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Influence of Specific Energy on Microstructure and Properties of Laser Cladded FeCoCrNi High Entropy Alloy

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Abstract: Specific energy is a key process parameter during laser cladding of high entropy alloy (HEA); however, the effect of specific energy on the microstructure, hardness, and wear resistance of HEA coating has not been completely understood in the literature. This paper aims at revealing the influence of specific energy on the microstructure and properties of laser cladded FeCoCrNi high entropy alloy on the Ti6Al4V substrate, and further obtains feasible process parameters for preparation of HEA coating. Results indicate that there are significant differences in the microstructure and properties of the coatings under different specific energy. The increase of specific energy plays a positive role in coarsening the microstructure, promoting the diffusion of Ti from the substrate to HEA coating, and subsequently affects the hardness of samples. The HEA coating is mainly composed of the face-centered cubic phase and body-centered cubic phase, precipitating a small amount of Fe-Cr phase and Laves phase. Metallurgical bonding is obtained between the base metal and the coatings of which the bonding region is mainly composed of columnar crystal and shrinkage cavities. The microhardness of the HEA coating reaches 1098 HV, which is about 200% higher than that of the TC4 substrate, and the wear resistance is significantly improved by the HEA coating.

Keywords: laser cladding; high entropy alloy; specific energy; phase transformation; wear resistance

1. Introduction

Titanium alloy has been widely used in the aerospace industry due to its superior advantages of low density, high strength, and anti-corrosion performance [1–4]. However, the service life of the titanium alloy structural part is restricted by the insufficient wear resistance and hardness. Therefore, the surface strengthening of titanium alloy has attracted massive attention from researchers worldwide [5,6]. High entropy alloy (HEA), as a promising multi-component alloy, has drawn considerable attention to the repair of seriously worn aircraft flap slide due to its outstanding comprehensive properties, which is attributed to its effect of high entropy, lattice distortion, and slow diffusion [7–9]. HEA rapidly attracts massive attention in material science since it was first reported [10–12]. HEA has created an unexplored area of alloy compositions and exploited the potential to influence solid solution phase stability through the controlling of configurational entropy.

Preparation of HEA coating on titanium alloy is a feasible method to improve surface hardness and wear resistance of titanium alloy. At present, the main technologies used to prepare HEA
coating include thermal spraying [13,14], laser/plasma cladding [15–18], physical vapor deposition [19], and powder metallurgy [20,21]. Among the above HEA coating methods, laser cladding has advantages such as high efficiency, reliable metallurgical bonding, high material utilization ratio, and excellent performance [22,23]. Therefore, laser cladding of HEA coating has been widely adopted for repairing and strengthening the titanium alloy structural parts.

The mechanism of surface strengthening by HEA was reported in the literature. Huang et al. [24,25] investigated the structure and properties of high entropy alloys; results indicated that the wear resistance of the cladding layer was significantly improved due to the second phase strengthening. The effect of the cladding process on the microstructure and properties of the HEA coatings was reported in the literature. Joseph et al. [26] conducted a comparative study between arc melting and laser melting; the microstructure and properties of the HEA coatings were found to be significantly different under different processes, but the compression experimental results were not much different. The effect of chemical compositions on the microstructure and properties of the HEA coatings was reported in the literature. Jiang et al. [27] conducted a comparative study on microstructure evolution and wear behavior of the laser cladding CoFeNi$_2$V$_{0.5}$Nb$_{0.75}$ and CoFeNi$_2$V$_{0.5}$Nb HEA coatings. Cai et al. [28] studied the alloying elements and dilution rates on the microstructure and properties of high entropy alloy cladding layers; results indicated that the migration of the Fe element from the matrix to the cladding layer could make the mixing entropy of CoCrNi coating close to the theoretical mixing entropy of FeCoCrNi high entropy alloy. The effect of laser power on the microstructure and properties of the HEA coatings was reported in the literature. Shu et al. [29] studied the effect of laser power on microstructure, mechanical and chemical properties of the CoCrBFeNiSi HEA coating; results indicated that the amorphous content in the coatings had a significant influence on microhardness, wear resistance, and corrosion resistance. Sui et al. [30] investigated the effect of specific energy on the microstructure and properties of laser cladded TiN/Ti$_3$AlN-Ti$_3$Al composite coating; results revealed that the dilution rate of the coating increased with the increase of specific energy, the microhardness of the composite coating was approximately three times higher than that of the substrate, and the wear resistance was improved remarkably under optimum specific energy 58.3 J/mm$^2$. In summary, previous studies mainly focus on the thermal stability, oxidation resistance, microstructure evolution, mechanical properties, and wear behavior of the HEA coating, however, the effect of specific energy on microstructure, hardness, and wear resistance of HEA coating has not been completely understood in the literature.

