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Plasma cladding of Stellite 6 powder on Ni76Cr19AlTi exhausting valve

ZHU Yuan-zhi(朱远志)[1,2], YIN Zhi-min(尹志民)[2], TENG Hao(滕 浩)[2]

1. School of Material and Metallurgy, Wuhan University of Science and Technology, Wuhan 430081, China;
2. School of Materials Science and Engineering, Central South University, Changsha 410083, China

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Abstract: Heavy duty engine valve head was prepared by Ni76Cr19AlTi alloy. It was coated by cobalt-base alloy on the surface to promote its wear-resistance. Hardness tester, metallograph, scanning microscopy, energy spectrum and X-ray diffraction were used to analyze the mechanical properties, the microstructure of the welds and the coated layer of cobalt-base alloy. The results show that the grains are obviously coasened in the side of Ni76Cr19AlTi alloy in the welds and it contains a typical dentritic structure in the side cobalt-base alloy. It is found that micro-strain in weld is stronger than that in heat-effected-zone. Micro-strain in nickel-base alloy is stronger than that cobalt-base alloy. There are not obvious imperfects in the weld. Hardness in cobalt-base alloy is more than 390HV and the major carbides in cobalt-base alloy are Cr_7C_3 and W_2C.

Key words: engine valve; nickel-base alloy; cobalt-base alloy; plasma cladding; microstructure; mechanical property

1 Introduction

Nickel-base alloy is an attractive alloy in industries for its high corrosion resistance and high strength[1−5]. However, its adhesive wear resistance is not so high [6−10]. Therefore, surface treatment is necessary if the alloy is used as friction materials.

Ni76Cr19AlTi alloy is a nickel-base alloy with ultra-high strength. Heavy-duty engine valve can be prepared with this alloy for its high strength even at high temperatures. To enhance the alloy’s wear-resistance, Stellite 6 powder is decided to be coated on this alloy by plasma arc. A lot of researches have been done about the mechanical properties and microstructure of this nickel-base alloy internationally[11−13]. Some researches have also been done on wear-resistance of Stellite 6 cobalt-base alloy[14−16]. However, very few studies have been done about the cladding of Stellite 6 powder on Ni76Cr19AlTi alloy.

After cladding of Stellite 6 alloy, the property of the coatings and its interface with Ni76Cr19AlTi valve is very important to compound engine valve. Therefore, properties and microstructure of coatings and the interface between coatings and valve were mainly studied in this paper.

2 Experimental

Ni76Cr19AlTi alloy bar was provided by Shanghai Materials Researching Institute. The diameter of the Ni76Cr19AlTi bar was 16 cm. The received bar was soluted at 1 080 ℃ for 8 h and then was forged into exhausting valve. Stellite 6 powder was provided by Stellite Corp. Ltd. The powder was coated on the head of the exhausting valve by plasma arc. Chemical compositions of Ni76Cr19AlTi alloy and Stellite 6 powder are listed in Table 1.

Table 1 Chemical compositions of Ni76Cr19AlTi alloy and Stellite 6 powder (mass fraction, %)

Alloy	C	Ni	Cr	Co	W
Ni76Cr19AlTi	0.04	Bal.	19.36	−	−
Stellite 6	1.2	2.5	30	Bal.	5
Alloy	Si	Ti	Al	Fe	
Ni76Cr19AlTi	−	2.11	1.94	0.64	
Stellite 6	1.5	−	−	2.5	

Photographs of compound exhaust valves are shown in Fig.1.

Corresponding author: ZHU Yuan-zhi; Tel: +86-27-63976403; E-mail: tozyzl@163.com

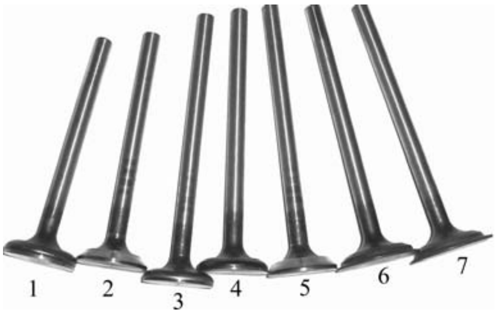

Fig.1 Compound exhaust valve: 1−6 Coated valve; 7 Un-coated valve

The properties of the coatings and interfaces were studied by hardness tester, metallograph, scanning electronic microscopy and X-ray diffractometry.

