FeCoNiAlTiCrSi high entropy alloy coating prepared by laser cladding

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Abstract. A FeCoNiAlTiCrSi high entropy alloy coating was cladding on the surface of Q235 steel by laser using FeCoNiAlTiCrSi as basic alloy powder in which B, C, and Y_2O_3 were added as a in situ synthesized elements. The results show that the 2mm thickness coating with no crack and pores was prepared under the optimized laser process parameters that the power is 1380W, spot size is 6mm × 4mm, scanning speed is 6mm/s, overlapping rate is 36% and shielding gas velocity is 1.5L/min. The structure is mainly composed of FCC and TiC particle phase, the size of the TiC particle synthesized in-situ is about 0.5μm-3μm. The average microhardness of coating is $450HV_{0.2}$, The dispersed TiC particles play the role of strengthening and toughening. The 2 mm thickness FeCoNiAlTiCrSi high entropy alloy coating prepared by this laser cladding method has good hardness and toughness.

Introduction

Multi element high entropy alloy is composed of n (n＞＝5) of a metal or metal and non metal that was proposed by Ye Junwei, a professor in Taiwan, in 1995. It has the characteristics of metal materials through smelting, sintering, laser cladding or other methods [1]. According to Boltzmann's hypothesis, the molar entropy of solid solution alloys composed of n equivalent element is as follows: $\Delta S_{conf}=R\ln(n)$,where R is gas constant, n is number of elements. As Boltzmann's law shown, the mixing entropy will increase with the growth of n[2]. Generally, high entropy alloys (HEAs) are defined as the alloys that contain at least five principal elements with each elemental concentration ranging from 5 to 35 at.%, and $\Delta S_{conf}>1.61R$. The micro structure of high entropy alloy is relatively simple and it's not easy to form intermetallic compounds. In the as cast and fully tempered state HEAs can be precipitated nanocrystals phase and amorphous structure. These particular structure with proper composition can offer HEAs with promising applications due to high strength, high hardness, good wear resistance and corrosion resistance [3-8] in industry.

In this paper, we use the laser cladding method and design the multi element high entropy alloy composition. In other words, it is based on Fe, Co, Ni, Ti, Cr, Si ,Al high entropy alloy powder by adding C, B, Y_2O_3 and so on in situ particle formation components to form a composite alloy powder system.The microstructure features, in situ particle phase composition, hardness mechanism of the coating are studied. This work provide reference for laser cladding high thickness high entropy alloy coating with good strength and toughness.

Experimental Process and Method

The substrate material used in the experiment was Q235 steel. The Fe, Co, Ni, Cr, Al, Si, C, B, and Y_2O_3 were used as components of laser cladding coating, and these elements were chemical reagent (purity >99%) with a particle diameter of 200 mesh. The research of this experiment alloy molecular formula is $FeCo_2Ni_2Al_{0.5}TiCr\ Si_2$. According to the in situ reinforced design, the multi elements alloy composition constitution is shown in table 1, which is mainly based on seven element alloy elements, adding C, B and Y_2O_3 to form a new type of composite powder.

Table 1 The components of the alloy powder (wt.%)

Element	Ni	Cr	Co	Fe	Al	Ti	Si	B	C	Y_2O_3
Content	23.97	10.63	24.05	11.37	2.73	9.78	11.47	3	2	1.5

The powder fractions were accurately weighed using an electronic balance to form designed composition as shown in Table 1, then mixed together for 8 hours in a ball milling tank to produce the composite powder. The oxides were removed from the surface of Q235 steel using polishing machine. The surface roughness of Q235 steel increased with the coarsening of surface, and the adhesion between the pre-coating and the substrate became better. The powder was evenly coated on the surface of Q235 with each preset 0.8mm thickness, then drop a moderate volume ratio for the mixed binder 20:1 acetone and 502 glue to place a few minutes for precoating. After acetone being completely volatile, samples were taken to laser cladding, the final preparation of the sample thickness reached 2.5mm through the method of multilayer cladding.

The experiment laser was the FL-Dlight02-3000W semiconductor produced by XiAn Juguang Company, the wavelength is 973nm，the laser spot size is 6mm × 4mm. The coating was deposited under the protection of 0.2Mpa side blowing argon.

