The microstructure and properties of Cr/Ni alloying layer after surface alloying treatment induced by continuous scanning electron beam process

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Abstract: The surface alloying of scanning electron beam can improve the microstructure and mechanical properties of steel materials. In this paper, Cr/Ni alloying treatment was performed on 35CrMo alloy structure steel by using continuous scanning electron beam to improve surface performance. The influence of scanning electron beam technology on the structure of alloy layer is studied, and the influence of coating thickness on the structure and properties of the alloying layer is discussed. The results show that the surface of 35CrMo steel is composed of alloying layer, heat affected zone and matrix. The microstructure of the alloying layer is short columnar crystal, equiaxed crystal and acicular martensite. The surface hardness can reach 770HV when the coating thickness is 5\textmu m, which is 2 times of the matrix. With the increase of Cr/Ni coating thickness, the surface of sample hardness decreases, and the corrosion resistance of the sample increases.

1. introduction

35CrMo steel is a medium-carbon alloy structural steel was created in order to satisfy a need of manufacturing industry for high static strength, impact toughness and high fatigue limit through tempering treatment. Due to its technical features, 35CrMo steels are largely employed on applications of manufacturing important parts of various machines with impact, bending and torsion and high load. However, after tempering treatment, the surface hardness of 35CrMo steel is low, the corrosion resistance is poor, which is difficult to meet the requirements in some fields, limiting its application ranges.

Surface alloying is an effective method to improve the surface mechanical properties of steel parts[1-3]. At present, surface alloying by laser beam surface technology and ion implantation are commonly used[4, 5]. However, these methods generally have the disadvantages of low energy utilization, low energy penetration depth, low efficiency and taking a long time[5-8]. Electron beam surface alloying is a new technology of surface modification due to its high energy utilization rate, less pollution and small deformation of workpiece, it uses continuous scanning electron beam technology to rapidly dissolve one or more alloy elements into the matrix, and uses energy transformation and microstructure change to
obtain alloy layer with special properties[9-11]. The alloy layer not only has strong binding force, dense structure, but also greatly improve hardness[12].

In recent decades, a number of studies have demonstrated electron beam surface alloying properties. Wu et al. [13] discussed the effects of Ni alloying by pulsed electron beam, Ni coating is prepared on the surface of Ti-6Al-4V steel by electroplating, Ti2Ni and TiNi are formed in the alloying area after electron beam treatment, and the grains of the alloying area are refined to have distorted lattice, which greatly improve the hardness of the workpiece surface. Wei et al. [14] achieved surface Cr-Ni alloying of Ti6Al4V alloys by double-glow plasma surface metallurgy technology, after plasma alloying, the tensile strength of Ti6Al4V was about 2.1% higher than the solid solution annealing state. However, the fatigue life of Ti6Al4V after plasma alloying process declined.

In this study, the Cr/Ni powder coating was prepared on the surface of 35CrMo steel by air plasma thermal spraying technology, and then the surface alloying of 35CrMo steel was carried out by continuous scanning electron beam process (CSEBP). The effects of the coating thickness on surface microhardness, microstructure, phase composition and corrosion resistance were discussed.

2. Material and methods

2.1 Material preparation

A commercial available 35CrMo steel was selected as the matrix material. The samples of 35CrMo steel were machined into 50×50×50 mm cubes. Before the electron beam alloying treatment, all samples should be underwent heat treatment. The quenching process: heating up to 850±20℃ for 1 h and oil-cooled. The tempering process: heating up 650±20℃ for 1 h and air-cooled. The chemical composition of the steel was given in Table 1.

| Table 1 | chemical composition of 35CrMo steel (wt.%) |
|---------|-------------------------------------|
| C       | 0.32~0.40                           |
| Si      | 0.17~0.37                           |
| Mn      | 0.40~0.70                           |
| Cr      | 0.80~1.10                           |
| Mo      | 0.15~0.25                           |
| Ni      | ≤0.30                               |
| P       | ≤0.035                              |
| S       | ≤0.035                              |