3 Results and analysis

3.1 Hardness of interface

A compound valve is sectioned vertically, as shown in Fig.2.

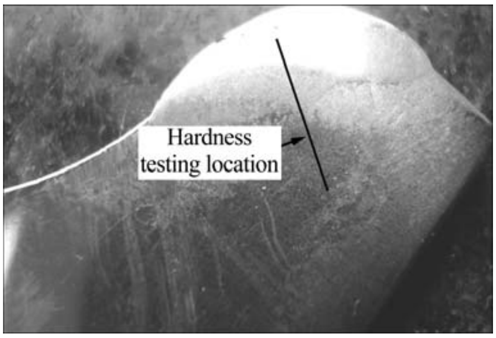

Fig.2 Vertical section of coatings

Fig.2 shows that there are no obvious metallurgical imperfections in the coatings and at the interface between the coatings and the nickel-base valve.

Hardness was tested along vertical direction of the interface. Hardness was tested along vertical direction of the interface and the value is shown in Fig.3.

Fig.3 shows that the value of the interface between the coatings and nickel-base alloy is the lowest because this interface undergoes the highest temperature in cladding and the grains here are coarsened[17−18]. The hardness is almost constant at side of nickel-base alloy crossing the interface, and increases stably from the interface to the outside of the cobalt-base coatings. It is probably because that the content of cobalt-base alloy is increased and the size of grains is lowered from the interface to the outside of the coatings.

3.2 Microstructure of interface

Microstructure of the interface between coatings and nickel-base alloy valve is shown in Fig.4.

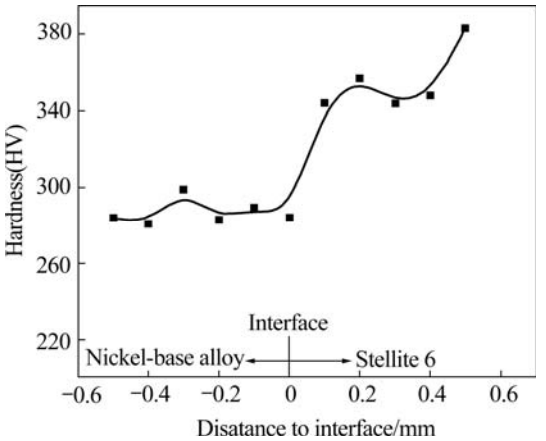

Fig.3 Hardness in different locations perpendicular to interface

Fig.4 shows that the size of grains at the interface is 80−100 nm, much bigger than that in matrix of the nickel-base alloy. Maybe, in this region, the alloy undergoes the highest temperature in cladding and the cooling rate is the lowest after cladding, therefore the grains grow bigger and bigger in cooling. On side of cobalt-base alloy, just adjacent to the interface, there is a transitional region in a shape of belt, where the grains are in narrow and longitude shape. These grains are bigger than those in the outside layer of cobalt-base coatings. This transition region is a location where nickel-base alloy is melted with cobalt-base alloy because the nickel-base alloy is stirred by plasma arc. And just because this melting, the amount of carbides in cobalt alloy is lowered[19−21]. Thus, the mechanical property of the interface is promoted because too much carbides can lower the impact toughness of an alloy. In the outer layer of the coatings it can be seen a typical solidification structure—a dendritic structure. On the side of nickel-base alloy, from the interface to the center of the valve, there is a 300 μm heat-affected zone where the grains are in a size of about 15−20 μm, a little bigger than those in matrix of the nickel-base alloy, 10 μm.

3.3 Phases in Stellite 6 coatings

3.3.1 X-ray analysis

Phases in the coatings were analyzed by XRD. The XRD pattern is shown in Fig.5.

