Microstructure and properties of $Fe_{0.5}$NiCoCrCuTi high entropy alloy coating prepared by laser cladding

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Abstract: The $Fe_{0.5}$NiCoCrCuTi high entropy alloy coating was prepared by laser cladding on 40Cr steel surface. The microstructure, hardness, wear resistance and corrosion resistance of $Fe_{0.5}$NiCoCrCuTi high entropy alloy were investigated by means of scanning electron microscopy and energy dispersive spectroscopy (SEM/EDS), micro/Vickers hardness tester, friction and wear tester and electrochemical workstation. Experimental results show that $Fe_{0.5}$NiCoCrCuTi high entropy alloy is mainly composed of coating, heat affected zone and the substrate. The coating has no pores, cracks and other defects, metallurgical bonding with substrate; the coating is mainly composed of two kinds of lamellar microstructure morphology, the grains closely arranged, fine particles are distributed on the grain surface. There is element segregation in the coating, but to a relatively small extent. Under the combined action of fine -grained strengthening, solid solution strengthening and precipitation strengthening, the $Fe_{0.5}$NiCoCrCuTi coating has high hardness, the maximum surface hardness is 857 HV, about 3.3 times as much as the 40Cr steel. High hardness and fine scale precipitates provided a guarantee for the wear resistance of the coating. The corrosion resistance of $Fe_{0.5}$NiCoCrCuTi high entropy alloy coating in 3.5% NaCl and 0.5 mol/L in H_2SO_4 solutions are excellent, compared with 304 stainless steel, the corrosion current density were decreased by 2 and 3 orders of magnitude respectively, the corrosion potential were shift toward positive direction for 0.230 V and 0.161 V respectively.

Key words: laser cladding; high entropy alloy; coating; microstructure; microhardness; wear resistance; corrosion resistance

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激光熔覆 $Fe_{0.5}$NiCoCrCuTi 高熵合金涂层的微观结构及性能

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摘　要: 采用激光熔覆工艺在 40Cr 钢表面制备了 $Fe_{0.5}$NiCoCrCuTi 高熵合金涂层,利用带有能谱的扫描电子显微镜(SEM/EDS)、显微/维氏硬度计、摩擦磨损试验机、电化学工作站等对 $Fe_{0.5}$NiCoCrCuTi 高熵合金微观结构进行分析并测试其硬度、耐磨性能、耐蚀性能。结果表明:$Fe_{0.5}$NiCoCrCuTi 高熵合金试样主要由涂层、热影响区及基体组成,涂层无气孔、裂纹等缺陷,与基体呈冶金结合;涂层主要由两种

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形貌的片状组织组成,晶粒排列紧密,晶粒表面分布着细小的粒子;涂层出现元素偏析,但程度较小;细晶强化、固溶强化、析出强化的共同作用使得$Fe_{0.5}$NiCoCrCuTi涂层具有高硬度,表面最高硬度为857 HV,约为基体40Cr钢的3.3倍,高硬度及细小尺度析出物为涂层的耐磨性提供了保证;$Fe_{0.5}$NiCoCrCuTi高熵合金涂层在3.5% NaCl和0.5 mol/L H_2SO_4溶液中的耐蚀性能优异,与304不锈钢相比,自腐蚀电流密度降低两三个数量级,自腐蚀电位分别正移0.230、0.161 V。
关键词:激光熔覆; 高熵合金; 涂层; 微观结构; 显微硬度; 耐磨性; 耐蚀性

0 Introduction

Chinese Taiwan scholar Yeh J W [1-2] broke through the traditional concept of material design and proposed the concept of high entropy alloys. It was found that high entropy alloys have higher entropy values and are not easily diffused by atoms, and easily obtain solid solution phases and nanostructures with high thermal stability, and even amorphous structures, its performance is better than traditional alloys [3-5]. The high entropy effect brings a series of excellent properties to multi-principal alloys, such as high hardness, high wear resistance, high corrosion resistance, high resistivity[6-9]. Therefore, it has become the current research hotspot. The high entropy alloy is a new kind of alloy that can be synthesized, processed, analyzed, and applied, and has important academic research value and broad industrial application prospects.