2.2. Equipment and experimental methods

In this experiment, the plasma spraying provided a feasible way to add Chromium (Cr) and Nickel(Ni) elements by film deposition before scanning electron beam treatment, the ratio of chromium to nickel was 2:3. Prior to the deposition, the matrix was cleaned by ethanol and acetone, and the surface of the matrix was sandblasted by 24 mesh white corundum sand to enhance the adhesion strength between the coating and matrix, the parameters of sandblasting process: pressure was 0.6MPa, sand blasting distance was about 100mm. Cr/Ni powder, 99.99% in purity(3μm particle size), was spread onto the 35CrMo steel samples using SX-80 model plasma spraying equipment, the parameters of process: the power is 52kw, the current is 500A, the voltage is 70V, the powder feeding speed is 40L/min, the spraying distance is about 60mm, and the moving speed is 400mm/s. The thickness of the coating was measured to be 5±1μm, 25±1μm, 45±1μm[10, 15-18]. The obtained coating was then treatment with continuous scanning electron beam in circular sweep mode. The electron beam experiments were performed on HDZ-6F electron beam installation unit(Fig. 1), performance parameters of the electron beam machine at the follow: accelerated voltage 0~120kV, electron beam current 0~120mA, scanning speed of the electron gun 0~100mm/s, scanning frequency 0~1000HZ. According to the phase transition melting temperature of 35CrMo steel and the principle of electron beam energy deposition, the electron beam process parameters are selected in Table 2[9, 19-21]. The diameter of the electron beam is 0.1mm, scanning circle diameter is 8mm.
Table 2. The electron beam process parameters

| Number | Accelerated voltage (kV) | Beam current (mA) | Coating thickness (μm) | Scanning speed (mm/s) | Scanning frequency (HZ) |
|--------|--------------------------|-------------------|------------------------|-----------------------|------------------------|
| 1      | 60                       | 8                 | 5                      | 5                     | 180                    |
| 2      | 60                       | 10                | 25                     | 5                     | 180                    |
| 3      | 60                       | 12                | 45                     | 5                     | 180                    |

Fig. 1. Schematic diagram of continuous scanning electron beam alloying

The metallographic samples were mechanically wet grind with SiC abrasive papers 320, 600, 1500 and 2000, then polished with 0.5μm diamond paste and etched with 4% solution of HNO3 in ethanol for 10 s. The cross section morphology and microstructure was observed by Quanta FEG 450 scanning electron microscope. The phase structure was examined using a Bruker D8 Advance diffractive with Cu-Kα radiation. The microhardness measuring was carried out by means of device HMV-ZT microhardness tester with a load of 1kg, time is 10 s. Electrochemical corrosion test was carried out by potentiostatic method and PS-268A electrochemical measuring instrument.

3. Results

Fig. 2 (a) shows the surface of 35CrMo steel consists of three parts: alloying layer, heat affected zone and matrix. Fig. 2 (b) shows the microstructure of the alloy layer is approximately equiaxed crystal and short columnar crystal, because the temperature of the alloy layer is the highest in the process of scanning electron beam treatment, and it is above the transformation temperature, the structure in this region is fully austenitized, and the structure is highly refined under the effect of self-quenching. The microstructure of the alloy layer is equiaxed and short columnar crystal, and all of them are uniform and dense. In addition, the structure grains in this region are coarse in the middle part of the alloying layer, while the grains near the surface layer and the interface with the heat affected zone are relatively small. Fig. 2 (c) shows the microstructure of the heat affected zone is acicular martensit, the main reason is that the heating temperature in this area is low, the structure is not fully austenitized. Fig. 2 (d) shows the microstructure of the matrix is pearlite and troostite.
According to the principle of metal solidification, the solidification structure of metal depends on two kinds of heat flow. When there is a positive temperature gradient between liquid and solid, directional solidification occurs. The latent heat of crystallization is dissipated by solid, and the microstructure of liquid metal after solidification is columnar crystal. When the crystal is surrounded by supercooled liquid and the temperature gradient at the solid-liquid interface is negative, the solidification is not directional. The latent heat of crystallization is dissipated by the surrounding liquid, and the microstructure after solidification is equiaxed crystal. It can be seen that the surface layer reaches a very high temperature, and the crystal nucleus is difficult to form during the melting and crystallization process of the alloying area, due to the thermal effect of the electron beam. The temperature at the bottom of the alloying layer is relatively low, and there is a positive temperature gradient between the solid and liquid. Because of the influence of "self quenching", the heat dissipation near the heat affected zone is faster, and the fine short columnar crystals are formed, as shown in Fig. 3(c). Moreover, the grains grow along the direction of temperature gradient from low to high to the middle of the alloying layer, forming long columnar crystals. In the middle of the alloying layer, the temperature is relatively higher than that of the top and bottom of the alloying layers due to the long high temperature residence time. During the solidification process, there is a negative temperature gradient at the solid-liquid interface, and the grain growth direction is not obvious, forming more approximately equiaxed crystals and short columnar crystals, as shown in Fig. 3(b). When approaching to the top of the alloying layer, due to the influence of heat conduction and radiation, the temperature gradient at the top decreases and the direction of heat dissipation is not obvious, but the degree of supercooling is high, forming fine equiaxed grains with non spontaneous nucleation, as shown in Fig. 3(a).

