Surface hardening of CrCoFeNi high-entropy alloys via Al laser alloying

Shuyuan Gou\textsuperscript{a}, Shunchao Li\textsuperscript{b}, Hailei Hu\textsuperscript{a}, Youtong Fang\textsuperscript{c}, Jiabin Liu\textsuperscript{a,c}, Weiping Dong\textsuperscript{b,d} and Hongtao Wang\textsuperscript{c}

\textsuperscript{a}School of Materials Science and Engineering, Zhejiang University, Hangzhou, People’s Republic of China; \textsuperscript{b}College of Engineering, Zhejiang Normal University, Jinhua, People’s Republic of China; \textsuperscript{c}Centre for X-mechanics, Faculty of Engineering, Zhejiang University, Hangzhou, People’s Republic of China; \textsuperscript{d}Key Laboratory of Intelligent Operation and Maintenance Technology & Equipment for Urban Rail Transit of Zhejiang Province, Jinhua, People’s Republic of China

ABSTRACT

Undeformed face-centred cubic (FCC) high-entropy alloys (HEAs) always possess excellent plasticity but low hardness. In this work, Al alloying on the surface of a CrCoFeNi FCC HEA is realized by laser alloying technique. An Al\textsubscript{1.5}CoCrFeNi body-centred cubic (BCC) HEA is \textit{in-situ} generated on the surface of the FCC HEA. The well-bonding BCC HEA layer possesses a hardness as high as 536 HV. The hard surface results in a much lower wear rate of the Al-alloyed specimen than the pristine specimen. This study provides a simple strategy to harden the FCC HEAs by \textit{in-situ} formation of BCC HEA through laser alloying.

IMPACT STATEMENT

A laser alloying technology to harden CrCoFeNi FCC HEA by \textit{in-situ} formation of BCC HEA.

1. Introduction

The conception of high-entropy alloys (HEAs) was first proposed by Yeh in 2004 [1]. Instead of one principal element in traditional alloys, HEA contains more than four elements in near-equiatomic proportions, providing a near-infinite compositional space. Over the decades, various HEAs have been developed involving 3d transition element HEAs [2,3] and refractory metal HEAs [4,5]. The majority of HEAs exhibit a single-phase or multi-phase solid solution although some intermetallic compounds are introduced in HEAs to enhance mechanical properties [6–8]. CrCoFeNi, a HEA with a single FCC phase, is one of the most widely studied HEAs so far [9–11]. It exhibits relatively low strength in the conventional arc-melting production process (yield strength of \(\sim 140\) MPa) [9]. The influence of additional elements on CrCoFeNi has been investigated (e.g. Mo, Al, V, Nb, Ta) [8,12,13]. In particular, the addition of Al element can cause a shift in the stability of the FCC and BCC phase, which changes the mechanical properties significantly [14–16]. With the increase of Al content, strength is enhanced at the expense of ductility [17]. Hence, it is conceivable that both good ductility of FCC phase and high hardness of BCC phase can be achieved by appropriate design and construction of FCC/BCC heterogeneous materials. For CrCoFeNi FCC alloy, BCC
phase transition induced by Al permeation is an interesting and simple thought. However, unlike traditional steel carburization, it is relatively difficult to permeate Al due to its bigger atom size than carbon atom. Laser surface treatment, as a branch of additive manufacturing, has been applied widely in surface modification. The deposited surface layer is capable of improving the surface properties on the basis of preserving the bulk properties. Most researches are focused on conventional steel or titanium substrates [18–20]. Chai et al. [21] achieved gradient equiaxed grain distribution into Zr sheet by combining laser surface treatment, rolling and annealing recently. In this work, Al1.5CoCrFeNi was in-situ synthesized on the surface of CrCoFeNi sheet via Al laser alloying. The wear resistance of the Al-alloyed surface shows remarkable improvement versus pristine specimen. Besides, microstructural details of equiaxed grains within the surface layer are investigated. To the best of our knowledge, this work is the first attempt to harden CrCoFeNi HEA by laser alloying. We expect this method can be extended to other HEAs, given that Al element is a BCC stabilizer for most HEA systems, thereby promoting their application.