Specific energy (E) is a key process parameter during laser cladding of HEA on the TC4 substrate. Specific energy is calculated by using the Equation: $E = P/(V \times D)$, where P (W) is the laser power, V (mm/s) is the scanning speed, and D (mm) is the laser spot diameter [30]. In this study, the influence of specific energy on the microstructure, phase transformation, hardness, and wear resistance of laser cladded FeCoCrNi HEA on the TC4 substrate will be systematically investigated, and the mechanism of surface strengthening lying in the laser cladding process will also be revealed, feasible process parameters for preparation of HEA coating will be obtained.

2. Materials and Methods

In this research, the experimental setup for the laser cladding process consists of a laser system (made in Shanghai, China), a 6-axis KUKA robot (made in MS, USA), a water-cooling machine to ensure the normal operation of the laser system, and a protection chamber to control the argon environment with less than 60 ppm oxygen content. Overall, the equipment of laser cladding is shown in Figure 1.

During the laser cladding process, the high entropy alloy powder and the surface substrate are subjected to the radiation of a high-energy laser beam, which quickly melts, diffuses, and solidifies to form a cladding layer that combines well with the substrate. The detailed schematic diagram of laser cladding is shown in Figure 2.
Figure 1. Equipment of laser cladding experiments: (a) laser cladding system with a KUKA robot, protection chamber, and water-cooling machine; (b) laser head; (c) laser system.

Figure 2. Schematic diagram of the experimental setup for the process.

In this paper, TC4 is used as the matrix material, and self-developed FeCoCrNi high entropy alloy is used as the powder material. The spherical pre-melted FeCoCrNi powders of 15–53 μm were produced by vacuum gas atomization under the Ar atmosphere. The element compositions of the substrate and HEA powder are shown in Table 1.

| Materials            | Ti   | Fe   | Co   | Cr   | Ni   | Al  | V   |
|----------------------|------|------|------|------|------|-----|-----|
| TC4 Substrate        | Bal. | ≤0.15| –    | –    | –    | 4.96| 3.70|
| FeCoCrNi powder      | –    | 24.44| 26.18| 22.43| Bal. | –   | –   |

Meanwhile, reasonable control of the process parameters is essential for achieving the desired performance. However, the properties of laser cladded coating are affected by numerous factors, such as the laser scanning speed and laser power. Therefore, this paper introduces the concept of specific energy, which can reflect the changes in laser power and scanning speed at the same time. The selected laser cladding parameters are shown in Table 2.
specific energy, which can reflect the changes in laser power and scanning speed at the same time. The selected laser cladding parameters are shown in Table 2.

| Case | Laser Power (W) | Scanning Speed (mm/s) | Beam Diameter (mm) | Specific Energy (J/mm²) |
|------|-----------------|-----------------------|-------------------|-------------------------|
| 1    | 900             | 11                    | 2                 | 40.9                    |
| 2    | 1050            | 9                     | 2                 | 58.3                    |
| 3    | 1250            | 7                     | 2                 | 89.3                    |