Fig.5 shows the matrix of the coatings is a solution of cobalt-base alloy. Diffraction peak of Cr_7C_3 and W_2C can be observed in this XRD pattern. This result is coincident with the metallograph result.

3.3.2 Investigation of carbides by SEM and EDX

Carbides were investigated by scanning electronic microscopy and energy dispersive X-ray analysis(EDX). Micrographs and composition of carbides in the coatings are shown in Fig.6.

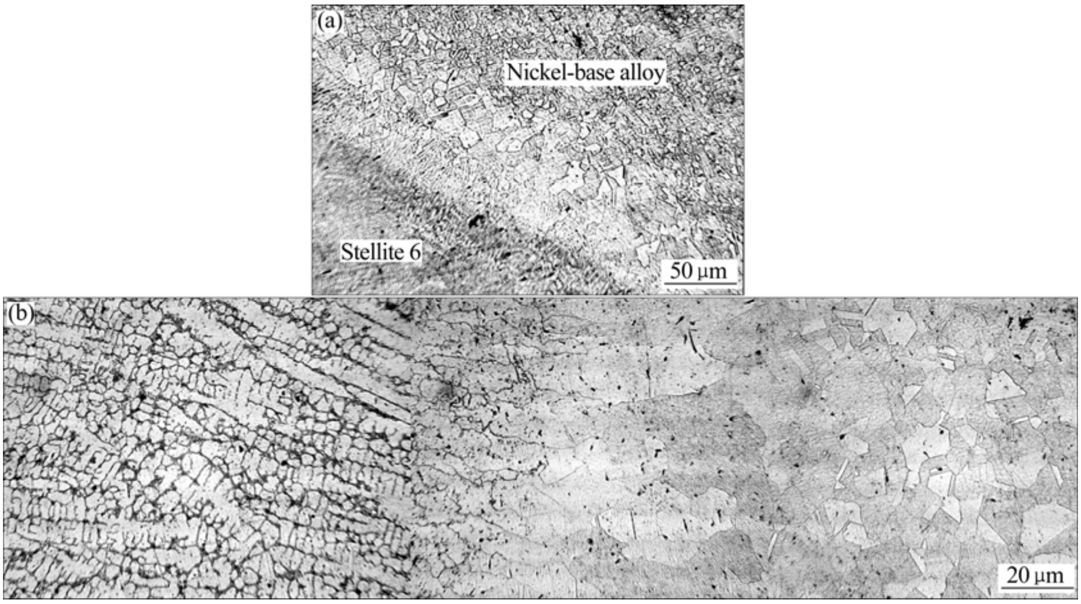

Fig.4 Microstructures of interface: (a) Low magnification; (b) High magnification

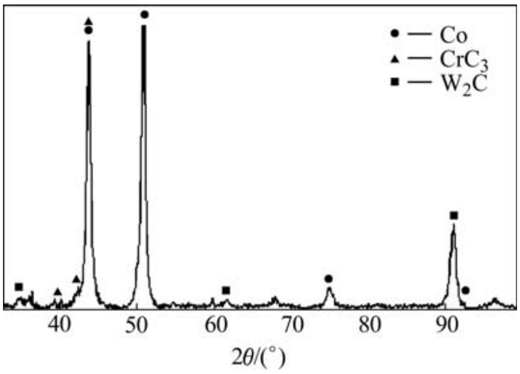

Fig.5 XRD pattern of cobalt-base coatings

It can be seen in Fig.6 that carbides are mainly distributed on grain boundary. These carbides include carbides formed at a temperature higher than the eutectoid temperature of the alloy and carbides precipitated at just eutectoid temperature or at temperatures lower than that temperature. EDX results show that these carbides mainly are Cr_7C_3 and W_2C, and the Cr_7C_3 is much more than W_2C because the content of chrome is much more than that of tungsten in the alloy. These carbides have a high hardness and can enhance the wear-resistance of the coatings.