2. Materials and methods
A laser alloying apparatus was used to carry out the Al laser alloying on a CrCoFeNi sheet. The corresponding apparatus in this work consists of a fibre laser system, a powder feeder, a KUKA six-axis robot and a cladding head with three beams surrounding the central powder feeding system (Figure S1(a)). The used laser is a continuous fibre laser with a maximum output power of 4500W and a laser wavelength of 1080 nm. Laser intensity distribution is flattened beam with a superposition of multi-modes. The beam diameter is 1.5 mm at their focus. The parameters during laser processing were set as follows: laser power of 1350 W, a scanning speed of 0.06 m/s, a powder feed rate of 1.15 g/min, a shielding argon flow rate of 0.8 L/min, a distance from the cladding head to the workpiece of 15 mm (at the focus), an angle between cladding head and workpiece of 80 ± 0.5° and an offset value of 300 μm.

The alloying material was Al powder with a size distribution of 50–100 μm (Figure S1(b)). FCC phase is identified from the XRD pattern (Figure S1(c)). The CrCoFeNi sheet was produced by arc melting. Before laser alloying, the sheet was processed through homogenization annealing (1000°C for 4 h followed by water quenching), cold rolling (90% reduction) and subsequent annealing (1000°C for 2 h followed by water quenching). The ultimate dimension of the sheet is approximately 100 × 50 × 1.5 mm³. During laser processing, the top layer of the CrCoFeNi sheet was melted to form a molten pool and mixed with the molten Al powder under the impact of Marangoni convection. Then an Al-alloyed layer was achieved on the CrCoFeNi sheet.

After laser processing, a cross-sectional sample was cut along Y–Z plane and prepared by the conventional metallographic method. Phase characterization was carried out by X-ray diffraction on Cu Kα radiation (XRD, Shimadzu 6000). The microstructure was analysed using an optical microscope (OM, LEICA DMLM), scanning electron microscope (SEM, HITACHI, SU-8010) equipped with an energy dispersive spectrometer (EDS, Oxford X-max80) and Electron Back-Scattered Diffraction (EBSD, Hikari XP). Vickers microhardness tests at a load of 0.05 kgf and a dwell time of 10 s were performed to measure the hardness distribution along the depth of the specimen.

The wear test was conducted on an HSR-2M friction testing machine at the condition of dry friction. The friction pair was ZrO2 with a diameter of 6 mm. The size of specimens for the wear test was Φ 25 mm. The parameters of the wear test were: a loading of 5 N, a sliding speed of 5 m/min, and a duration of 20 min. The three-dimensional diagrams were reconstructed on a LEICA DCM3D laser confocal microscope. Five sectional profiles of the wear tracks were recorded to calculate average wear rates. The wear rate (δ) was calculated by the following equation [20]:

$$\delta = \frac{\Delta V}{\Sigma W} = \frac{\Delta V}{F_n \cdot d}$$

(1)

where $\Delta V$ indicates wear volume (m³), $W$ is work (J), $F_n$ represents applied load (N), and $d$ indicates sliding distance (m).

3. Results and discussions
Figure 1(a) shows the XRD pattern of the CrCoFeNi alloy after annealing. As can be seen, the CrCoFeNi alloy is composed of a single FCC phase. Fine grains with an average size of 50 μm and homogeneous element distribution were obtained in the CrCoFeNi alloy (Figure 1(b,c)).

Figure 2(a) shows the SEM cross-sectional image of the Al-alloyed specimen. No visible cracks and defects is found in the surface layer. The corrugated interface indicates the metallurgical bond between the surface layer and substrate. The thickness of the surface layer is approximately 620 μm. Figure 2(b) shows elemental distributions along the depth of the cross-section, encompassing both the surface layer and substrate. Distributions of Fe, Co, Cr, Ni, Al elements are relatively uniform in the surface layer, suggesting the sufficient mixture of
those elements. An area of 200 × 200 μm² was used for composition quantification in the surface layer and the result is shown in Table 1. It can be seen that the chemical composition of the surface layer is approximately Al₁.₅CoCrFeNi. The XRD result confirms that the surface layer is composed of BCC/B2 phase (Figure 2(c)), as many previous studies show [14,22]. Figure 2(d–f) shows the EBSD characterizations of the area near the interface between the surface layer and substrate. The surface layer is composed of BCC phase, which is consistent with XRD results, while the substrate remains FCC phase (Figure 2(d)). The Inverse pole figure (IPF) map in Figure 2(e) reveals that the surface layer is mainly composed of equiaxed grains with random orientation, rather than oriented columnar grains which are commonly found in the additive manufacturing (AM) alloys [23,24] (Given that three-dimensional scale of grains, the X–Y, X–Z planes are also examined and found to be characterized by fine equiaxed grains likewise). Besides, the statistical grain size of the surface layer (d_{surf}) is approximately 12 μm on a Gauss distribution, as shown in Figure 2(f).