After laser cladding, specimens were cut along the transverse sections, then they were ground and polished to 0.06 μm using colloidal silica, and subsequently they were electrolytically etched using the standard Kroll’s reagent (HF:HNO₃:H₂O = 1:2:6) with 10 s. The crystal structure and lattice parameters of the laser cladding products and TC4 substrate were discussed from the corresponding XRD patterns. The XRD was tested on a Bruker D8 ADVANCE (made in Karlsruhe, Germany) Bragg-Brentano diffractometer with an X-ray wavelength of 1.54 Å. The microstructural research and chemical analysis of the laser cladded samples are performed using an FEI Inspect-F Scanning Electron Microscope (made in Hillsboro, OR, USA) equipped with an energy-dispersive spectroscopy (EDS) detector. The microhardness tests were performed using an HVS50 hardness tester, with 15 s load application time and under loads of 1000 g. Meanwhile, the wear experiments were carried out at room temperature using CFT-I type fretting friction and wear machine (made in Shanghai, China) with a normal load of 30 N, a motor speed of 300 t/min, and a wear time of 10 min. Besides, Si₃N₄ ceramic balls with a radius of 3 mm were used as the friction pair.

3. Results and Discussions

3.1. Macro Morphology

Based on the selected experimental parameters in Table 2, a high entropy alloy laser cladding experiment was carried out. The macro morphology of the cladding layer under different specific energies is shown in Figure 3. It can be seen from Figure 3 that as the specific energy increases, the surface quality of the cladding layer changes significantly. In order to investigate the influence of specific energy on the cladding layer, the cross-sections of each high entropy alloy laser cladding layers are shown in Figure 4.

![Figure 3. Surface morphology of high entropy alloy laser cladding layer under different specific energies. (a) 40.9 J/mm²; (b) 58.3 J/mm²; (c) 89.3 J/mm².](image-url)

During the laser cladding process, affected by the influence of surface tension and wetting, a parabolic morphology was formed during the rapid solidification process. It can be seen from Figure 4 that the specific energy of laser cladding has a significant impact on the cladding layer morphology, specifically related to the cladding layer morphology size, that is, the cladding layer reinforcement (H), width (W), and melting depth (h). The test results are shown in Table 3. The results show that the specific energy has an important effect on the volume of the molten pool, which is specifically expressed in the reinforcement, width, and melting depth. With the increase of specific
energy, the size of the molten pool will increase accordingly. The penetration and width of the molten pool increase with higher specific energy, while the reinforcement does not show any regularity with higher specific energy.

Table 2. Laser cladding experiment parameters.

| Case | Laser Power (W) | Scanning Speed (μm/s) | Beam Diameter (mm) |
|------|----------------|-----------------------|-------------------|
| 1    | 40.9           | 58.3                  | 89.3              |
| 2    | 58.3           | 0.58                  | 4.04              |
| 3    | 89.3           | 0.28                  | 4.18              |

Figure 4. Transverse section of the high entropy alloy laser cladding layer under different specific energies. (a) 40.9 J/mm²; (b) 58.3 J/mm²; (c) 89.3 J/mm².

Table 3. The size of the cladding layer under different specific energy.

| Case | E/(J/mm²) | H/(mm) | W/(mm) | h/(mm) |
|------|-----------|--------|--------|--------|
| 1    | 40.9      | 0.58   | 3.69   | 0.15   |
| 2    | 58.3      | 0.8    | 4.04   | 0.35   |
| 3    | 89.3      | 0.28   | 4.18   | 0.55   |

3.2. Phase Transformation

X-ray Diffraction (XRD) is a commonly used phase analysis method [31,32]. The XRD patterns of the pre-placed powders and the FeCoCrNi coatings are shown in Figure 5, which shows that the HEA coatings are mainly composed of the FCC phase and BCC phase, precipitating a small amount of Fe-Cr phase and Laves phase, while the raw powders possess the single-phase FCC crystal structure only. The addition of the Ti element influences the valence electron concentration (VEC) inside the FeCoCrNi high entropy alloy, thus inhibiting the formation of the FCC phase in the cladding layer. Meanwhile, the atomic size of the Ti element is quite different from that of Fe, Co, Cr, Ni, which is beneficial to the formation of the BCC phase. It is also can be found from Figure 5 that the addition of the Ti element causes the change of the lattice constant of the FCC phase. This is also due to the above-mentioned atomic size. Compared with other elements, Ti has a larger atomic radius. Therefore, its addition led to severe lattice distortion, thereby increasing the lattice constant of the FCC phase.

