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ARTICLE

Effects of Annealing on the Microstructure and Wear Resistance of $AlCoCrFeNiTi_{0.5}$ High-entropy Alloy Coating Prepared by Laser Cladding

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Abstract: Annealing behavior of $AlCoCrFeNiTi_{0.5}$ high entropy alloy coatings prepared by laser cladding was investigated. The specimens were annealed at 900 ℃ for 5 h. The microstructure and wear resistance of the as-annealed and as-cast specimens were investigated. The XRD results indicate that the as-annealed $AlCoCrFeNiTi_{0.5}$ high entropy alloy coating is composed of $Al_{80}Cr_{13}Co_7$, Co_3Ti, and AlFe solid solution phase. The SEM results and EDS data show that a typical spinodal decomposition structure with uniform composition is formed after annealing treatment. The average Vickers micro-hardness of the as-annealed coatings could reach 9890 MPa which is increased by about 73.5% compared with that of the as-cast coatings. The abrasion resistance testing shows that the abrasion loss of the as-annealed coatings is reduced by 92.5% and the wear width is reduced by 50% compared with the values of as-cast coatings.

Key words: high-entropy alloy; annealing; wear resistance; laser cladding

High-entropy alloys (HEAs), which are defined as alloys containing at least five principal elements with atomic concentration between 5% and 35%, have broken the traditional alloy design concept based on one or two principal components and emerged as a new research frontier in the metallic materials community[1]. According to recent study, the high entropy alloys have high lattice deformation and high mixing entropy so that the phases number of the frozen high entropy alloys is less than that forecasted by the equilibrium fraction. At the same time, high entropy alloys may form a simple fcc or bcc solid solution and nano-scale precipitation or amorphous. Therefore, high entropy alloys may possess high strength, high hardness, abrasion resistance, corrosion resistance, and oxidation resistance at high temperature[2,3]. Y. P. Lu[4] and his research team had proposed a novel strategy to design HEAs using the eutectic alloy concept and successfully produced the bulk alloy ingot, which can be readily adapted to large-scale industrial production of HEAs with simultaneous high fracture strength and high ductility. Y. Dong et al[5,6] investigated the effects of vanadium and Molybdenum element addition on the microstructure and mechanical properties of $AlCoCrFeNiV_x$ and $AlCrFeNiMo_x$ respectively. W. R. Wang[7] et al have studied the $Al_xCoCrFeNi$ alloys with different aluminium contents. The result shows that with the increase of aluminium content, the phases in the alloys contain not only a simple fcc solid solution, but also bcc ones as main phases. Xiaoyan Luo [8] et al have studied the hardness and the electrochemical characteristics of the $AlFeCoNiCrTiV_{0.5}$. The result shows that with the change of the annealing temperatures, alloy phases change and the phase transformation point is 900 ℃ during the annealing treatment of the alloy. Wei Li[9] and his research team investigated the effects of Ti contents on the microstructure and properties of high entropy alloys; the microstructure is optimized, and the hardness reaches its maximum when Ti content is x=0.5 for $AlCoCrFeNiTi_x$. Xiaoyan Luo [8] and Y. F. Wang [10] et al confirmed that the alloys had a good comprehensive mechanical property when annealing temperature was 900 ℃

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and Ti content was x=0.5 for $AlCoCrFeNiTi_x$ alloys. However, the studies of wear resistance are not reported for these alloys in recent years. Laser cladding is a rapidly developed surface treatment technique, which takes great advantages of rapid solidification velocity, fine microstructure, excellent metallurgical bonding, and little intermixing with the substrate. H. Zhang et al[11] have prepared 6FeNiCoCrAlTiSi high-entropy alloy coating by laser cladding and investigated the influences of high temperature annealing treatment on the structure, mechanical, and electrical properties of the coating. We have prepared $AlCoCrFeNiTi_{0.5}$ high-entropy alloy coatings by laser cladding. The purpose of this study is to investigate the effects of annealing on the microstructure and wear resistance of the $AlCoCrFeNiTi_{0.5}$ coatings.

