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Full Length Article

Modified criterions for phase prediction in the multi-component laser-clad coatings and investigations into microstructural evolution/wear resistance of FeCrCoNiAlMox laser-clad coatings

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ABSTRACT

Based on the analyses of a large number of investigations related to laser cladding, the modified criterions in terms of the atomic size difference (δ), the mixing enthalpy (ΔH_{mix}), the mixing entropy (ΔS_{mix}) and the specific laser energy (K) had been proposed to precisely predict phase constituents of the multi-component laser-clad coatings fabricated in a typical nonequilibrium state. The criterions were followed: $10.8 \le \Delta S_{mix} \le 16.2\,J{\cdot}K^{-1}{\cdot}mol^{-1}$, $-17 \le \Delta H_{mix} \le 7$ $kJ{\cdot}mol^{-1}$, $0 \le \delta \le 14$ and $0.04 \le K \le 0.14\,kJ{\cdot}mm^{-2}$, in which the simple solid solution was obtained in a multi-component alloy coating prepared by laser cladding. Among them, δ as the most important criterion was double that proposed in the previous studies, K as a new criterion was first proposed. Moreover, FeCrCoAlNiMox (x = 0.25, 0.75, 1.00, 1.25 and 1.50) high-entropy alloy (HEA) coatings were synthesized on 45# steel substrates by laser cladding, and the investigations into the effect of Mo on dilution rates, macro morphologies, microstructures and mechanical properties (microhardness and wear resistance) of the coatings were carried out. Results showed that the dilution rates of the coatings presented the increasing tendency with the increase in x. The coatings with x = 0.75/1.00 were composed of the single solid solution with a BCC structure. Besides the solid solution, an intermetallic compound rich in Fe and Mo (CrFeNiMo) was also formed in the other three coating with x = 0.25/1.25/1.50. A model was established to estimate the content of each component in the coatings, based on which ΔS_{mix}, ΔH_{mix} and δ were further calculated. The calculated results of the four parameters (δ, ΔH_{mix}, ΔS_{mix} and K) in the five coatings confirmed the validity of the above criterions. With the increasing in x, the average microhardness of the coatings (660, 664, 706, 681 and 642 $HV_{0.2}$) was first increased and then decreased. The maximum value was obtained in the coating with x = 1.00, which was improved about 3.5 times when compared with that of the substrate (about 200 $HV_{0.2}$). The average friction coefficient (0.514, 0.462, 0.443, 0.494 and 0.503), wear volumes (0.281, 0.154, 0.119, 0.177 and 0.254 mm^3) and wear rates (8.29, 5.64, 4.41, 6.28, and 7.43 $mm^3{\cdot}N^{-1}{\cdot}m^{-1}$) of the coatings also confirmed that the coating with x = 1.00 exhibited the optimum wear resistance among the five coatings, which were significantly improved when compared those of the substrate (0.579, 0.34 1 mm^3 and 8.42 $mm^3{\cdot}N^{-1}{\cdot}m^{-1}$).

1. Introduction

Multi-component high-entropy alloys (HEAs) consisting of at least five principal elements were reported by Yeh et al. [1] in 2004, which are usually composed of simple solid solution phases like FCC and BCC. Nowadays, HEAs have gradually become a new research hot in the designing field of metal materials due to their remarkable mechanical properties, outstanding corrosion resistance and excellent wear resistance [2,3]. Wear and corrosion are essentially two surface dependent properties; hence, some bulk materials can be endowed with excellent wear and corrosion resistance by fabricating a thin layer of HEAs on their surfaces without affecting the bulk materials [4]. With the development of surface modifying techniques in recent years, laser processing [5–7], electrochemical deposition [8,9], spraying technology [10,11], magnetron sputtering [12,13], etc. all have been successfully applied to prepare the HEAs coatings/films on different substrates (such as Fe-based, Mg-based, Cu-based, etc.). Among them, laser cladding with rapid heating and cooling rates contributes to the formation of the simple solid solution in the coating by restraining the nucleation of various competing undesired compounds. Moreover, the

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laser-clad coating can reach up to a higher level in thickness (≥1 mm) and has a very strong metallurgical bonding with the substrate [14], when compared with the other surface modification techniques.

