Full length article

# Laser surface alloying of FeCoCrAlNi high-entropy alloy on 304 stainless steel to enhance corrosion and cavitation erosion resistance

S. Zhang [a,*], C.L. Wu [a], C.H. Zhang [a], M. Guan [b], J.Z. Tan [b]

[a] School of Materials Science and Engineering, Shenyang University of Technology, Shenyang 110870, Liaoning, PR China
[b] Shenyang Blower Works Group Corporation, Shenyang 110869, Liaoning, PR China

ABSTRACT

FeCoCrAlNi high-entropy alloy coating was synthesized with premixed high-purity Co, Cr, Al and Ni powders on 304 stainless steel by laser surface alloying, aiming at improving corrosion and cavitation erosion resistance. Phase constituents, microstructure and microhardness were investigated using XRD, SEM, and microhardness tester, respectively. The cavitation erosion and electrochemical corrosion behavior of FeCoCrAlNi coating in 3.5% NaCl solution were also evaluated using an ultrasonic vibrator and potentiodynamic polarization measurement. Experimental results showed that with appropriate laser processing parameters, FeCoCrAlNi coating with good metallurgical bonding to the substrate could be achieved. FeCoCrAlNi coating was composed of a single BCC solid solution. The formation of simple solid solutions in HEAs was the combined effect of mixing entropy ($\Delta S_{mix}$), mixing enthalpy ($\Delta H_{mix}$), atom-size difference ($\delta$) and valence electron concentration (VEC), and the effect of $\Delta S_{mix}$ was much larger than that of the other factors. The microhardness of the FeCoCrAlNi coating was ~3 times that of the 304 stainless steel. Both the corrosion and cavitation erosion resistance of the coating were improved. The cavitation erosion resistance for FeCoCrAlNi HEA coating was ~7.6 times that of 304 stainless steel. The corrosion resistance was also improved as reflected by a reduction in the current density of one order of magnitude as compared with 304 stainless steel.

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## 1. Introduction

Conventional alloys are mainly composed of one or two principal elements via the addition of minor elements to improve their properties, such as Fe-, Al-, Mg-, Ni- and Ti-base alloys. The use of only one or two principal elements has restricted the number of alloys that can be studied and utilized. Different from the conventional alloy design concept, Yeh et al. [1] proposed the concept of high-entropy alloys (HEAs) in 2004 for the first time, breaking the bottleneck stage of conventional alloy design concept. HEAs are defined as solid-solution alloys that contain at least five principal elements, but no more than 13 principal elements with the concentrations of each principal element lying between 5 and 35 at%. According to Yeh and Zhang et al. [2,3], HEAs exhibit simple solid solutions with BCC and/or FCC structure(s), nano-structure or even amorphous, instead of intermetallic compounds or other complex phases, which might be attributed to the effect of high mixing entropy. However, some intermetallic compounds can also form in certain HEAs [4], indicating that the formation of simple

solid solutions in HEAs might not solely depend on the high mixing entropy. Then Guo et al. [5,6] proposed the solid-solution formation rules and improved the theory of HEAs according to the Hume-Ruthery rule. Previous studies have revealed versatile properties of high-entropy alloys, such as high hardness [7], good thermal stability [8], excellent wear and corrosion resistance [9,10]. Taking the $Al_{0.2}Co_{1.5}CrFeNi_{1.5}Ti$ HEA as an example [11], the hardness of $Al_{0.2}Co_{1.5}CrFeNi_{1.5}Ti$ HEA is similar to that of SUJ2 bearing steel and lower than that of SKH51 high-speed steel, but the wear resistance of the former is 3.6 and 2 times higher than that of the two steels, respectively.

Among the previous HEAs studied, HEAs are usually synthesized by arc melting technology or casting methods [4,10,11]. However, the cost of HEAs bulk material may be much higher due to the addition of expensive alloying elements. In view of this point, surface modification technology provides a solution to the problem which could yield a judicious combination of surface and bulk properties, while consuming only a small amount of expensive elements to improve the alloy properties [12]. Recently, it is reported that high-entropy alloy coatings with the thickness of ~1.7 μm were synthesized by magnetron sputtering [13], but the thickness was too thin to meet the mechanical requirements in field applications. Recognizing this, laser surface alloying was

attempted because of its unique features such as the rapid melt-ing-solidification process ($10^4$–$10^6$ K s$^{-1}$), which contributed to the formation of non-equilibrium phases, a dense coating bonded metallurgically to the substrate and homogeneity in micro-structures. In addition, the thickness of the coating can reach the millimeter range [14,15].