3.3.3 Composition at interface

Composition at the interface of coatings and nickel-base alloy valve was analyzed by EDX. The results can be seen in Fig.7.

From Fig.7, it can be seen that there is an obvious transitional region of chemical compositions. In this region, the content of nickel varies in a smooth curve and the content of chrome changes in a straight line. The content of tungsten, carbon and cobalt also varies in a straight line, but there is a sharp change in these content lines. On the left side of the point of sharp change, the content of these three chemical elements is almost zero. On the right side, the content of the three elements rises in straight line. At some points, the content of carbon and tungsten or carbon and chrome is abnormally higher than that of other location, which means that there are carbides of tungsten or chrome at these points.

4 Discussion

4.1 Growth of grains at interface

In a region of 150 μm width, grains are bigger than those in the outside of this region, which means the grains undergo a higher temperature or longer time. It is well known that the temperature at the tip of plasma arc is the highest. Maybe this region just contacts with the tip of plasma arc. Usually the temperature of plasma arc is higher than 2 000 ℃, which means that metals in this region melt. The grains grow large in solidification. According to Ref.[22], size of grains depends on the growth rate of the grains. If the growth rate is R, then it can be calculated by the following equation[22]:

$$R = \frac{D}{x}\ln\left(\frac{\Delta T_{\mathrm{f}}}{\Delta T_{\mathrm{f}} - \Delta T_{\mathrm{c}} - G \cdot x}\right) \tag{1}$$

where D is the diffusion coefficient; x is the distance from the boundary of solid to that of liquid; G is the thermal gradient; ΔT_{f} is the temperature range of solidification of the alloy; ΔT_{c} is the difference between the actual temperature and the temperature of solidification of the alloy. The temperature in the region

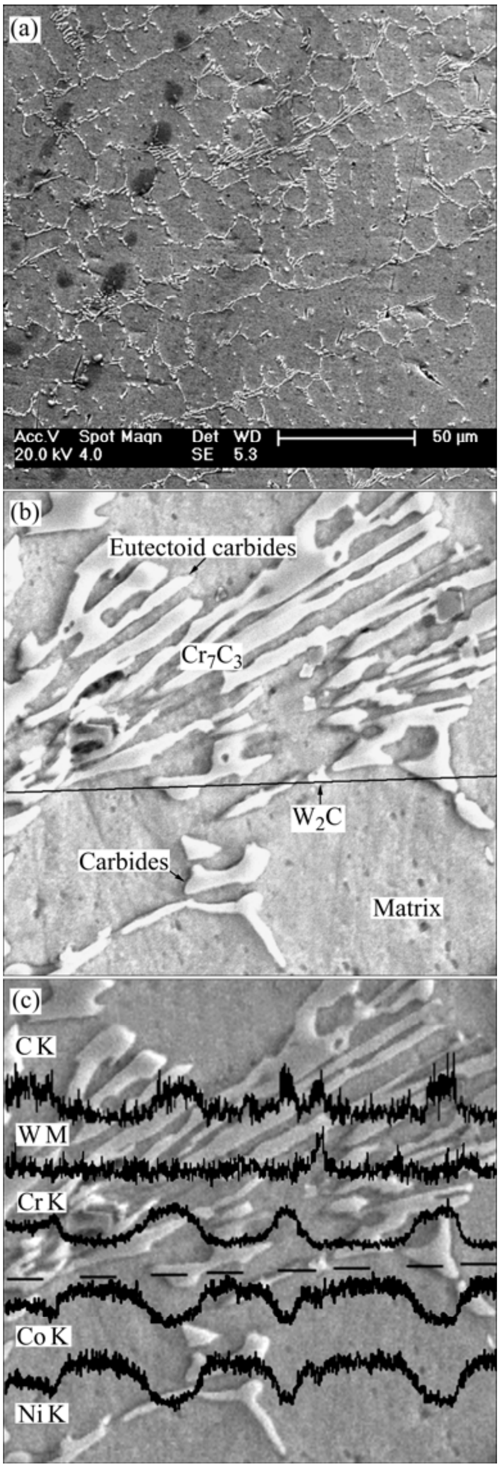

Fig.6 Micrographs (a)−(b) and composition (c) of carbides in Satellite 6 coatings

contacted with tip of plasma arc is the highest, which means that the values of ΔT_c and D are the highest, thus leading to a high growth rate in this region. Furthermore, this region is in the bottom of the coatings and the heat is difficult to be transferred to the outside, which means that this region undergoes a long period at high temperatures. Therefore large grains can be seen in this