1 Experiment

The alloy powder was mixed with Al, Co, Cr, Fe, Ni, Ti alloy powders and the purities are above 99.9% for each one. The composition of $AlCoCrFeNiTi_{0.5}$ alloy is shown in Table 1. The substrate material for laser cladding is industrial pure iron.

The $AlCoCrFeNiTi_{0.5}$ high entropy alloy coatings were prepared by laser cladding with HGL-6000 CO_2 multi-functional numerically-controlled laser processing machine. The alloy powder for laser cladding was uniformly mixed by an agate mortar machine and preheated at 100 ℃ for 24 h. The powder was preset on the base material and the thickness of the powder layer was 1.0 mm. The laser power was 3500 W, the scanning speed was 300 mm/min, and the spot diameter was 5 mm. The cladding process was shielded with argon. The specimens were then annealed at 900 ℃ for 5 h. The specimen structures were identified via x-pert power X-ray diffraction (XRD) with Cu radiation operating at 40 kV/30 mA and a scanning step of 0.065 and 2θ changed from 10° to 70°. The XRD patterns were analyzed by High Score plus. The ground and polished specimen were etched in a solution of aqua regia for 5 to 20 s. The microstructures were observed with a HITACHS-3400 N SEM. Vickers hardness was measured by a HITACHS-3400 N Vickers hardness tester with a loading force of 4.9 N and a loading time of 15 s. The wear resistance was measured by a CSM-TRIBOMETER friction wear tester with normal load force of 13 N and reciprocating speed of 10 cm/s. The reciprocating linear distance was 24 mm and the friction pair was SiN.

2 Results and Discussion

2.1 Effect of annealing on crystal structure

Fig.1 shows the X-ray diffraction profiles of as-cast and as-annealed $AlCoCrFeNiTi_{0.5}$ high-entropy alloy coating. The results reveal a remarkable influence of annealing on the crystal structure evolution of the $AlCoCrFeNiTi_{0.5}$ high entropy alloy. Fe_2Ti and $Co_{4.00}$ with simple fcc solid solution structure form in the as-cast specimen. After annealing at 900 ℃, AlFe with bcc structure and $Al_{80}Cr_{13}Co_7$ and Co_3Ti compounds appear. According to the formula of interplanar spacing, the lattice parameter of AlFe solid solution is 0.290 nm, which is slightly less than that of bcc-Fe (a=0.293 nm). Meanwhile, some Fe atoms of bcc-Fe are replaced by Al atoms and formed AlFe phase. The similar phase was also observed in L12-Co_3Ti intermetallic compounds[12]. Yuan Liu et al[13] reported that compounds and ordered substitutional solid solutions formed when $\Delta H_{mix} < 0$, while disordered solid solutions formed when $\Delta H_{mix} \approx 0$. The mixing enthalpies of Al-Fe, Co-Ti and Fe-Ti atomic pairs are less than 0. According to ΔH_{mix} formula[14], the mixing enthalpy ΔH_{mix} of $AlCoCrFeNiTi_{0.5}$ high-entropy alloy is –17.92 kJ/mol, which is between –40 kJ/mol and 10 kJ/mol. Therefore, simple transpositional solid solutions are obtained in the investigated alloy system [15]. Both fcc and bcc transpositional solid solutions form in the annealed coatings, while only fcc solid solutions appear in the as-cast coatings.

Table 1 Composition of $AlCoCrFeNiTi_{0.5}$ alloy (at%)

Number	Al	Co	Cr	Fe	Ni	Ti
1#&2#	9.76	21.32	18.81	20.21	21.24	8.66

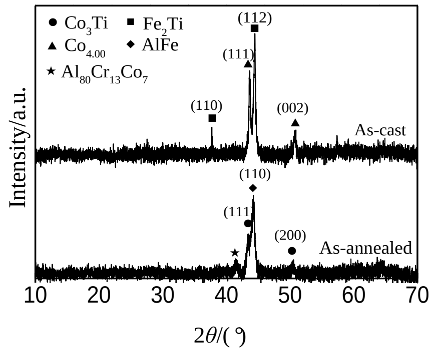

Fig.1 XRD patterns of as-cast and as-annealed $AlCoCrFeNiTi_{0.5}$ high-entropy alloy coating