The microstructure of laser cladding is a kind of rapid solidification structure. The basic characteristic is that the microstructure is fine and uniform, and the solid solubility of the matrix is increased. The energy of the laser radiation in the cladding process does not spread far enough, and the matrix material melts very little, which ensures that the cladding material does not diluted by the matrix, so that a low dilution rate of the cladding layer is obtained [10-12]. In this way, both the excellent performance of the original cladding material and the thermal effect on the substrate are minimized. Therefore, it can meet the requirements for the use of the material surface without changing the overall characteristics of the material.

In order to improve the surface properties of 40Cr steel, obtain a high entropy alloy coating with uniform composition and excellent performance, and expand the application range of high entropy alloys, a high-performance high entropy alloy laser cladding layer is fabricated on a low-cost substrate by using a laser cladding process.

1 Experiment

Fe, Ni, Co, Cr, Cu and Ti powder with high purity (greater than 99.5%) were used as cladding power. 40Cr steel was used as the substrate material. Before cladding, the 40Cr steel surface was treated by grinding machine, and cleaned by acetone to remove dirt and oil. The alloy powder were mixed in a ball and then pre-coated uniformly on 40Cr steel surface with a layer thickness of 1.0 mm. Laser cladding was carried out with laser processing machine. The processing parameters were: power P=1 800 W, scanning speed V=5 mm/s, spot diameter D=4 mm. The overlap rate of multi-track laser cladding is 35%. Argon was used as protection gas during processing.

The microstructures of $Fe_{0.5}$NiCoCrCuTi high entropy alloy coatings were investigated by field emission scanning electron microscope (SEM, JSM-6700F). Before observation, samples were sanded, polished and then treated by aqua regia. The chemical composition of studied area was analyzed by e nergy dispersive spectrometry (EDS). The hardness was measured by a microscopy/vickers hardness tester (TUKON2100). Hardness test from the coating surface, along the cross–section direction, until deep into the substrate; the distance between two test points is 0.1 mm, with 1.96 N loads, and duration of 15 s, measuring 5 sets of data, take the average as the final outcome. The wear resistance of the substrate and the high entropy alloy coating were measured using an ML–10 abrasive wear tester. The abrasive was a 360 mesh water sandpaper, loaded with 30 N, the wear morphology was observed by scanning electron microscopy. The potentiodynamic polarization curves of the studied coatings and substrate in 3.5% NaCl solution and 0.5 mol/L H_2SO_4 solutions were investigated by an electrochemical workstation (CHI660 D) at room temperature. Three–electrode system was used, in which the saturated calomel electrode is a reference electrode, auxiliary electrode is a platinum electrode and coating specimen is a working electrode, reserve the surface to be measured, and cover the rest with paraffin. The potential scan range of polarization curve was 0.3–1.7 V in 3.5% NaCl solution and 0.75–2.3 V in 0.5 mol/L H_2SO_4 solutions, respectively. The scanning rate was 1 mV/s.

2 Results and discussion

2.1 Microstructure

Figure1 shows the cross–sectional microstructure of $Fe_{0.5}$NiCoCrCuTi high entropy alloy coating. Fig.1(a) is a macroscopic photograph of a laser cladding coating; Fig.1(b) is a image of an alloy coating; Fig.1 (c) is a image of a bounding zone between coating and heat affected zone; Fig.1(d) is a image of the transition zone between the heat affected zone and the substrate.