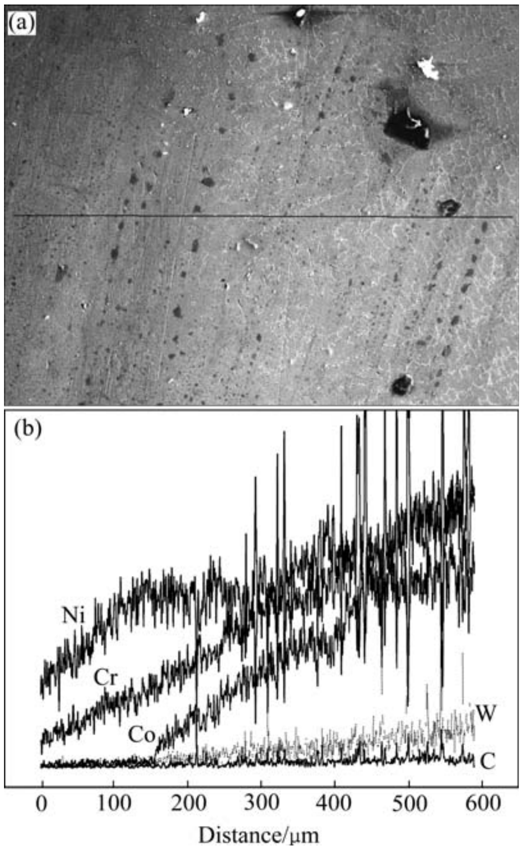

Fig.7 Chemical composition crossing interface: (a) Micrograph of interface; (b) EDX line scanning results

region.

4.2 Diffusion of elements crossing interface

The nickel-base alloy is on the left side of the interface and the cobalt-base alloy on the right, as shown in Fig.7. Therefore there is almost no tungsten and cobalt on the left. However, even on the right side, there is still a high content of nickel. Probably nickel transfers from the nickel-base alloy to cobalt-base alloy in cladding. It is because that plasma arc not only provides the two alloys a high temperature environment, but also mechanically stirs the molten nickel-base alloy and makes it transfer to the coatings.

4.3 Micro-strain crossing interface

Samples were cut down every 2 mm along a line vertical to the cladding interface in the coated valve by a line cutter. Then the samples were polished to get rid of the oxide on the surface, analyzed by a X-ray diffractometer, and scanned at a speed of 0.1(˚)/min. The XRD results are shown in Fig.8.

Fig.8 shows that the nearer the alloy to interface is, the wider the diffraction peak is. This means that the nearer to the interface, the higher the micro-strain in the alloy. Based on this XRD results, micro-strain and sizes