Microstructure and in situ particle

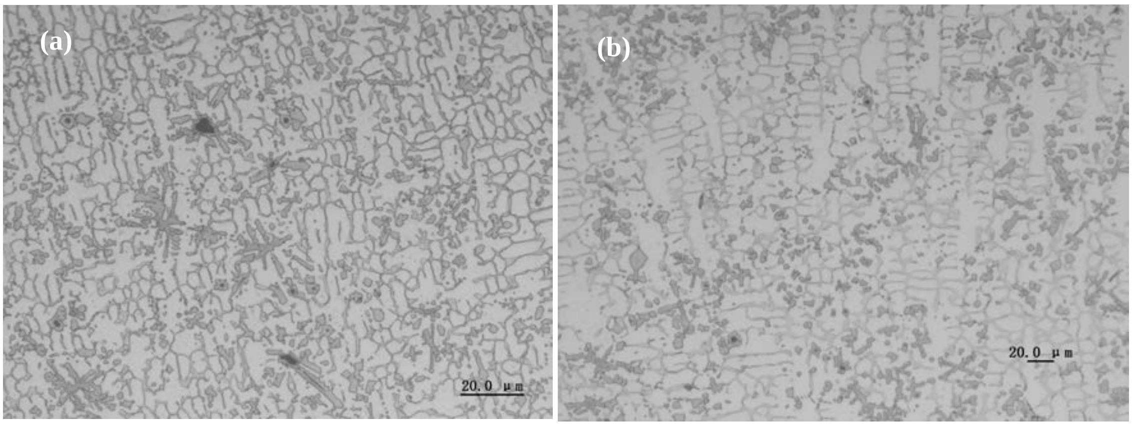

Fig. 1 OM image of laser cladding FeCoNiAlTiCrSi alloy coating:
(a)- the micro top;(b)- the middle part of the micro.

The microstructures of different positions of sample are shown in Fig.1. The microstructures near the top of deposition layer are mainly consist of the equiaxe grains and fine dendrites. Because the melting pools in the top of deposition were cooling by heat conduction of below deposition, surrounding air radiation and thermal convection, which causes growth of nucleation rate so that the grains on the top of deposition can become more finer as Fig. 1(a) shown. The primary grains grow to the liquid metal along the preferred growth direction which is vertical to the interface, which causing the formation of directional solidification dendrites. As presented in the Fig. 1(b).

Fig. 2 is the FESEM images and EDS analysis of the sample. As can be seen from the Fig. 2(a), precipitated particles distribute dispersively in the coating. Table 2 shows the EDS analysis of Fig. 2(b) different regions . According to Table 2, the point 1 is the matrix of the FeCoNiAlTiCrSi high entropy alloy, the point 2 is the in situ synthesized particles. The point 3 is rich in B and C phase.The matrix is mainly Fe, Co, Cr, Ni, Ti, Al, Si and other components and no obvious segregation of elements, the component analysis of point 2 is TiC phase, which are in the shape of black block, acicular and petaloid dispersed in the matrix. These are the evidence that in situ particle reinforced phase has been produced by laser metallurgy in the high entropy alloy matrix under the conditions of experimental design.

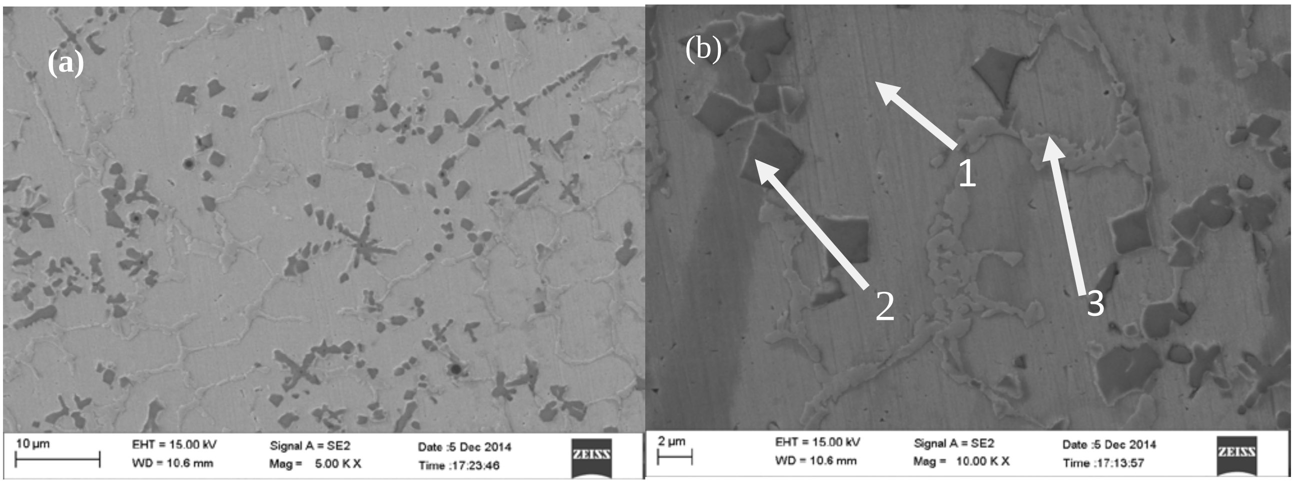

Fig. 2 FESEM images of in situ synthesized particles in FeCoNiAlTiCrSi alloy coating: (a)- the dispersed particles; (b)- EDS of different structure

Table 2 The EDS analysis results of different point (at.%)