2.2 Effect of annealing on microstructure

Fig.2 shows the microstructures of as-cast and as-annealed $AlCoCrFeNiTi_{0.5}$ alloy coatings in the center of the coatings. Fig.2a shows that the as-cast coatings consist of bulk dendrites and primary α phases, which is similar to the research results of Qunhua Tang et al [16]. This phenomenon indicates that dislocation, grain boundary and interface defects possibly exist within the as-cast alloys, which precipitate high thermodynamic free energy in unsteady state. The micro-structure of the annealed specimen is fine and typical spinodal decomposition structures are formed in the interden-drite[7,13,17]. EDS data of different regions of the coating are given in Table 2. Fig.2a shows that titanium segregates in the primary α phases because of rapid solidification during laser cladding and segregation character of titanium. The segre-gation of titanium has been eliminated in Fig.2b. Fe_2Ti and $Co_{4.00}$ solid solutions are formed in the dendrite and interdendrite,

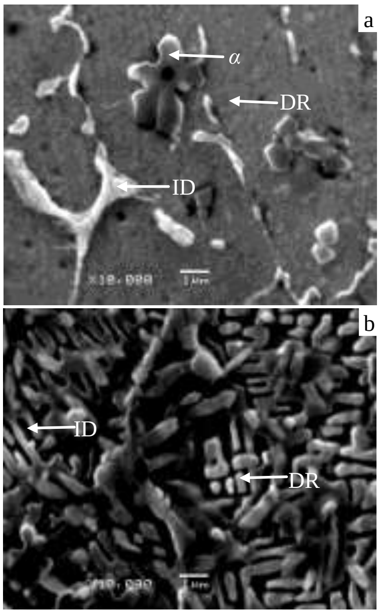

Fig.2 Microstructures of as-cast and as-annealed $AlCoCrFeNiTi_{0.5}$ alloy coating

Table 2 EDS data of different regions of the coating in Fig.2 (at%)

Condition	Region	Al	Co	Cr	Fe	Ni	Ti
As-cast	DR	12.11	13.49	13.79	42.48	13.84	4.31
	ID	9.77	14.23	27.47	34.55	11.55	2.44
	α	24.75	5.57	7.96	11.68	5.49	44.55
As-annealed	DR	17.01	13.00	17.96	36.88	14.24	0.91
	ID	23.90	13.41	12.81	28.09	20.68	1.12

respectively, in Fig.2a. Grain boundary is devoured and typically spinodal decomposition microstructures form in the annealed coating. The formation of the spinodal decomposition microstructures is related to stress field formed by grain boundary, dislocation, vacancy etc in the as-cast sample. The contents of Al and Fe are rich in dendrites. The elasticity modulus of Al and Fe are different in spinodal decomposition microstructures, the whole system forms nonuniform elasticity modulus and AlFe will separate out in anisotropic state. Similar results were reported by Ziqing Weng et al[18] in their study on annealed FeCrNiCoMn high-entropy alloy coating prepared by laser cladding.

2.3 Effect of annealing on Vickers hardness

Fig.3 shows the hardness of as-cast and as-annealed $AlCoCrFeNiTi_{0.5}$ coating. The average Vickers hardness of the as-annealed specimens is 9890 MPa, which is increased by 73.5% compared with that of the as-cast specimen. Hardness increasing is mainly because of solute strengthening and precipitated strengthening. Firstly, complex phase $Al_{80}Cr_{13}Co_7$ and AlFe solid solution with bcc structure form in the annealed alloy, which can enhance hardness by increasing lattice distortion and preventing slippage. Similar results were