Figure 5. XRD patterns of as-alloyed powder and high entropy alloy (HEA) coatings.
Besides, Ti and Co\Cr elements have a low composite enthalpy, hence, the excessively high temperature inside the molten pool provides an opportunity for the reaction between the elements. There is a great possibility for the Ti element in Case 3 to be combined with the Co element and Ni element to form (Co, Cr)\textsubscript{2}Ti Laves phase (as shown in Figure 5). However, the Ti element content in Case 1 is extremely small, and the XRD test result is the phase on the top of the cladding layer, so no detection results are consistent with the detection results of the high entropy alloy powder, and no obvious BCC phase and Fe-Cr phase are detected. As the specific energy increases, the Ti element content gradually increases, so the BCC characteristic gradually becomes obvious, and Fe-Cr can be detected. When the specific energy is too large, the Laves phase inside the cladding layer is significantly precipitated.

3.3. Microstructure

Based on the substantial investigation on the macro morphology and phase transformation, the effect of specific energy on the crystal growth and microstructure is figured out in this research. Figure 6 presents the SEM morphology of the coatings obtained under the condition of different specific energy. Metallurgical bonding has been obtained between the base metal and the coatings of which the bonding region is mainly composed of columnar crystal and shrinkage cavities, as shown in Figure 6. There is a slight increase in the width of the bonding region from 25.5 \textmu m to 60 \textmu m at the function of specific energy varied from 40.9 to 89.3 J/mm\textsuperscript{2}. With regard to the thermal cycling process, the increase of specific energy leads to the decrease of actual cooling rate and thus provides an opportunity for the mixing of HEA alloy and TC4 substrate. As implied in the detailed image, the transformation from columnar crystal to the cavities is an important feature in this region. It also can be concluded from Figure 6g–i that there are obvious differences in the size of columnar crystals under different specific energy. There is a significant increase in the width of the columnar crystal zone from 3.2 \textmu m to 12.1 \textmu m at the function of specific energy varied from 40.9 to 89.3 J/mm\textsuperscript{2}. It is attributed that the higher heat provides more energy for the growth or coarsening of sub-grain. Thus, the columnar crystals grow larger slightly with the increase of specific energy.

The microstructure at the top of the HEA laser cladding layer under different specific energies is presented in Figure 7. Meanwhile, the chemical composition of different regions, which are shown in Figure 7, is exhibited in Table 4. It can be seen from Figure 7 and Table 4 that there is a slight difference between Case 1 and Case 2, while Case 3 shows an obvious difference. The microstructure of Case 1 is composed of the Fe-Cr phase (point A) and matrix. Compared to Case 1, the rich-Ti phase is formed with the higher specific energy which provides a promotion to the melting of the TC4 substrate. However, the extremely high specific energy results in sufficient reaction between powders and substrate. Thus, the (Ni, Co, Ti)-rich phase is formed because of the more negative $\Delta H_{\text{mix}}$.