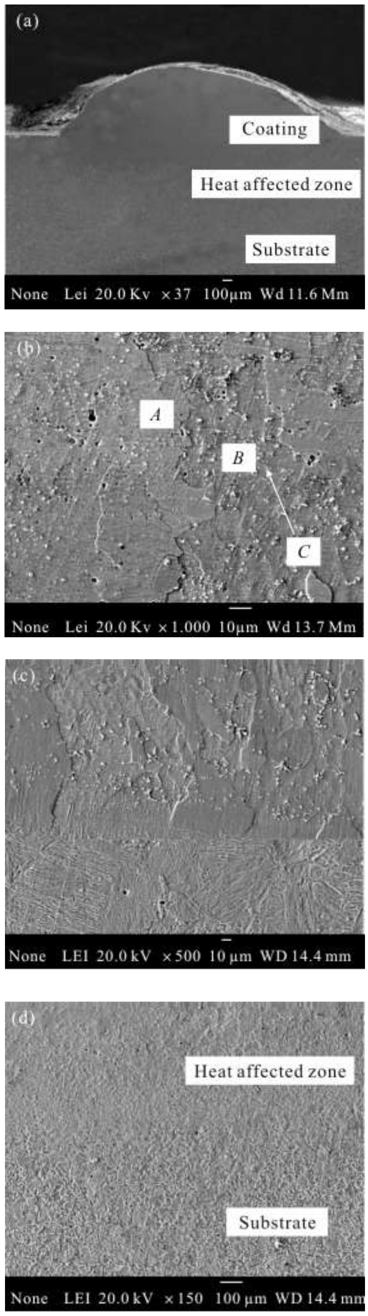

Fig.1 Microstructure images of the high entropy alloy′s coating: (a) macroscopic morphology; (b) coating; (c) bounding zone of coating and heat affected zone; (d) transition between heat affected zone and substrate

As shown in Fig.1 (a), the high entropy alloy laser cladding coating has a spherical shape, no defects such as cracks and air holes in the coating. The surface of the 40Cr steel melts a small part due to the injection of high energy laser beam, and then solidifies with the alloy powder. The bonding zone between the coating and substrate shows an arc shape. The heat affected zone is near the bonding part and the matrix below the heat affected zone.

As shown in Fig.1(b), the microstructure of the high entropy alloy coating mainly consists of two kinds of flaky microstructures. The crystal grains are closely arranged, fine-grained particles are distributed on the surface of the crystal grains. The alloy powder is instantaneously melted by the irradiation of a high energy laser beam, and the arrangement of various elements contained in the melt areas disordered. When solidified, under cooling effect of the 40Cr steel substrate, the diffusion and rearrangement of multiple elements become much harder than traditional alloys, so fine-grained precipitates formed.

As shown in Fig.1(c), the cladding coating is well bonded with the substrate, provides a guarantee for the excellent performance of the coating. The microstructure of the coating is finer than that in the heat affected zone. The reason is that, the alloy powder melts instantaneously under the rapid heating of the high energy laser beam. With the rapid cooling of the substrate, the molten alloy powder and matrix solidify instantaneously. Because of the rapid cooling rate, the crystal structure in the molten pool is not enough to grow up, thus forming a fine microstructure.

As shown in Fig.1(d), the microstructure of the heat affected zone is finer than that of the substrate. The reason is that, the microstructure of heat affected zone changed under the thermal effect of the laser beam. Far away from the heat affected zone, it is hardly affected by heat, so it is still the original microstructure.

The EDS analysis of lamellar microstructure (*A*), (*B*) and fine precipitate (*C*) in Fig.1(b) is shown in Tab.1.

Tab.1 EDS analysis results of high entropy alloy coating (atom fraction/%)

Region	Fe	Ni	Co	Cr	Cu	Ti
Nominal composition	9.10	18.18	18.18	18.18	18.18	18.18
A	19.82	16.16	15.75	12.68	10.20	25.39
B	15.78	18.89	20.18	15.12	20.69	9.34
C	8.12	30.25	26.11	23.20	6.21	6.11

EDS analysis showed that the content of Fe and Ti elements in lamellar microstructure (*A*) were higher than the theoretical content, and the content of Cr and Cu elements were lower than the theoretical content, and the content of the other elements were equal to the theoretical content. The content of Fe in lamellar microstructure (*B*) was higher than that of the theory content, while Ti content is lower than the theoretical content, and the content of the other elements were equal to the theoretical content. The fine precipitate (*C*) is rich in Ni, Co and Cr elements, and is deficient in Cu and Ti elements. The surface of 40Cr steel is partially melted under the action of high energy laser beam, and the content of Fe element increases with the interaction of the alloy powder after melting. The analysis shows that the coating element appears segregation, but the degree is small.

Figure 2 shows the morphology of the large area laser cladding coating. It can be seen that the large area coating is intact and no defect, which guarantees the performance of the coating.

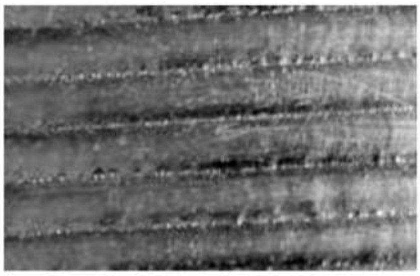

Fig.2 Morphology of large area $Fe_{0.5}NiCoCrCuTi$ high entropy alloy laser cladding coating

2.2 Microhardness

Figure 3 is the microhardness distribution curve of $Fe_{0.5}NiCoCrCuTi$ high entropy alloy. It can be seen that the hardness distribution curve is ladder shaped, corresponding to the cladding coating, the heat affected zone and the substrate respectively.