Element	B	C	O	Al	Si	Ti	Cr	Fe	Co	Ni	Y
1	5.39	5.93	1.52	5.4	5.05	12.28	8.51	15.27	20.3	20.35	0
2	1.16	50.64	0	0.03	0.1	45.65	0.83	0.54	0.58	0.47	0
3	20.40	19.97	0.00	0.50	7.39	9.51	3.72	5.71	14.10	18.69	0.01

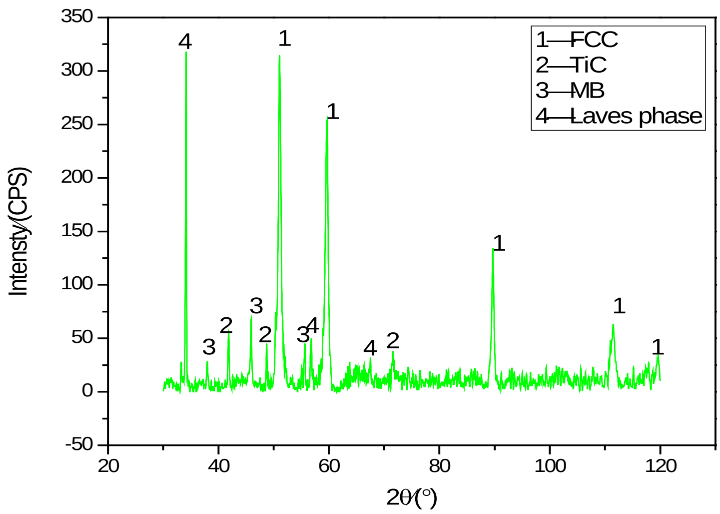

Fig.3 XRD pattern of laser cladding FeCoNiAlTiCrSi high entropy alloy coating

Hardness and phase analysis

The XRD analysis of the samples is shown in Fig. 3，as can be seen from the analysis, the structure of the laser cladding FeCoNiAlTiCrSi high entropy alloy coating is mainly composed of simple FCC solid solution (FeCoNiAlTiCrSi), the in situ formatting TiC phase, in situ formatting TiC phase, the MB(M:Ni、Cr、Ti) phase and laves phase(Y_2O_3). So that adding B, C and other high entropy alloy elements formed in situ reinforced phase. So that adding B, C and other high entropy alloy elements formed in situ reinforced phase. Under high energy of laser, Y_2O_3 will decompose, free Y and other elements to form Laves phase precipitates at grain boundary[9].There are no intermetallic compounds. This shows that successfully prepared high entropy alloy in situ reinforced under the experimental conditions.

Fig. 4 is distribution of sample's micro-hardness. The hardness distribution of sample is uniform and relatively high with the average of $450HV_{0.2}$. The addition of Y_2O_3 can refine the grain size, so as to effectively promote the improvement of strength and toughness. At the same time, the formation of solid solution phase and in situ particle which can pin the grain boundaries and hinder dislocation motion greatly improve the hardness. Consequently, the FeCoNiAlTiCrSi high entropy alloy coating with good strength and toughness can be prepared under this condition.

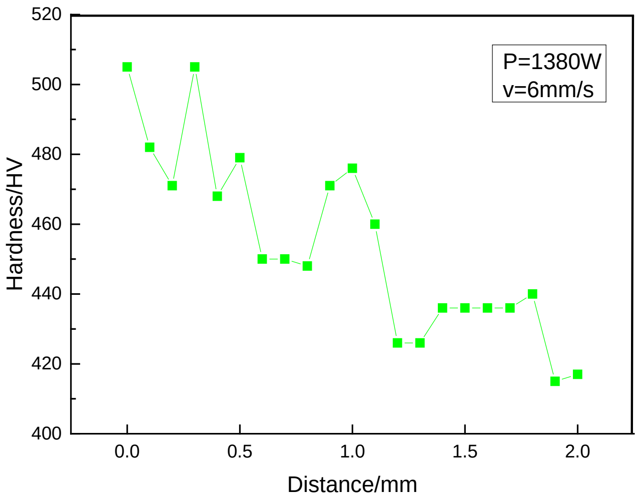

Fig. 4 the hardness distribution of laser cladding FeCoNiAlTiCrSi alloy coating

Conclusion

The optimal laser cladding parameters for this test are shown as follows: laser power is 1380W; spot size is 6mm×4mm, scanning speed is 6mm/s, and overlapping ratio is 36%; Argon shielding gas velocity is 1.5L/min. A in situ particle enhanced FeCoNiAlTiCrSi high entropy alloy (HEA) coating with 2mm thickness is successfully prepared on the surface of Q235, there are no pores and cracks in coating. The structure is mainly composed of FCC and TiC particle phase, the size of the TiC particle synthesized in-situ is about 0.5μm-3μm. The average microhardness of coating is $450HV_{0.2}$, The dispersed TiC particles play the role of strengthening and toughening. The FeCoNiAlTiCrSi high entropy alloy coating prepared by this laser cladding method has good hardness and toughness.

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