Fig. 3. Grain morphology and distribution in the alloying layer, (a) the top of the alloying layer, (b) the middle of the alloying layer, (c) the bottom of the alloying layer.
There is another kind of special equiaxed grains in the alloying layer, as shown in Fig. 4. Such equiaxed grains are located at the intersection of the tip of multiple columnar grains. Although they have the initial conditions for nucleation and growth, they are squeezed by the surrounding grains, and the nuclei lose the space for continuous growth, forming a special kind of equiaxed grains. This kind of equiaxed grain is closely related to another grain growth mode in the alloying layer. In the local region of the alloying layer, there are obvious dislocation structures. The reason of dislocation formation is that during the solidification and crystallization process of the alloying layer, the grain structure at the top and bottom of the alloying layer grows to the middle of the alloying layer at the same time, because of the difference of their preferred growth directions, when they reach the middle of the alloying layer, the top of the grain structure growing from the two directions contacts, a certain extrusion stress is produced, and the growth trend slows down. The recrystallized grain structure is easier to form equiaxed, and difficult to grow, and the grain is fine.

![Special equiaxed crystal](image)

**Fig. 4. Special equiaxed crystal**

**4. Discussion**

4.1 Effects of coating thickness on the microstructure of the alloying layer

Microstructures of alloying layers with different Cr/Ni coating thicknesses are shown in Fig. 5. Fig. 5 shows that the Cr/Ni coating thickness is different, the microstructure of the alloying layer of the sample is different after scanning electron beam treatment. Fig. 5 (a) shows the microstructure of the alloying layer is acicular martensite, and less surface dendrite and short columnar fine grains, when the Cr/Ni coating thickness is 5 μm. Fig. 5 (b) shows the microstructure of the alloying layer is mainly equiaxed crystal and columnar crystal when the coating thickness is 25 μm. Fig. 5 (c) shows the microstructure of the alloying layer is mainly columnar crystal when the coating thickness is 45 μm.

![Effects of coating thickness on the microstructure of the alloying layer](image)

**Fig. 5. Effects of coating thickness on the microstructure of the alloying layer**

(a) 5 μm, (b) 25 μm, (c) 45 μm

Causes of the presented phenomenon were analyzed. With the increase of the coating thickness, the relative content of Cr/Ni alloy elements increases gradually in the alloying layer, the content of Cr/Ni alloy elements of the alloying layer is the lowest after scanning electron beam alloying when the coating thickness is 5 μm, the effect on MS point of martensitic transformation temperature is the lowest, forming more acicular martensite. When the coating thickness is 25 μm and 45 μm, the content of Cr/Ni alloy
elements of the alloying layer is higher, the effect of alloy elements on MS point of martensitic transformation temperature is greater, forming a mixed structure of the equiaxed and columnar grains.