Based on the above analysis, it can be concluded that the addition of Al cause a shift in the stability of an FCC and BCC phase in the surface layer. In previous studies, many researchers were committed to predicting the phase stability for different HEA systems as a function of composition. Zhang et al. [25] investigated the impact of the atomic size difference and the mixing enthalpy on the phase stability and found the solid solutions tend to form when \(-15 \text{kJ/mol} < \Delta H_{\text{mix}} < 5 \text{kJ/mol}, 1\% < \delta < 5\%\). Guo et al. [12] showed valence electron concentration (VEC) can be used to predict the phase stability in HEAs by:

\[
\text{VEC} = \sum_{i=1}^{n} C_i (\text{VEC})_i
\]

where \(C_i\) denotes the atomic percentage of component \(i\), \((\text{VEC})_i\) denotes the VEC value of component \(i\).

As such, FCC phase exists at \(\text{VEC} \geq 8\) while BCC phase exists at \(\text{VEC} < 6.87\). The VEC of Al₁.₅CoCrFeNi and CrCoFeNi can be calculated based on Equation (2). The results show that CrCoFeNi has a VEC of 8.25, falling in the FCC stable area, while Al₁.₅CoCrFeNi has a VEC of 6.83, just inside the BCC stable area. The required parameters for the calculations are from Ref. [12]. The phases predicted by the VEC rule are consistent with the XRD results (Figure 1(a) and Figure 2(c)).

According to the classical solidification theory, crystal morphology is mainly dependent on the original composition of an alloy, temperature gradient in solid/liquid interface (\(G\)) and solidification velocity (\(R\)). A high \(G/R\) ratio often facilitates the formation of columnar grains while a low \(G/R\) ratio facilitates the formation of equiaxed grains. In the laser AM process, \(G\) values are often extremely high up to \(10^3 \text{K/mm}\) [26] compared to approximately 1 K/mm in mould casting [27]. Therefore, the final microstructures in AM process tend to be dominated by columnar grains. However, laser scanning speed in this work (60 mm/s) is relatively higher than that in the

\[\text{Figure 1. (a) XRD pattern, (b) microstructures and (c) the corresponding elemental distribution of the CrCoFeNi alloy after annealing.}\]
general AM process (\(< 10\) mm/s). That means the solidification rate becomes higher, decreasing the $G/R$ ratio thereby promoting the formation of equiaxed grains.

Wang et al. [14] fabricated Al$_{1.5}$CoCrFeNi ingots using the vacuum arc remelting method. It exhibited similar equiaxed dendrite structure but with a much larger grain size of more than 100 \(\mu\)m compared to the current study (12 \(\mu\)m). Figure 2(g) shows equiaxed dendrite morphology inside grains. EDS reveals the enrichment of Al in the dendrite core and Cr segregates in interdendritic regions (Figure S2). The dendrites show irregular morphology, some of which are flowery while others are spherical, suggesting that dendrite fragmentation occurred during solidification [28,29]. The reason for the dendrite fragmentation phenomenon is that the neck of dendrite is thinner than other regions, which is unstable due to surface tension difference. During the subsequent solidification process, thicker regions would grow up at the expense of thin regions, as Ostwald ripening. On the other hand, when a negative temperature gradient exists in front of the solid/liquid interface during solidification, the crystallize latent heat would spread out from liquid phases radially. In the case of extreme undercooling, fine dendrites would be fused due to recalescence when the crystallised latent heat is released. These dendrite fragments can be natural nucleation sites for new grains, resulting in the ultimate fine equiaxed grain microstructure. Hunt [30] and Gäumann et al. [31] also suggested that high density of nucleation sites can be conducive to
the formation of equiaxed grains despite high $G$ values. Chai et al. showed that rapid non-equilibrium solidification during laser processing is conducive to grain refinement \[32\].

The in-depth observation was conducted by TEM to reveal phase structures in the surface layer (Figure 2(h–i)). The diffraction pattern shows superlattice diffraction spots derived from B2 ordered structure. Dark field images taken from the (100) superlattice spot show the different morphology of the dendrite and interdendrite regions: spherical nanosized particles in the dendrite areas vs. cuboid and lath-shaped participates in the interdendrite areas, which is similar to Linden et al.’s results \[19\].