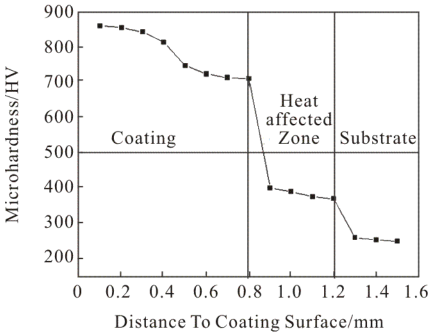

Fig.3 Microhardness of high entropy alloy

The microhardness of $Fe_{0.5}NiCoCrCuTi$ high entropy alloy obtained by laser cladding is significantly improved. The highest hardness of the alloy surface is 857 HV, about 3.3 times as that of the 40Cr steel. Under the effect of rapid laser heating and rapid cooling, the microstructures is very fine and compact, and plays a role in refinement strengthening. Rapid solidification can increase the solid solution limit. In addition, the difference of the atomic radius in the element makes the lattice distortion more serious, strengthening the solid solution strengthening effect. Fine scale precipitates play a role in precipitation strengthening.

2.3 Wear resistance

The weight loss per unit area before and after wear is used to characterize the wear performance. The smaller weight loss of per unit area, the better wear resistance. It is calculated that the weight loss per unit area of 40Cr steel matrix is 3.4 times as that of $Fe_{0.5}NiCoCrCuTi$ high entropy alloy coating. Table 2 illustrates wear parameters of 40Cr and $Fe_{0.5}NiCoCrCuTi$ high entropy alloy coating. Figure 4 show the wear morphology of 40Cr steel substrate and $Fe_{0.5}NiCoCrCuTi$ high entropy alloy coating. It can be seen that the substrate wear is serious, resulting in deep furrows, and trivial metal particles falling off from the surface. The wear of $Fe_{0.5}NiCoCrCuTi$ high entropy alloy coating is relatively light, it has worn scratches, but the depth of the worn scratches is shallow and the width is narrow, indicating that the wear resistance of the coating is better.

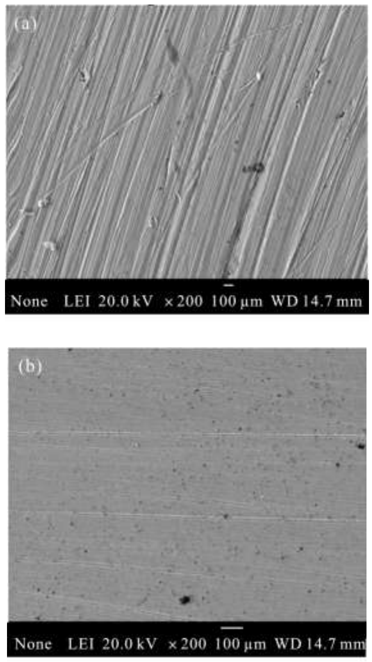

Fig.4 Wear morphologies: (a) 40Cr steel; (b) coating

Tab.2 Wear parameters of 40Cr and high entropy alloy coating

Sample	Wear area/ mm^2	Weight before wear/g	Weight after wear/g	Weight loss/g
40Cr	100	23.000	20.126	2.874
$Fe_{0.5}NiCoCrCuTi$ coating	100	25.000	24.155	0.845

The abrasive wear is mainly caused by the micro cutting of the abrasive particles on the surface of the material. The abrasive particles are pressed into the surface by the normal load, and the abrasive particles are plow on the surface when they are relatively slid. Thus, the debris are formed[13]. There is little chance that the debris will be cut once from the metal surface, most of them cause surface fatigue damage through repeated loads, resulting in small particles falling off from the surface.

The reason for the good wear resistance of $Fe_{0.5}$NiCoCrCuTi high entropy alloy coating is that the high entropy alloy coating has a good metallurgical bonding with the matrix, the high hardness of the alloy coating and the fine particles precipitated in the coating also play a role in improving the wear resistance.