Fig. 6. XRD of the alloying layer with different coating thickness

4.2 Effects of coating thickness on phase composition of the alloying layer

To further explore the phase analysis of the alloying layer with different Cr/Ni coating thicknesses was performed by an X-ray diffractometer. The results are shown in Fig.6. When the coating thickness is 5μm, the alloying layer is mainly composed of α-Fe, the microstructure is acicular martensite. When the coating thickness reaches 25μm, the alloying layer is mainly composed of Fe/Cr/Ni solid solution and residual alloy austenite phase. When the coating thickness reaches 45μm, the main phase of the alloying layer is also the Fe/Cr/Ni solid solution and the residual alloy austenite phase, but the content of the Fe/Cr/Ni solid solution and the residual alloy austenite phase is more than that of 25μm. When the coating thickness reaches 25μm, NiCr2O3 phase is produced in the alloying layer, and the content of NiCr2O3 increases with the increase of the coating thickness, this shows that the nickel in the coating reacts with the oxygen in the air to generate more NiO.

4.3 Effects of coating thickness on the microhardness of the alloying layer

Fig.7 shows that the distribution laws of sectional microhardness of electron beam alloying samples with different Cr/Ni coating thicknesses along the depth direction are similar. The microhardness of the surface along the depth increases gradually in the beginning and then gradually declines. It can be seen from the Fig.7, the surface microhardness of the alloying layer is 770HV, 672HV and 450HV, the surface microhardness decreases gradually respectively with the increase of the coating thickness. Within 100μm from the surface, the rate of microhardness increase gradually increases with the increase of the coating thickness, which is closely related to the microstructure and phase composition of the alloying layer. When the coating thickness is 5μm, the main reason of the high microhardness is acicular martensite formed on the alloying layer. There is little difference between the microhardness of the three coating thicknesses in the heat affected zone.
4.4 Effects of coating thickness on the corrosion resistance of the alloying layer

Fig. 8 shows the dynamic potential polarization curves of samples with three coating thicknesses after CSEBP treatment. It can be seen from Fig. 8 that the current density decreases with the increase of potential during the cathodic polarization process. The samples with 5μm coating thickness start to enter into anode polarization when the self corrosion potential \( E = -836 \text{mV} \), the samples with 25μm coating thickness start to enter into anode polarization when the self corrosion potential \( E = -775 \text{mV} \), the samples with 45μm coating thickness start to enter into anode polarization when the self corrosion potential \( E = -742 \text{mV} \), with the increase of the coating thickness, the self corrosion potential is higher, the corrosion resistance is better.

Combined with the previous analysis of the microstructure and phase composition, the main cause to improve the corrosion resistance of the material surface is the solid solution formed by Cr/Ni element and matrix. When the coating thickness is more thick, more solid solutions are formed in the alloying layer after CSEBP treatment, the passivation film formed on the surface in the electrochemical corrosion process is thicker, the passivation effect is more obvious, the corrosion resistance is stronger.

5. Conclusions

In this paper, alloying treatment was carried out on 35CrMo steel to improve its hardness and corrosion resistance by continuous scanning electron beam. The effects of the Cr/Ni coating on the microstructure, phase composition, microhardness, and corrosion resistance of the alloying layer were investigated. The research results provide references for the applications of scanning electron beam.
(1) After alloying the 35CrMo steel surface with Cr/Ni using a continuous scanning electron beam, the surface of 35CrMo steel consists of three parts: alloying layer, heat affected zone and matrix. The microstructure of the alloy layer is approximately equiaxed crystal and short columnar crystal, the microstructure of the heat affected zone is acicular martensite, the microstructure of the matrix is pearlite and troostite.

(2) The microstructure in the top of the alloying layer is fine equiaxed grains, the microstructure in the middle of the alloying layer is approximately equiaxed crystals and short columnar crystals, the microstructure in the bottom of the alloying layer is fine columnar crystals. When the coating thickness reaches 25 μm, NiCr2O3 phase is produced in the alloying layer, and the content of NiCr2O3 increases with the increase of the coating thickness.

(3) With the increase of Cr / Ni coating thickness, the content of columnar crystal in the alloying layer increases, the hardness of the sample surface decreases, and the surface corrosion resistance increases.

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