EDS analysis is then carried out along the path from the upper layer to the substrate as marked in Figure 8. Little fluctuation in the relative concentration curves of Cr, Co, Fe, Ti, and Ni elements is found in the upper and middle layers in the coatings. However, the content of all the elements increased and decreased sharply, respectively, in the bottom layers of the coatings, especially in the bonding region. As the content of Ti elements in the substrate is much higher than that of the coatings, the obvious dilution effect by the substrate upon the cladded coatings led to the increase of Ti elements and the formation of the bonding region. Besides, the element change of the sample with lower specific energy is strongly sharper than that with a higher specific energy. Among the experiments, increasing specific energy leads to an increase in the dilution ratio. More melted substrate metal is melted to give birth to a higher dilution rate and thus less obvious difference in the chemical composition between the HEA coating and substrate.
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Figure 6. (a) SEM image of the transverse section of Case 1, (b) SEM image of the transverse section of Case 2, (c) SEM image of the transverse section of Case 3, (d) high-magnification SEM image of bonding region in Case 1, (e) high-magnification SEM image of bonding region in Case 2, (f) high-magnification SEM image of bonding region in Case 3, (g) high-magnification SEM image of the localized region marked in (d), (h) high-magnification SEM image of the localized region marked in (e), (i) high-magnification SEM image of the localized region marked in (f).

Figure 7. SEM images of laser cladded coatings in different region. (a) Case 1, (b) Case 2, (c) Case 3.

Table 4. The chemical composition of different points in Figure 7.

| Case | Point | Al(at%) | Ti(at%) | V(at%) | Cr(at%) | Fe(at%) | Co(at%) | Ni(at%) |
|------|-------|---------|---------|--------|---------|---------|---------|---------|
| 1    | A     | 1.8     | 6.95    | 1.1    | 35.58   | 25.63   | 16.70   | 12.25   |
|      | B     | 1.75    | 17.06   | 0.047  | 20.78   | 21.43   | 19.92   | 18.59   |
| 2    | A     | 2.20    | 7.99    | 0.83   | 36.49   | 24.53   | 15.04   | 12.92   |
|      | B     | 2.42    | 16.54   | 0.7    | 21.37   | 20.69   | 19.71   | 18.58   |
|      | C     | 2.85    | 47.08   | 0      | 17.70   | 12.78   | 10.65   | 8.93    |
| 3    | A     | 09.51   | 40.34   | 02.29  | 09.95   | 07.58   | 15.56   | 14.97   |
|      | B     | 09.97   | 61.57   | 02.30  | 08.54   | 06.11   | 05.29   | 06.22   |
3.4. Hardness

Figure 9 presents the hardness depth profile in the transverse cross-section of the laser clad coating. The hardness was tested with a load of 1000 g. The variation of hardness reflects the coating microstructure and element changes, which are responsible for the hardness variation. Due to the interaction between the multi-principal elements that will promote the internal fine-grain strengthening, dispersion strengthening, and solid solution strengthening of the alloy during the solidification process, the hardness of the HEA coating is much higher than that of the Ti6Al4V substrate. The hardness of FeCoCrNi coating exceeds 850 Hv when the parameters of Case 1 and Case 2 are selected. Results indicate that a better FeCoCrNi coating is obtained than that from the literature [28]. Meanwhile, Figure 9b shows that the average hardness of HAZ is slightly higher than the substrate. This increase is likely to be attributed to the localized metallurgical changes that occur in the HAZ associated with the rapid heating and cooling above the α-β phase-transition temperature of this specific alloy but below its melting point. It can also be seen that the microhardness of HEA coating in Case 3 is significantly lower than that in Case 1 and Case 2, which is related to the element content in coatings, as shown in Figure 8. The content of Ti is much higher than the other element, hence the balance of high entropy is broken.
3.5. Wear Resistance

Figure 10 shows the wear morphology of the sample surface after the above-mentioned wear resistance test. It can be seen from the figure that the surface wear of the TC4 substrate is very serious, and there are pits and adhesive materials, which is attributed to the that under the action of plastic deformation and large pressure, the surface material of the substrate will adhere to the surface of the friction pair and transfer during the sliding process. Therefore, pits and adhesive materials are formed. In addition, deep furrows were also found. This is because metal particles caused by wear will adhere to the surface of the friction pair, thereby forming grooves on the surface of the substrate. Meanwhile, the main component of the cladding layer of Case 3 is the Ti element, so there is not much difference in the wear morphology. Compared with the TC4 matrix, it shows slight adhesion wear and abrasive wear. A large amount of Laves phase is distributed in the cladding layer, which increases the hardness of the cladding layer, so abrasive wear is effectively suppressed. XRD results show that a HEA solid solution phase is generated in the cladding layer, which improves the plasticity of the material, and the adhesion wear is also suppressed.

