processing. Zhang et al. [20] deposited FeCoCrAlNi high-entropy alloy coating on 304 stainless steel by laser surface alloying. The parameters of mixing entropy (ΔSmix), mixing enthalpy (ΔHmix), atom-size difference (δ) and valence electron concentration (VEC) play a major role in the formation of simple solid solutions. Shon et al. [21] synthesized AlFeCrCoNi HEA alloy on aluminum by laser cladding through using a pre-coating process. They controlled over dilution by combinations double layered coating and higher energy input, while the coating still existed cracks. Meng et al. [22] fabricated AlCoCrCuFeNi high-entropy alloy on the AZ91D surface by using the LMI techniques and the wear resistance was significantly improved. The quality of a

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cladding layer mainly depends on several parameters including laser power, laser beam size, scanning speed, and powder feed rate, which has an influence on the temperature of the clad interaction zone. Moreover, laser cladding is an open-loop technique, which means the quality relies heavily on the skills of the operator. Post-processing is always expensive and time consuming [23].

In recent years, laser-induced breakdown spectroscopy (LIBS) has become one of the online analytical and diagnostic techniques [24]. This technique based on laser ablation of the sample and the analysis by optical emission spectroscopy of the plasma formed. Some advantages of the LIBS technique have demonstrated its unique versatility, such as: rapid and real-time analysis, allowing fast contact-less analysis of almost any type of material, in situ analysis with no sample preparation required, and its relatively low cost [25–27]. Lednev et al. [28] used EDS and LIBS techniques profiling of major components in the multilayer wear resistant coatings, a good correlation between EDS element mapping and LIBS data was established with minor difference explained by different sampling depth. Varela et al. [29] analyzed the characterization of laser claddings based on hard facing alloys and partial dilution of some WC spheres in the coating by using LIBS technique. The behavior of hardness can be explained by LIBS maps which evidenced the partial dilution of some WC spheres in the coating. Song et al. [30] used operating parameter conditioned support vector regression (SVR) method to improve the composition prediction performance during laser process. The SVR methods showed a stable and accurate performance.

Previous reports found that the segregation of copper was due to the enthalpy of mixing between copper and the other main elements were more positive [31,32]. The melting of aluminum matrix resulted in Al enrichment within the coating during the laser processing [33]. In this study, we decrease the atomic percentage of aluminum and copper, then deposit Al0.5FeCu0.7NiCoCr high-entropy alloy coatings on aluminum by laser cladding. The effect of laser processing parameters on the phase formation, substrate dilution and microstructure was investigated by a combination of XRD, LIBS and EDS techniques.

2. Experimental procedure

The 5083 aluminum with dimensions of 60 mm × 20 mm × 10 mm was selected as the substrate material, and then cleaned with acetone to remove surface dirt and oil. The Al, Cr, Fe, Ni, Cu and Co elemental powders had a purity of 99.5% with a size range of 44–149 um (−100 / +325 mesh) as cladding materials. Alloy powder mixed with the aid of a ball mill for 2 h in an argon atmosphere. The mixed powders were then placed onto the surface of aluminum alloy, using ethyl alcohol as binders, and then dried in an oven at 80 °C for 8 h. The thickness of the power was approximately 0.8 mm. Laser cladding was carried out using a Nd: YAG laser of 1.06 um wavelength, and laser beam diameter of 2 mm. With a series of optimization trail runs, the processing parameters were: laser power was 1.1 kW, scanning speed were 270 mm/min, 360 mm/min, 450 mm/min and 630 mm/min. High purity argon gas at a flow rate 10 L/min was used to prevent oxidation. The fiber optic spectrometer was based on the AvaBench-75 optical platform designed, the ambient temperature of the spectrometer was minimal. The wavelength was ranging from 200 to 950 nm, and integration time 100 ms.

After the laser cladding, metallographic samples were sectioned perpendicular to the scanning track with a Wire cut Electrical Discharge Machining (WEDM) machine. The structural features of HEA alloy samples were examined by a EMPYGREAN X-ray Diffraction analysis system (XRD) with Cu Kα radiation at 40 kV and 30 mA. XRD patterns were taken at 2θ angles from 20° to 90° at a scanning rate 4°/min. HEA coatings morphology and microstructure were analyzed by scanning electron microscope (SEM, JSM6510F) equipped with energy dispersive spectroscopy (EDS). The microhardness was measured by MH-60 Vickers Hardness Tester with a load of 200 g and a duration time of 10 s.

3. Results and discussion

3.1. XRD analysis

Fig. 1 shows the patterns of the Al0.5FeCu0.7NiCoCr high-entropy alloy coating with different scanning speeds. Phase analysis revealed the existence of Al peak (fcc1) and HEA phase (fcc2, bcc). In the present study, the Gibbs free energy is used to calculate the formation of high-entropy and can be expressed as:

$$\Delta G_{\mathrm{mix}} = \Delta H_{mix} - T\Delta S_{mix} \tag{1}$$

where $\triangle G_{\mathrm{mix}}$ means mixing Gibb's free energy, $\triangle H_{\mathrm{mix}}$ is the mixing enthalpy, T is the absolute temperature, and $\triangle S_{\mathrm{mix}}$ is the entropy of mixing.

As we know that the $\triangle H_{\mathrm{mix}}$ demonstrate the tendency for ordering or cluster, and the $\triangle S_{\mathrm{mix}}$ at a given temperature indicated the tendency for the formation of disordered solid solutions (DSS) [34]. Furthermore, several investigations proposed that the solid solution formation can be determined based on these parameters including atomic size difference (δ), electronegativity difference ($\triangle\chi$) and valence electron concentration (VEC) [35], which can be expressed as:

$$\Delta \mathrm{H}_{\mathrm{mix}} = \sum_{i=1, i\neq j}^{n} \Omega_{ij} c_i c_j \tag{2}$$

$$\Delta \mathrm{S}_{\mathrm{mix}} = -R\sum_{i=1}^{n} c_i \ln(c_j) \tag{3}$$

$$\mathrm{T}_{\mathrm{m}} = \sum_{i=1}^{n} c_i (T_m)_i \tag{4}$$

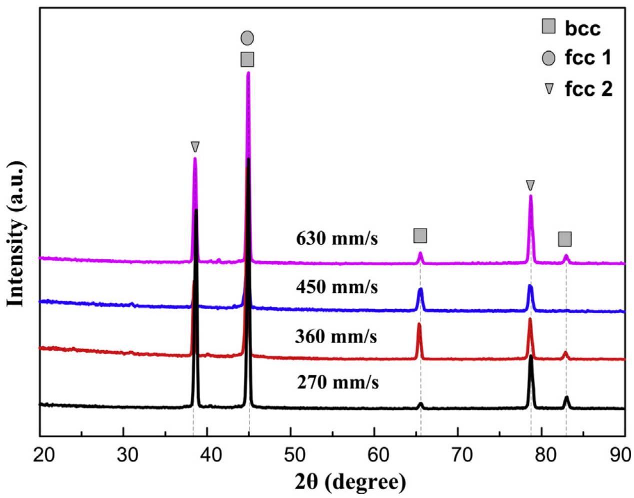

Fig. 1. XRD patterns of the HEA coating.