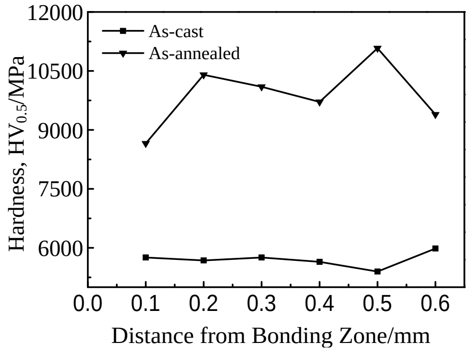

Fig.3 Hardness of $AlCoCrFeNiTi_{0.5}$ alloy coating

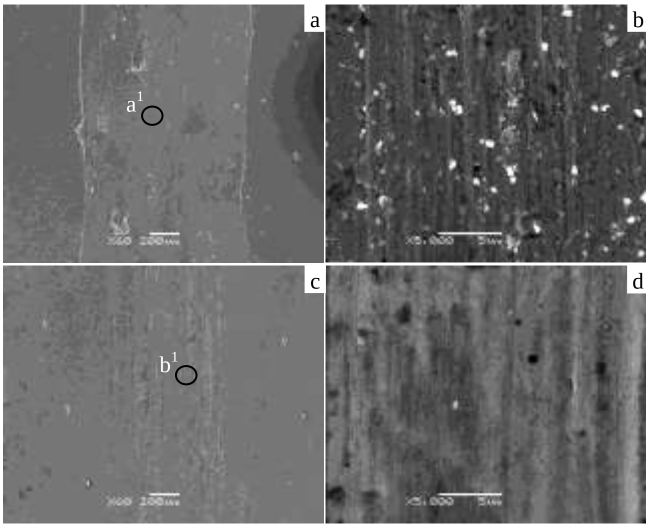

Fig.4 SEM micrographs of polishing scratch foras-cast (a, b) and as-annealed (c, d)

given by Ziqing Weng et al [18]. Secondly, fine and uniform spinodal decomposition microstructures lead to much higher hardness in as-annealed coatings.

2.4 Effect of annealing on wear resistance

Fig.4 shows SEM micrographs of grinding crack. Fig.4a and 4b show that the wear width in the as-cast sample is twice the size of that in as-annealed sample. Meanwhile, the wear scar of the annealed sample is relatively smooth and shiny, which indicates that the fine spinodal decomposition microstructures form a compact protective film on the surface. The mass loss of the as-annealed sample is 0.4 mg, which is decreased by 92.5 % compared with that of the as-cast sample. Solid solution with bcc structure and typical fine spinodal decomposition microstructures are formed in the as-annealed coating, which increases wear resistance because of solute strengthening and precipitated strengthening.

3 Conclusions

1) $AlCoCrFeNiTi_{0.5}$ high entropy alloy coatings are prepared

by laser cladding and annealed at 900 ℃ for 5 h. The phases of the annealed samples are Co_3Ti and solid solutions with bcc structure, which are superior to those in as-cast coating.

2) Fine and uniform components spinodal decomposition microstructures are formed in the annealed coatings, while the microstructures of the as-cast samples are coarse dendrites and primary α phases. The compositional variation is decreased and the segregation of titanium disappears in the as-annealed sample.

3) The average Vickers hardness of the annealed samples is 9890 MPa, which is increased by 73.5% compared with that of the as-cast samples. The mass loss is decreased by 92.5% and the wear width is decreased by 50% for the annealed samples.

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退火对激光熔覆 $AlCoCrFeNiTi_{0.5}$ 高熵合金涂层组织和耐磨性的影响

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摘　要：对激光熔覆$AlCoCrFeNiTi_{0.5}$高熵合金涂层进行900 ℃退火，保温5 h处理。主要对退火前后样品的微观结构和耐磨性进行研究。XRD结果表明，退火后的$AlCoCrFeNiTi_{0.5}$高熵合金涂层，其相组成有Co_3Ti和bcc结构的AlFe固溶相，出现典型的成分均匀的网状调幅分解组织；退火后的平均显微硬度达到9890 MPa，比退火前提高了73.5%；耐磨性测试结果显示，退火后磨损量比退火前降低了92.5%，磨损宽度是退火前的50%。

关键词：高熵合金；退火；耐磨性；激光熔覆

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