Laser direct deposition ZrO_2 particle reinforced Fe60 alloy coating

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Abstract. The ZrO_2 particle reinforced Fe60 alloy coatings were deposited on the surface of steel by laser using Fe60 self-fluxing spherical alloy powder adding mass fraction of 0.1%, 0.3%, 0.5%, 0.7%, 0.9% content ZrO_2 powder. The structure and hardness of the samples were analyzed by the means of OM、SEM、XRD、micro-hardness tester. Experimental results show that: ZrO_2 powder in Fe60 alloy powder can alleviate the generation of cracks effectively in the process of laser direct deposition, Fe60 alloy coating with high Cr content was prepared successfully on the steel substrate, and the coating formed good metallurgical bonding with the Q235 steel, and the thickness of the coating is up to 6mm. The phases of the deposited coating composed of Cr_7C_3, α- Fe, {Fe, Cr} solid solution, ZrO_2, and Fe_3C. ZrO_2 particle play an important role in phase transformation toughening and dispersion toughening, the cracks in the sample has been eliminated due to addition of ZrO_2 ceramic powder. The coating with 0.5% ZrO_2 particle had fine crystal structure without cracks, and the hardness is up to 817HV. Therefore, the adding ZrO_2 ceramic particles to Fe60 alloy powder is an effective way to eliminate cracks and improve the hardness in the laser direct deposition Fe60 alloy coating with high wear-resistant..

Introduction

Laser direct deposited Fe base alloy coating has been widely applied to prepare wear resistant coating on the surface of the steel, due to strong interface bonding and high performance[1,2]. With the rapid development of laser direct deposition technique in laser, material deposition, and deposition mechanism, the wear resistant coating with high thickness(≥3mm) deposited by laser on some key parts of high speed train and nuclear power equipment become a new development direction. However, laser cladding technique also had some disadvantages, e.g., the thermal stress which was induced in the course of laser cladding could lead to crack formation in the composite coatings [3]. Especially, it's easy to produce cracks in the laser cladding coating with high wear resistance, due to the high content of C and Cr element in the coating alloy, which often limits the industrial application of the coating [4], in addition, with the increase of coating thickness, crack sensitivity will increase. So how to solve the problem of crack is of great significance. Most methods for controlling cracks from the adjustment of the laser cladding process, composition extension, and the gradient coating design, have made someimportant progress. Kim et al found that a well uniform, crack-free coating of HAP/ZrO_2 composites had formed on Ti-alloy substrate by laser cladding [5], it proved that zirconia(ZrO_2) exhibited distinct effects on reinforcing coating and preventing cracking. The addition of V_2O_5 has an apparent effect on enhancing the toughness, refiningthe microstructure and reducing the cracking sensitivity of the coating [6].

So far, researches of lase rdirect deposition Fe base alloy coatings with high wear resistance mainly concentrated in thin layer,while the research reports of the wear-resisting coating with high thickness (≥3mm) are still less [7] . Because the thermal conductivity of ZrO_2 is lowest and the coefficient of thermal expansion is closer to the metal material, ZrO_2 is an important structural ceramic material. Zirconia has a different phase structureat different solidification molding conditions, and the four- zirconia phase in the external force with aphase to monoclinic phase characteristics. Ceramic particle reinforced iron matrix composites are one of the most promising wear resistant materials for tough conditions[8]. but the toughening effect of iron-based with zirconia has not been reported. Therefore, to study the development of wear-resistant coating on the steel of the ball mill liner with high strength and high toughness, and to solve the crack problems of the Fe-based alloy laser cladding coating, the new experiment need to be done. In this paper, Fe60 iron base self- fluxed spherical alloy powder work as laser direct deposition powder material, the Fe60 alloy coatings with high hardness and thickness were deposited on the surface of Q235 steel by semiconductor laser at room temperature. The powder of the experiment with 0.1%, 0.3%, 0.5%, 0.7%, 0.9% ZrO_2 ceramics powder respectively, to explore the mechanism of the ZrO_2 on the coating of the steel.

Experimental Materials and Methods

Materials and methods of the samples preparation.

The substrate is Q235 steel, its size is 200× 100×10mm, the surface oxide film of substrate was removed by a grinding wheel. The deposited layer material was mass fraction of 0.1%, 0.3%, 0.5%, 0.7%, 0.9% ZrO_2 of Fe60 alloy, the size of the particle is 140 to 200 mesh, and the chemical composition is as shown in Table 1.

Table 1 Chemical composition of Fe60 powder

Element	B	C	Si	Cr	Ni	W	Fe
Content(wt.%)	1.5-2.5	4.0-4.5	2.0-3.0	24-30	4-6	2-3	Bal.