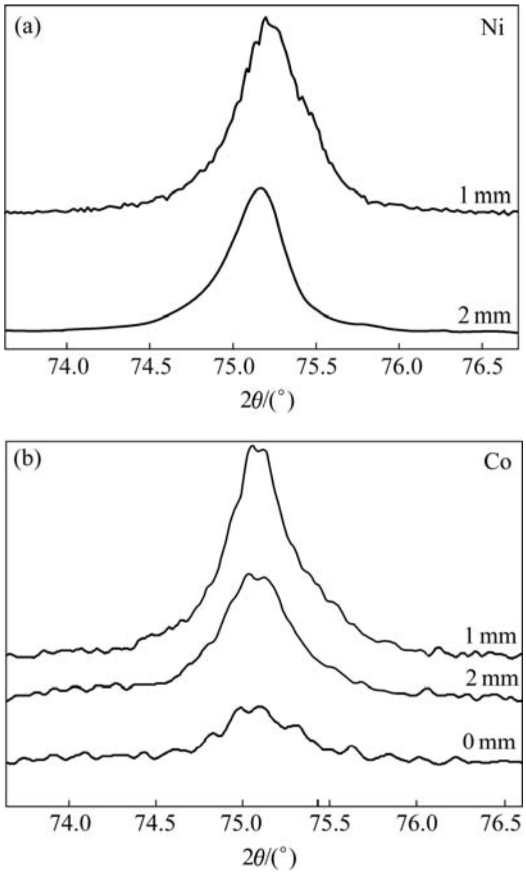

Fig.8 XRD patterns of alloy at different distances to cladding interface: (a) Nickel-base alloy side; (b) Cobalt-base alloy side

of sub-grains in different locations can be calculated by the attached software of the XRD system. The results can be seen in Fig.9.

Fig.9 shows that micro-strain at the interface is the highest, and the sub-grains size is the smallest in this location. The farther to the interface, the lower the micro-strain is, and the bigger the sub-grain size is. The micro-strain in this case mainly comes from the stress for the difference of expansion coefficient in different locations caused by the deference of chemical compositions and thermal stress caused by thermal gradient near the interface.

4.4 Comment on property and microstructure of coatings

The microstructure of the interface and the coatings shows that there are no obvious metallurgical imperfects in it. For the Dilution of nickel-base alloy at the interface, brittleness of the interface is eliminated. A great deal of carbides in the coatings is favorable to a high wear-resistance. The hardness of the coatings is almost HV390. Empirically, as to heavy-duty engines, the hardness of valve should be about HRC40 that almost equals to HV390. Therefore the hardness of this compound valve can satisfy the need of heavy-duty engines.

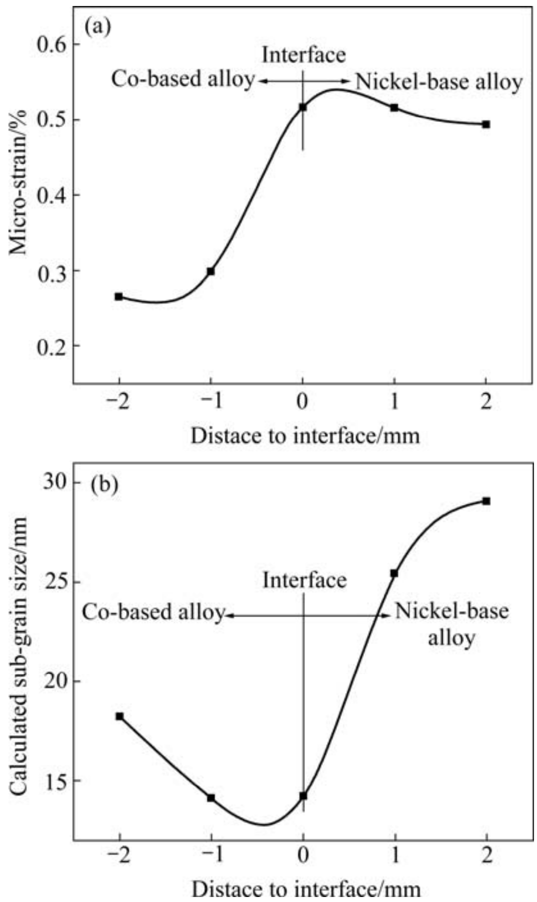

Fig.9 Micro-strain (a) and sub-grain size (b) in different locations

5 Conclusions

1) Interfaces between nickel-base alloy valve and coatings were studied. Results show that the property and microstructure of interfaces are improved for the dilution of nickel-base alloy at the interface by plasma arc. Carbides such as Cr_7C_3 and WC enhance wear-resistance of the coatings. The micro-strain at the cobalt side in weld is stronger than that in heat-effected zone.

2) The hardness of the coatings is almost HV390. The lowest value of hardness at the interface is about HV300. The hardness of the coated compound valve can satisfy the need of heavy-duty engines.

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