Up to now, quite a considerable number of HEAs coatings were fabricated on the different materials, among which Fe-based materials accounted for more than 70 percent. The FeCrCoNiTi HEAs coatings were synthesized on 45# steel substrates by laser cladding [15]. Massive FCC and a tiny quantity of BCC were formed in the coating. BCC phase with high hardness was regarded as the pinning skeleton and effectively inhibited the plastic deformation of the coating during wear. As a result, the wear volume of the coating was reduced by almost half ($5.0 \times 10^{-6}\,\mu m^3$) when compared with that of the substrate ($8.1 \times 10^{-6}\,\mu m^3$). A HEA coating was prepared on Q235 steel by laser cladding high-purity Co, Cr, Al and Cu powders [16]. Both the wear volume and the specific wear rate of the coating were an order of magnitude lower than those of the substrate under a dry sliding condition (the wear volumes of the substrate and HEA coating were $2.96 \times 10^{-7}\,\mu m^3$ and $1.61 \times 10^{-6}\,\mu m^3$, respectively, the specific wear rates of the substrate and HEA coating were $5.48 \times 10^{-5}\,mm^3 \cdot Nm^{-1}$ and $2.98 \times 10^{-6}\,mm^3 \cdot Nm^{-1}$). This was mainly attributed to the increase in hardness of the coating, which was 3 times of that of the substrate. The other HEAs laser-clad coatings had also been explored to improve wear resistance of the Fe-based materials with low hardness (CrCoNiAlMoBx (FCC + BCC) [17], FeCrCoNiMoTi$_{0.75}$Si$_{0.25}$ (BCC) [18], FeCrNiCoMnB (FCC) [19], FeCrCoNi (FCC) [20], Al$_{0.5}$CrFeCoCuNi (FCC) [21], FeCoCrNiB (FCC) [22], AlCoCrFeNiTi$_{0.5}$ (FCC and BCC) [23], MoFeCrTiWAl (BCC) [24], etc.).

Present investigations mainly focus on the selection and optimization of the constituents of the HEAs laser-clad coatings, based on which a correlation between constituents and microstructures/properties is established. It is very essential to confirm the suitable addition contents of different constituents in the coatings, where the simple solid solutions with the optimum solid solution strengthening were synthesized. The determination of the suitable addition contents mainly depends on a large number of experiments, which will take a great cost and tedious work. It is very necessary to establish the criterions to precisely predict phase constituents of the HEAs laser-clad coatings, based on which the compositions can be confirmed easily. The similar criterions in terms of the atomic size difference (δ), the mixing enthalpy (ΔH_{mix}) and the mixing entropy (ΔS_{mix}) had been established [25–30] based on numerous experimental data. Unfortunately, those proposed criterions are mainly suitable to characterize the formation ability of the simple solid solution in the multi-component HEAs fabricated by the traditional method such as casting or arc melting with a comparatively cooling rate. Compared with those methods, laser cladding can be regarded as a typical non-equilibrium processing technique due to its rapid heating and cooling rates. The significant difference in cooling rate is bound to cause the significant change in phase constituent [31,32]. Therefore, whether the present criterions are suitable to laser cladding should be validated, based on which the modified criterions should be proposed.

In this study, the FeCrCoAlNiMox HEAs coatings were synthesized on 45# steel by laser cladding, the effects of Mo on microstructural evolution and wear resistance were investigated in detail. The optimum value (x) was confirmed, in which the coating composed of the single solid solution exhibited the optimum wear resistance. Moreover, based on the analyses of a large number of data reported in the references related to laser cladding, the modified criterions were proposed to characterize the formation ability of the simple solid solution in the HEAs coatings fabricated by laser cladding.