Preparation of experiments.

The experiment system of the FL-Dlight02-3000W semiconductor laser and coaxial powder feeding was used. The optimal parameters: laser power is 1600W, scanning speed is 180mm/min, laser spot diameter is 6×4mm, powder feed amount is 8.4g /min, and overlapping ratio is 30%. During the time of experiment, the each sample was deposited 11 layers to form 7 mm thickness coating on the steel substrate. To prevent oxidation, Ar is used as the protective gas.

Experimental analysis.

The coating was cut to 10×10mm by wire–cut electrical discharge machining to obtain cross-sections of vertical laser scanning direction. The samples mounted in denture powder after washed were ground by 100# to 2000# sandpapers, polished with diamond power and etched by a Kroll's (1 mL HNO_3 and 3 mL HCl) during seven seconds. Microstructures were characterized using a OLYMPUS-GX71 optical microscope (OM). Micro-hardness was measured using a 401MVDTM microhardness tester at a load of 1N and an indentation time of 10s. Phase identification was performed using Rigaku SmatLab-9000 X-raydiffractometer (XRD). The optimal parameters:X-rays target is Cu, Kα ray tube voltage is 45Kv, tube current is 200mA, the angle range is 20°~100°, scanning speed is 2°/min.

Results and discussion

Microstructure of the Fe55 alloy coating.

Fig. 1 is the metallographic photos of samples with different concentration ZrO_2 ceramicpowders. Fe60 is wear-resistant alloy with high C and high Cr, so crack is easy to produce in the process of laser deposition. Because the sample cool rapidly, so the temperature gradient become bigger. Due to the coefficient of thermal expansion and the shrinkage rate of the material aredifferent, the produced thermal stress, microstructure stress, constraint stress leading to the coatingcan't shrink freely, resulting in cracks. Laser cladding experiment in the ceramic plate can minimizethe heat loss, reduce the temperature gradient, therefore, the possibility of cracks decreased. ZrO_2 has the effect of phase transformation toughening and dispersion toughening, which can improve the toughness of the cladding layer and eliminate the crack significantly. At the same time, the thermal conductivity of

ZrO_2 is close to that of metal materials, so it is an important structural ceramics,which can avoid the stress caused by the difference of material properties, and prevent the crack ofthe coating effectively. As shown in the Fig.1(a), the cracks exist in the cladding layer with 0.3%ZrO_2 powder, may be because the content is too low, and the toughening effect is not significant. Fig.1(b) shows the microstructure of the grain is more small with 0.5% ZrO_2 ceramic powder, and the fine grain strengthening and the dispersion strengthening reduce the possibility of cracks. Fig.1(c) and (d) is the OM images of samples with different ZrO_2 powder, such as the content of ZrO_2 is 0.7% and 0.9%. Contrast with (b), the grain is bigger, so the grain strengthening effect is not enough. At the same time, Fig. 2 also reflect the rule that ZrO_2 ceramic powder has the most obvious effect on the grain refinement of the laser direct deposition Fe based alloy coating.