**Figure 3.** (a) The microhardness distribution along the depth direction. (b) The friction coefficient variations vs test time of the pristine specimen and Al-alloyed specimen in a dry friction condition. (c–d) The three-dimensional program across the wear track of the pristine specimen (c) and Al-alloyed specimen (d). (e) Wear volumes and wear rates of the pristine specimen and Al-alloyed specimen.
Figure 3(a) shows the microhardness distribution of the specimen along the depth direction after laser alloying. The average hardness value of the surface layer is $\sim 536$ HV, about three times that of the substrate ($\sim 182$ HV). As mentioned above, the addition of Al causes a shift of phase stability and induces the formation of BCC phase in the surface layer. BCC phase usually exhibits a higher hardness than FCC phase [33]. Besides, refined microstructures in the surface layer can also make a contribution to hardness. Figure 3(b) shows the friction coefficient variations of the pristine specimen and Al-alloyed specimen as a function of test time. The mean friction coefficients of the pristine specimen and Al-alloyed specimen are 0.76 and 0.60, respectively. As shown in the 3D morphologies of both specimens (Figure 3(c,d)), the wear depth of the Al-alloyed specimen decreases remarkably versus the pristine specimen. Severe abrasive wear and local adhesive wear are observed on the worn surface of the pristine specimen, whereas the Al-alloyed specimen is just polished slightly. The wear volumes of the pristine specimen and the Al-alloyed specimen measured from Figure 3(c,d) are $1.69 \times 10^{-10}$ and $0.26 \times 10^{-10}$ $\mu$m$^3$, respectively. The specific wear rates of both specimens are calculated to be $3.38 \times 10^{-13}$ and $5.26 \times 10^{-14}$ m$^3$/N·m, respectively (Figure 3(e)). According to Archard’s law [34], the wear resistance of materials is proportional to surface hardness. Therefore, the hard surface of the Al-alloyed specimen is responsible for the reduction of 80% in wear rate regarded to the pristine specimen.

Figure 4 shows worn surface morphologies of the pristine specimen and the Al-alloyed specimen. The insets in Figure 4(a,c) are the corresponding counterface balls after the wear tests. Ploughing grooves along the wear direction and adhesive layers are observed on the worn surface of the pristine specimen (Figure 4(a,b)). During the sliding process, the specimen underwent severe plastic deformation under the combined action of normal force and tangential force. From the image of worn ball (the inset in Figure 4(a)), a mass of materials transferred from the pristine specimen are observed on the ball surface. Therefore, the wear mechanism of the pristine specimen is predominantly adhesive wear, which is prevalent in soft and ductile materials [35]. Besides, the process of wear was accompanied by oxidation due to heat through friction, evidenced by the high content of oxygen element on the worn surface (Table 2). In contrast, the worn surface of the Al-alloyed specimen is relatively smooth with shallow scratches and debris, representing the improved wear resistance (Figure 4(c,d)). As mentioned above, good wear resistance is attributed to BCC phase formation in the Al-alloyed specimen. High hardness of BCC phase exhibits strong resistance to plastic deformation.

**Figure 4.** Worn surface morphologies of the pristine specimen (a, b) and Al-alloyed specimen (c, d). The insets in (a) and (c) are optical micrographs of the corresponding worn balls after wear tests.
Table 2. Chemical compositions of the worn surface of the pristine specimen and Al-alloyed specimen (at.%).

| Specimen               | Fe    | Co    | Cr    | Ni    | Al    | O     |
|------------------------|-------|-------|-------|-------|-------|-------|
| Pristine specimen      | 9.57  | 9.55  | 9.82  | 9.42  | /     | 61.63 |
| Al-alloyed specimen    | 10.15 | 10.12 | 10.30 | 10.13 | 18.97 | 40.34 |

and then hinders the micro-cutting from the friction pair. Less adhesion can be seen on the surface of worn ball (the inset in Figure 4(c)). Besides, oxygen element is also detected on the worn surface (Table 2). Therefore, the wear mechanism of the Al-alloyed specimen is oxidation wear and slight adhesive wear.

4. Conclusion

In summary, the surface hardening of CrCoFeNi FCC HEA was achieved by in-situ synthesized BCC HEA via Al laser alloying. Al alloying leads to the shift of phase stability and generates the fine Al$_{1.5}$CoCrFeNi grains with BCC structure on the CoCrFeNi FCC substrate. The Al-alloyed surface has a microhardness three times that of the substrate, which is responsible for the much lower wear rate. This work opens a door for achieving surface hardening of FCC HEAs by simple laser alloying technology.

Data availability statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

Disclosure statement

No potential conflict of interest was reported by the author(s).

Funding

This work was supported by the National Natural Science Foundation of China [grant number 11725210] and the Fundamental Research Funds for the Central Universities [grant number 2018XZZX001-05].

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