2. Experimental procedures

45# steel was used as the substrate, which was machined into a cylinder of 50 mm in diameter and 10 mm in thickness. The substrate was ground with 300 grit sic abrasive papers to remove the surface contaminants, and then cleaned ultrasonically in acetone for 15 min. The high purity (higher than 99.5 wt.%) commercial powders of Mo, Cr, Co, Al and Ni were chosen as the precursors for laser cladding, which with different mole ratios (x = 0.25, 0.75, 1.00, 1.25, 1.50 in FeCrCoNiAlMox) were mixed for 8 h in a ball grinding mill. An YLS-5000 fiber laser system was used for laser cladding in the study, in which the wavelength of laser output is 1.06 µm. The laser wavelength is only a tenth of that (10.6 µm) in the traditional CO_2 laser frequently used for laser cladding. Some investigations had pointed out that the laser absorptivity of metals presented the incline tendency with the increase in laser wavelength [33,34]. Therefore, the fiber laser is more conductive to preparing the high-quality laser-clad coating. Laser cladding was carried out with the scanning speed of 5 $mm \cdot s^{-1}$, the output power of 3 kW and the spot diameter of 6 mm, which have been optimized to obtain a smooth coating surface with a uniform microstructure free of pores and cracks, and a good metallurgical bonding with the substrate.

Phase components of the coatings were identified by a PANalytical X 'pert Pro X-ray diffractometer (XRD) with Cu Kα radiation (λ = 0.1540560 nm). Microstructure of the coatings was characterized by a Hitachi S-3400 scanning electron microscope (SEM) equipped with a GENESIS EDAX energy-dispersive spectrometer (EDS). Microhardness across the whole cross sections of the coatings was measured by HXD-1000 TMSC/LCD Vickers microhardness tester with the load of 200 gf applied for 15 s. Room-temperature dry sliding wear behaviors of the substrate and coatings were investigated using a CFT-1 ultra-functional wear-test machine. The sliding time was 60 min, the applied load was 30 N and the reciprocating sliding speed was 0.1 $m \cdot s^{-1}$. The hard YG6 ceramic ball with a diameter of 5 mm was chosen as the counterpart. Considering that different roughness of the initial surfaces of the samples affected the test results directly, the surface zones of the samples were polished with 150 grit sic abrasive papers. The friction coefficient was recorded in real time during sliding. Worn morphologies of the samples were observed by SEM. Wear volumes of the samples were measured by a surface mapping profile meter coupled with the wear-test machine. Wear rates (L) of the samples were subsequently calculated by Archard's equation [35]:

$$L = \frac{V}{N \cdot d} \tag{1}$$

in which V signifies the measured wear volume (mm^3), N denotes the normal load (N) and d represents the total reciprocating distance (m).

3. Results and discussion

3.1. Modified criterions for predicting constituent phases in the laser-clad coating

Hume-Rothery rules [36,37], as the most important basic scientific theory for analyzing solid solubility, are widely used to establish the new solid-solution phase formation criterions in a multi-component alloy system. Based on the rules, Zhang et al. [25] proposed the criterions in terms of three parameters (the mixed entropy (ΔS_{mix}), the mixed enthalpy (ΔH_{mix}) and the atomic size difference (δ)), in which the simple solid solutions can be formed when they satisfy $12 \le \Delta S_{mix} \le 17.5\,J \cdot K^{-1} \cdot mol^{-1}$, $-19 \le \Delta H_{mix} \le 5\ kJ \cdot mol^{-1}$ and $0 \leqslant \delta \leqslant 6.5$. Based on the analyses of a large number of data obtained from numerous prepared HEAs, the convincing criterions including ΔS_{mix}, ΔH_{mix} and δ were proposed by Guo et al. [27], which can be expressed by $11 \le \Delta S_{mix} \le 19.5\,J \cdot K^{-1} \cdot mol^{-1}$, $-22 \le \Delta H_{mix} \le 7\ kJ \cdot mol^{-1}$ and $0 \leqslant \delta \leqslant 8.5$. It can be found that ΔS_{mix}, ΔH_{mix} and δ as the three most important parameters were frequently applied to establish the criterions in many studies.

The mixing entropy (ΔS_{mix}) plays a very important role in phase constituent of a HEA. ΔS_{mix} of a HEA is usually high due to the addition of multiple metal elements. When ΔS_{mix} exceeds the entropy of intermetallic compounds, the formation of intermetallic compounds will be