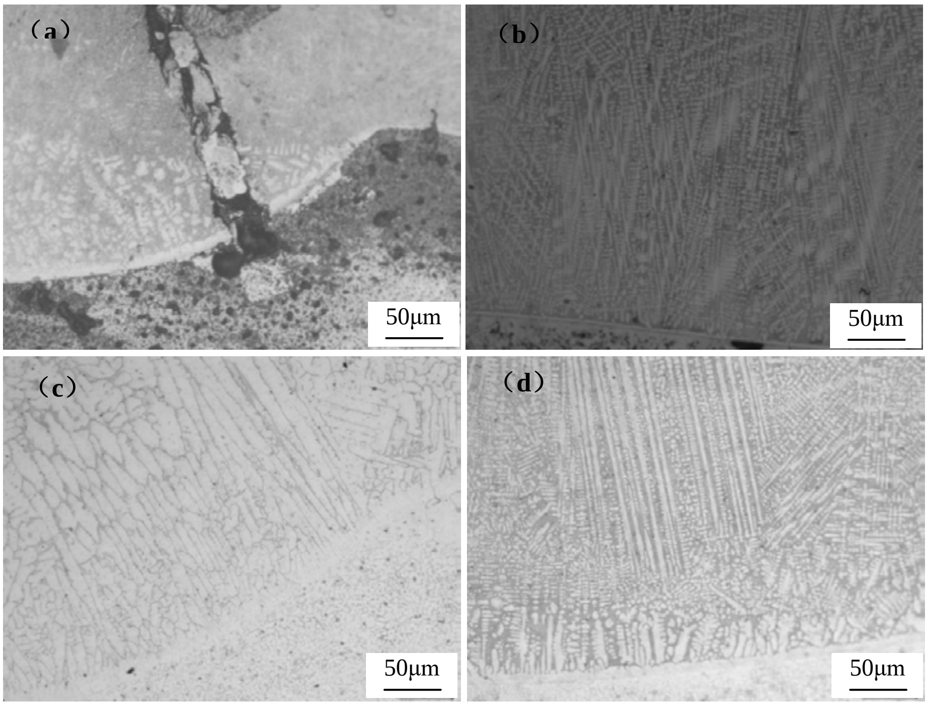

Fig.1The OM images of samples with different ZrO_2 powders
(a)-0.3%ZrO_2; (b)-0.5%ZrO_2; (c)-0.7%ZrO_2; (d)-0.9%ZrO_2.

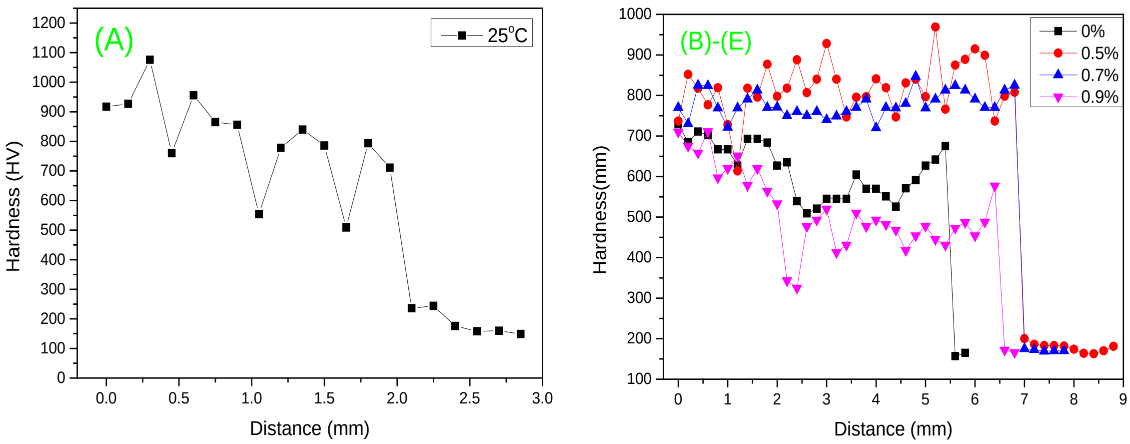

Fig. 2 Hardness curves of the samples with different ZrO_2 ceramic powders

Fig. 2 shows the hardness curve of the coating deposited with different ZrO_2 content. Fig. 2(a) is the hardness curve of the coating deposited with Fe60 purity powder at room temperature, there is a sudden drop in hardness mutation in the boundary layer and layer, which easily leads to the crack in the sample. Fig. 2 (b) is the hardness curve of the coating deposited with Fe60 purity powder. The trend of hardness curve dropping in the boundary of layer and layer slow, and the hardness curve is stable relatively. Fig. 2 (c) and (e) are the hardness curves of the coating deposited with Fe60 purity powder at room temperature. The powder respectively contain 0.5%, 0.7%, 0.9% ZrO_2 ceramic powders. The average hardnessof the sample with 0.5% ZrO_2 is up to 817HV. The average hardness of the sample with 0.7% ZrO_2 is up to 778HV. The average hardness of the sample with 0.9% ZrO_2 is up to 516HV. As the addition concentration of ZrO_2 increased, the hardness decreases. Hard particles precipitated phase and refinement organizations cause the coating with highhardness. Combined with Fig. 1, due to the effect of fast cooling, fine grain strengthening can be achieved, and the hardness of the coating is relatively high. And Fig.1 (b) shows the sample with 0.5% ZrO_2 ceramic powder can significantly refine the grain, improvehardness, and prevent sample cracking.