2.4 Corrosion resistance

Figure 5 is the potentiodynamic polarization curves of $Fe_{0.5}$NiCoCrCuTi high entropy alloy coating in 3.5% NaCl and 0.5 mol/L H_2SO_4 solutions. The corrosion kinetic parameters obtained by linear fitting are listed in Tab.3, where I_{corr} indicates corrosion current, E_{corr} indicates corrosion potential, I_{pp} indicates passivation potential, E_{pp} indicates passivation current density, R_p indicates polarization resistance.

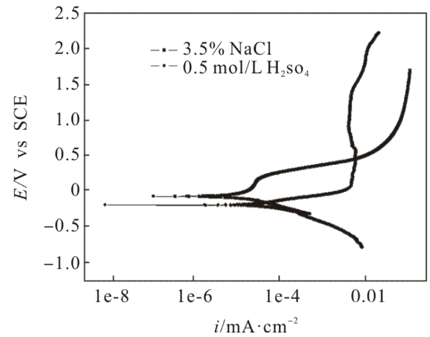

Fig.5 Dynamic potential polarization curves of high entropy alloy coating in 3.5% NaCl and 0.5 mol/L H_2SO_4 solutions

Tab.3 Corrosion dynamics parameters of high entropy alloy coating in 3.5% NaCl and 0.5 mol/L H_2SO_4 solutions

Corrosion solution	I_{corr}/mA·cm^{-2}	E_{corr}/V	I_{pp}/mA·cm^{-2}	E_{pp}/V	R_p/kΩ·cm^2
3.5% NaCl	1.12×10^{-6}	−0.008	7.15×10^{-6}	0.112	0.88
0.5 mol/L H_2SO_4	2.82×10^{-5}	−0.173	1.08×10^{-4}	0.286	1.72

It is known from reference [14] that the corrosion kinetic parameters of 304 stainless steel in 3.5% NaCl solution are: I_{corr}=3.50×10^{-4} mA/cm^2, E_{corr}=−0.238 V. According to the electrochemical theory, the lower corrosion current density and higher corrosion potential, the better corrosion resistance. Compared with 304 stainless steel, the corrosion current density of $Fe_{0.5}$NiCoCrCuTi high entropy alloy coating decreases 2 orders of magnitude, the corrosion potential is higher than 0.230 V, indicating that the corrosion resistance of the coating is excellent. The corrosion of NaCl on high entropy alloy coating is mainly the effect of Cl^-. In $Fe_{0.5}$NiCoCrCuTi high entropy alloy coating, Co, Ni and Cr are all strong corrosion-resistant elements, and it is easy to form passivating film on the alloy surface. It can effectively inhibit the Cl^- that adsorbed on the surface entering the interior and participating in the polarization reaction, thus slowing down the corrosion rate and improve the corrosion resistance. The corrosion resistance of the high entropy alloy coating is related to the passivation film and microstructure characteristics of the surface. The more dense and homogeneous of the passivation film, the stronger of the bonding with the alloy matrix, the better corrosion resistance of the coating.

It is known from reference [15] that the corrosion kinetic parameters of 304 stainless steel in 0.5 mol/L H_2SO_4 solutions are: I_{corr}=2.40×10^{-2} mA/cm^2; E_{corr}=−0.334 V. It can be seen that the corrosion current density of $Fe_{0.5}$NiCoCrCuTi high entropy alloy coating is 3 orders of magnitude lower than that of 304 stainless steel, and the corrosion potential of the coating is higher than

0.161 V, indicating that the corrosion resistance of the coating is excellent. The combination of Cr elements and Ni elements in $Fe_{0.5}NiCoCrCuTi$ high entropy alloy coating is beneficial to passivation and is stable in 0.5 mol/L H_2SO_4 solutions. Under the condition of rapid laser cooling, the grain can not grow up and form a tightly arranged crystal. Although the crystal is segregated, the degree is small, which will not lead to the obvious unevenness of the grain and grain boundary in the electrochemical properties, thus having excellent corrosion resistance.