Figure 10. The wear morphology of TC4 and coatings. (a) TC4, (b) Case 1, (c) Case 2, (d) Case 3.
Figure 10b,c are the wear morphology of Case 1 and Case 2, respectively. A nearly straight crack with a smooth fracture appearance can be found on the wear morphology of Figure 10b, so brittle fracture will likely occur under the action of larger pressure, which will seriously affect the practical application of Case 1. Therefore, sufficient specific energy is essential during laser cladding of FeCoCrNi high entropy alloy on the Ti substrate. Case 2 only suffered slight scratches during the wear process. Besides, as can be seen from the figure, the wear resistance of Case 2 is significantly higher than that of the TC4 matrix. This is because Case 2 has an equal proportion of elements, solid solution strengthening, and second phase strengthening, which results in a significant improvement in the wear resistance of the cladding layer.

Due to the obvious brittle fracture of Case 1, it is difficult to define the size of the wear region. Therefore, only the wear size statistics of the TC4 substrate and Case 2 and Case 3 are performed. The results are shown in Table 5. It can be seen that the wearing depth and width of the HEA cladding layer is significantly lower than that of the TC4, and the wear cross-sectional area is calculated using the probe of the friction-wear machine, and its wear rate was further calculated, as shown in Table 5. The results show that the HEA cladding layer plays a significant role in improving the wear resistance of the TC4 surface, which can effectively protect the matrix material. Results indicate that the wear resistance of Case 2 is improved by 5 times relative to the TC4 matrix, while the wear resistance of Case 3 is improved by 2.84 times. The reason is that as the hardness increases, the wear resistance of the material will also increase. Therefore, the feasibility and extent of improve wear resistance of titanium alloy by laser cladding of HEA is revealed. It is worth noting that the appropriate process parameters are limited to a small range during laser cladding of FeCoCrNi high entropy alloy on the Ti substrate.

### Table 5. The size of the wear region of the cladding layer and substrate under different specific energy.

|                  | TC4   | Case 3 | Case 2 |
|------------------|-------|--------|--------|
| Wearing depth(µm) | 116.3 | 68.6   | 27.3   |
| Wearing width(µm) | 954   | 569.8  | 366    |
| Wearing area(µm²) | 6.11×10⁴ | 2.15×10⁴ | 9.9×10³ |
| Wearing volume(mm³) | 0.305 | 0.107  | 0.050  |
| Wear resistance(mm³/s) | 5.08×10⁻⁴ | 1.78×10⁻⁴ | 8.33×10⁻⁵ |

### 4. Conclusions

FeCoCrNi HEA coatings have been successfully deposited directly on Ti6Al4V alloy using the laser cladding method. The microstructure evolution and enhanced properties of laser cladded FeCoCrNi HEA on TC4 substrate have been studied and the main conclusions are as follows:

1. The HEA coating is mainly composed of the FCC phase and BCC phase, precipitating a small amount of Fe-Cr phase and Laves phase. With the increase of specific energy, there is an intensification in the transformation from the FCC phase to the BCC phase and precipitation of the Laves phase.
2. Specific energy has an important influence on the cladding morphology. The coating width will increase with higher specific energy. Meanwhile, the length and width of the columnar crystal at the bottom of the cladding layer increase significantly with higher specific energy.
3. Attributed to the various strengthening mechanism, the microhardness of HEA coating reaches 1098 HV, which is about 200% higher than that of the TC4 substrate.
4. The appropriate process parameters are limited to a small range during laser cladding of FeCoCrNi high entropy alloy on the TC4 substrate. The wear resistance is significantly improved by the HEA coating by using optimized process parameters. The effect of scanning path and strategy of the microstructure and properties of laser cladded FeCoCrNi high entropy alloy are worth deeply investigation in the future.
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