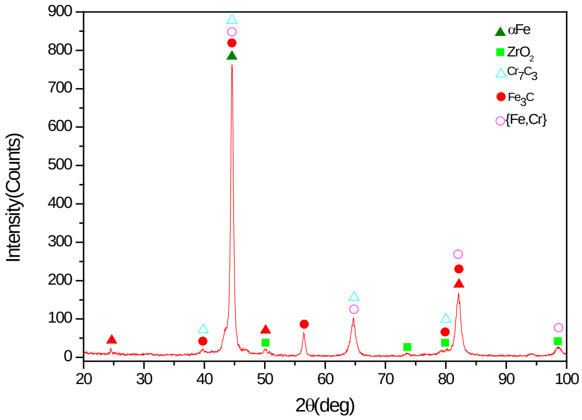

Fig. 3 The XRD pattern of the sample with

Fig. 3 is XRD pattern of the sample deposited with 0.5% ZrO_2 ceramic powders. It shows that the coating is mainly composed of Cr_7C_3, a-Fe, {Fe, Cr} solid solution, ZrO_2, Fe_3C and other phase. In the process of laser direct deposition, the Cr_7C_3 carbide as the strengthening phase plays a good role in improving the hardness of the coating. At the sametime, the presence of monoclinic ZrO_2 phase shows the occurrence of phase transformation toughening in the process of laser direct deposition. ZrO_2 with different morphology at different temperature, when the temperature is lower than 1100 ℃, it is monoclinic phase.As temperature rises, it is tetragonal phase; and when the temperature is higher than 2000 ℃, it is cubic phase. Stress-induced phase transformation toughening is the use of stress-induced tetragonal ZrO_2 martensitic transformation to improve the ceramics resilience. When ceramics containing tetragonal ZrO_2 particles crack, and stress concentration in the crack tip, so the stress is higher than the critical value. Resulting in ZrO_2 particles near the tip was pressed, generated 3% -5% expansion or contraction of the volume. Induced ZrO_2 tetragonal to monoclinic martensite phase can disperse tip stress effectively, and achieve the goal of toughening coating material.

Fig. 4 is the surface scanning photo with the 0.5%ZrO_2 ceramic powder. By the analysis, the enrichment of O and Zr elements can be seen clearly. Combined with the two photos of Zr and O element, the enrich position is consistent, which can infer the existence of ZrO_2. At this time, the observation of SEM images suggests that ZrO_2 gathered in the black spot area. In order to further verify the true existence of ZrO_2, the EDS analysis of the black dot region are carried.

Fig. 5 is the results of EDS, which shows that ZrO_2 exists in the deposition layer, rather than as the impurity phase in the black spot. In the table 2, the different composition also can show differentareas has different composition. According to the Fig. 5, the ZrO_2 exist in the boundary between layer and layer as the reinforced phase. ZrO_2 has the effect on the transformation toughening， which can reinforce the toughness and eliminate the cracks effectively.

Table 2 The EDS composition of the two black spot

Element		B	C	Si	Cr	Fe	Ni	O	Zr
1	**Wt%**	5.36	1.05	2.93	9.89	70.12	5.99	2.36	2.31
	At%	19.27	3.38	4.06	7.39	48.80	14.55	1.56	0.98
2	**Wt%**	7.50	1.15	0,44	19.56	69.56	1.69		
	At%	28.55	3.88	0.64	15.39	50.68	1.17		