Though the microstructure and mechanical properties of the AlCoCrCuFeNi HEAs system have been investigated [1], the rules of phase formation and cavitation erosion resistance have not been reported. It can be concluded that cavitation erosion is formed under the interaction of mechanical, chemical and electrochemical processes during water hammer effect. In most cases, the sy-nergistic effect between the mechanical and electrochemical processes plays an important role in contributing to the total mass loss [16,17]. Therefore, only the material with both good me-chanical property and good corrosion resistance may serve well under hydraulic condition. 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. [18]. The highest increase in cavitation erosion resistance could reach 12 folds. In comparison, laser surface melting of 316 L stainless steel could only bring about minimal increase in cavitation erosion resistance (20%). The in-crease was much higher by laser surface alloying [18]. NiCrSiB has been employed for laser surface alloying of stainless steel, aiming at improving the cavitation erosion resistance [19]. The resistance of laser surface-alloyed stainless steel using NiCrSiB was improved by factors of 7.4. Zhang et al. [20] have investigated the corrosion resistance of FeCoNiCrCu HEA coating prepared by laser technique. The NiCrSiB coating was selected for the comparison of the cor-rosion resistance. It was found that the FeCoNiCrCu coating was easier to be passivated and had a wider passive region and higher corrosion resistance compared to the NiCrSiB coating. The im-provement in corrosion resistance of the HEA coating could be attributed to its structure and the formation of very stable passive films. However, the total content of Ni, Cr and Co in the FeCo-NiCrCu coating was only about 60% that of the NiCrSiB coating. Therefore, the HEA coating has lower cost in preparation. In the present study, we have selected another high-entropy alloy sys-tem, FeCoCrAlNi, as a cavitation erosion resistant coating on 304 stainless steel. Compared with AlCoCrCuFeNi system, Cu was re-moved as it would lead to serious segregation and deteriorate corrosion resistance [21], and Fe in the substrate participated in the formation of solid solution during laser irradiation to form the FeCoCrAlNi HEA coatings. The results of the present study on rules of phase formation, microhardness, cavitation erosion and elec-trochemical corrosion resistance would provide essentials for further research and applications of HEA coatings.

## 2. Materials and experimental details

### 2.1. Material and specimen preparation

As-received 304 stainless steel in the form of plate with di-mensions of 40 mm × 20 mm × 10 mm was used as the substrate material. The nominal chemical composition in wt% is: 0.08 C; 19 Cr; 11 Ni; 1.0 Si; 2.0 Mn; 0.03 S; 0.035 P and Fe balance. The sub-strate was ground clean with 600 grade SiC paper to remove surface oxides or contaminants and then sandblasted to increase surface roughness for enhancing powder adhesion. Equiatomic ratios of the Co, Cr, Al, Ni powders of 99.9% purity and particle size ~45–100 μm were thoroughly mixed with the aid of a ball milling equipment in an argon atmosphere for 2 h before laser surface alloying. The mixed powders were then dried in an oven at 80 °C for 2 h and pre-

placed on the steel specimens with a thickness of approximate 500–600 μm. Laser surface alloying was carried out using a DL-HL-T5000B type continuous-wave $CO_2$ laser. With a series of optimi-zation trial runs, the following parameters at work piece were se-lected for subsequent laser processing: laser power=2 kW, laser spot diameter=3 mm, scanning speed=3–7 mm s$^{-1}$, and high-purity argon gas at a flow rate 15 L min$^{-1}$ was used as shielding gas to prevent oxidation. Coating over the entire substrate surface was obtained by overlapping the single-tracks at a 50% track-width. As a comparison, CoCrAlNi laser rapid prototyping alloy was also pre-pared by high-energy laser beam irradiation, similar to the HEA coating on 304 stainless steel.

### 2.2. Characterization of the coating

Cross-section of the HEA coating transverse to the laser tracks was prepared by the usual metallographic techniques and etched with 5 g $FeCl_3$ +50 mL HCl +100 mL $H_2O$ solution. The micro-structure and chemical composition of the samples were in-vestigated using scanning-electron microscope (SEM, Hitachi S-3400N), equipped with an energy-dispersive spectrometer (EDS). The constituent phases of the HEA coating and laser rapid prototyping alloy were identified using an X-ray diffractometer (XRD, Rigaku D/max2500Pc), with Cu K$_\alpha$ radiation and generated at a voltage of 30 kV and a current of 15 mA. The microhardness of the HEA coating was measured with a HVS-1000 Vickers hardness tester with a load of 2 N and a duration time of 10 s. Five mea-surements were made at each depth and the average hardness was calculated. The electrochemical corrosion behaviors of the coating and the substrate were investigated by potentiodynamic polar-ization measurements (PARSTAT 2273) in 3.5% NaCl solution (open to air) at 23 ± 2 °C. A saturated-calomel electrode (SCE) was em-ployed as the reference electrode and two parallel graphite rods served as the counter electrode for current measurement. The samples for the electrochemical corrosion were immersed in the electrolyte for 10 min prior to polarization to reach a steady-state condition. The electrode potential was increased at a rate of 1 mV/ s, starting from a potential which was 250 mV vs. SCE below the open-circuit potential. The samples for the cavitation erosion were polished with 2.5 μm diamond paste to ensure consistent surface roughness and then cleaned, degreased and dried before sub-sequent cavitation erosion. Cavitation erosion tests were carried out using ultrasonic-induced cavitation facility (HN-500M) con-forming to ASTM Standard G32–92 [22]. The samples were sub-jected to a series of cavitation erosion tests in 3.5% NaCl solution at 23 ± 2 °C. The frequency and the peak-to-peak amplitude were 20 kHz and 60 μm, respectively. The samples were held stationary below the vibrating stud with a separation of 1 mm between the sample and the vibrating stud. The surface of the vibrating stud was polished by 2.5 μm diamond paste in every intermittent per-iod of 30 min in order to keep a constant surface roughness. The sample was weighed at regular intervals and the weight loss was converted to a cumulative mean depth of erosion (MDE). The mean depth of erosion rate (MDER) was calculated at the end of the test period and the reciprocal of MDER was taken to be the cavitation erosion resistance (Re). These quantities for MDE, MDER and Re can be expressed as [23]:

$$MDE \ (\mu m) = \frac{\Delta W}{10\rho A} \tag{1}$$

$$MDER \ (\mu m \ h^{-1}) = \frac{\Delta W}{10\rho A \Delta t} \tag{2}$$