3 Conclusion

The m icrostructure of $Fe_{0.5}NiCoCrCuTi$ high entropy alloy coating is mainly composed of flaky structure, and the grains are closely arranged, and fine particles are distributed on the grain surface. The coating element is segregated, but the degree is small. The coating with high hardness under the combined action of refinement strengthening, solid solution strengthening and precipitation strengthening. The highest surface hardness of 857 HV, about 3.3 times of the substrate. It provides a guarantee for the wear resistance of the coating. The corrosion resistance of $Fe_{0.5}NiCoCrCuTi$ high entropy alloy coatings in 3.5% NaCl and 0.5 mol/L H_2SO_4 solutions are excellent. Compared with 304 sta inless steel, the corrosion current density decreases by 2 and 3 orders of magnitude respectively, and the corrosion potential is higher than 0.230 V and 0.161 V respectively.

References:

[1] Yeh J W, Chen S K, Gan J Y, et al. Formation of simple crystal structures in solid-solution alloys with multi-principal metallic elements [J]. ***Metallurgical and Materials Transactions A***, 2004, 35A: 2533-2536.

[2] Yeh J W, Chen S K, LIN S J, et al. Nanostructured high-entropy alloys with multi-principal elements - novel alloy design concepts and outcomes [J]. ***Advanced Engineering Materials***, 2004, 6: 299-303.

[3] Pham Thihongnga, Liu Hongxi, Zhang Xiaowei, et al. Microstructure and high-temperature wear behaviors of Co/TiC laser coatings on die steel [J]. ***Optics and Precision Engineering***, 2013, 21(8): 2048-2055. (in Chinese)

[4] Li Z M, Pradeep K G, Deng Y, et al. Metastable high-entropy dual-phase alloys overcome the strength - ductility trade-off [J]. ***Nature***, 2016, 534: 227-230.

[5] Ma Chen, Ma Zhuang, Gao Lihong, et al. Laser damage mechanism of flake graphite modified phenolic resin coating [J]. ***Chinese Optics***, 2017, 10(2): 249-255. (in Chinese)

[6] Qiu X W, Wu M J, Qi Y, et al. Microstructure and corrosion resistance of $Al_2CrFeCoCuNi_xTi$ high entropy alloy coatings prepared by laser cladding [J]. ***Infrared and Laser Engineering***, 2018, 47(7): 0706008.

[7] Qiu X W, Huang C X, Wu M J, et al. Structure and properties of AlCrFeNiCuTi six principal elements equimolar alloy [J]. ***Journal of Alloys and Compounds***, 2016, 658: 1-5.

[8] Hsu Y J, Chiang W C. Corrosion behavior of FeCoNiCrCux high-entropy alloys in 3.5% sodium chloride solution [J]. ***Materials Chemistry and Physics***, 2005, 92: 112-117.

[9] An Xulong, Liu Qibin, Zheng bo. Microstructure and properties of laser cladding high entropy alloy MoFeCrTiWAlxSiy coating [J]. ***Infrared and Laser Engineering***, 2014, 43(4): 1140-1144. (in Chinese)

[10] Liu Hongxi, Tao Xiaode, Zhang Xiaowei, et al. Microstructure and interface distribution of Fe-Cr-Si-B-C laser cladding alloy coatings assisted by mechanical vibration [J]. ***Optics and Precision Engineering***, 2015, 23(8): 2192-2202. (in Chinese)

[11] Zhang Min, Liu Chang, Ren Bo, et al. Microstructure and mechanical properties of porous Ni alloy fabricated by laser 3D printing [J]. ***Chinese Optics***, 2016, 9(3): 335-341. (in Chinese)

[12] Liu Hongxi, Leng Ning, Zhang Xiaowei, et al. Microstructure and wear behavior of WC/Co50 composite coatings on 40Cr cutting tool surface prepared by laser cladding [J]. ***Infrared and Laser Engineering***, 2016, 45(1): 0120001. (in Chinese)

[13] Zhang A J, Han J S, Su B, et al. Microstructure, mechanical properties and tribological performance of CoCrFeNi high entropy alloy matrix self-lubricating composite [J]. ***Materials & Design***, 2017, 114: 253–263.

[14] Li Wei, Liu Guizhong, Guo Jingjie. Microstructure and electrochemical properties of Al_xFeCoNiCrTi high-entropy alloys [J]. ***Foundry***, 2009, 58(5): 431–435. (in Chinese)

[15] Luo Xiaoyan, Liu Guizhong, Li Wei, et al. Microstructure and electrochemical properties of AlFeCoNiCrTiV_x high-entropy alloys [J]. ***Corrosion & Protection***, 2010, 31(5): 355–358. (in Chinese)