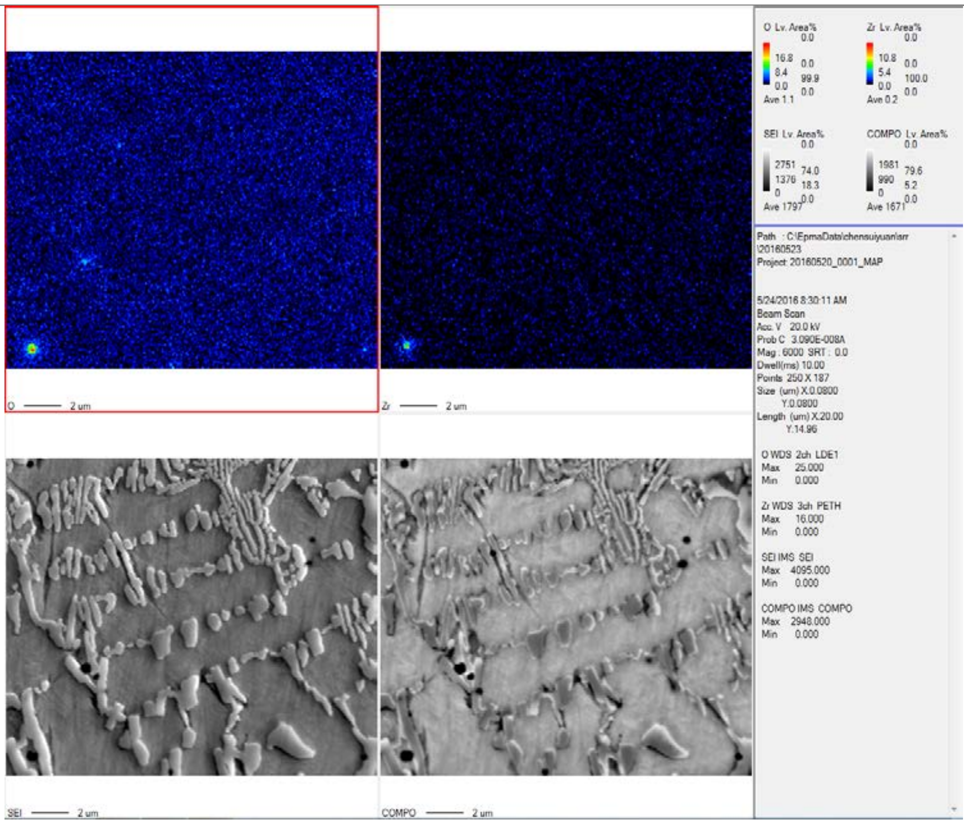

Fig. 4 The surface scanning of the coating deposited with 0.5% ZrO_2 ceramics powder

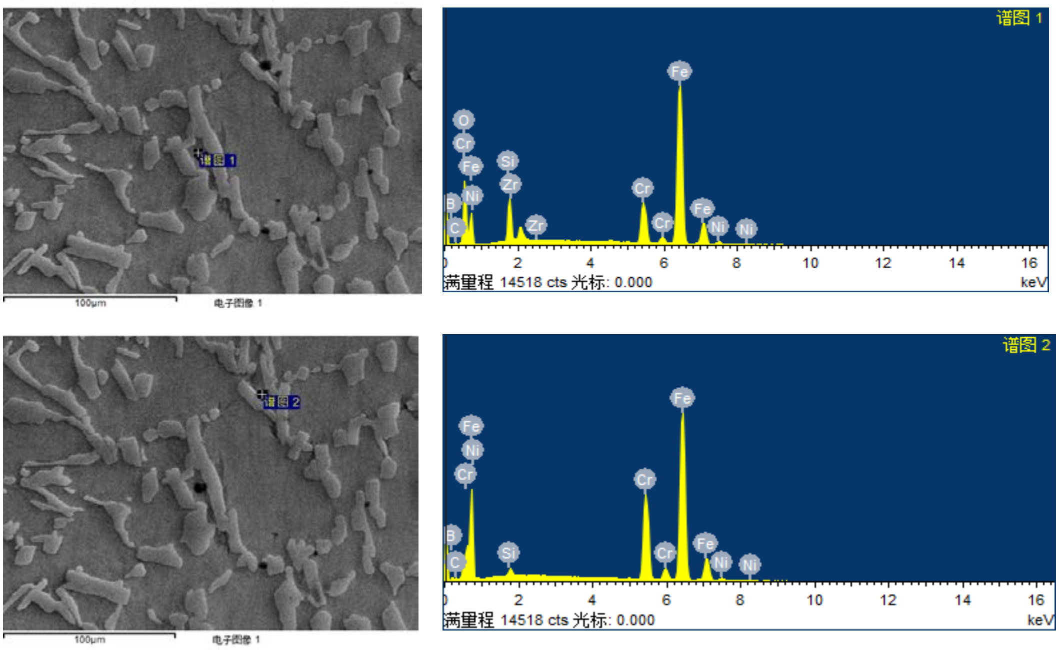

Fig. 5 The EDS analysis cureve of the coating depositied with 0.5%ZrO_2 ceramics powder

Conclusions

The Fe60 alloy coating was deposited on the surface of Q235 steel by semiconductor laser at room temperature by using optimized process parameters such as power of 1600w, scanning speed of 3 mm/s, multi-channel lap rate of 30%, laser spot diameter of 6×4mm, powder feed amount of 8.4g/min, overlapping ratio of 30%, and the protection of argon amount 0.2 Mpa.The phase of coating is composed of Cr_7C_3, α-Fe, {Fe,Cr}solid solution, ZrO_2, and Fe_3C. The main reinforcing hardness phases in the laser deposited coating is Cr_7C_3 and the main reinforcing tenacity is ZrO_2. ZrO_2 powder has good eliminating coating cracks role in the laser deposited Fe-based coating with high Cr and C content. So the sample has the good properties of strength and toughness, such as the high hardness, fine-grained structure and in-situparticle reinforcment. The sample with 0.5%ZrO_2 has the finest crystalline structure and nocracks, the hardness is up to 817HV and thickness is 8mm. ZrO_2 plays an important role in the phase transformation toughening, so it can slow down the crack growth trend and eliminate the cracks effectively in this Fe60 alloy coating.

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