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Influences of precursor constitution and processing speed on microstructure and wear behavior during laser clad composite coatings on γ-TiAl intermetallic alloy

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ABSTRACT

The effects of constitution of precursor mixed powders and scan speed on microstructure and wear properties were designed and investigated during laser clad $\gamma/Cr_7C_3/TiC$ composite coatings on γ-TiAl intermetallic alloy substrates with NiCr–Cr_3C_2 precursor mixed powders. The results indicate that both the constitution of the precursor mixed powders and the beam scan rate have remarkable influence on microstructure and attendant hardness as well as wear resistance of the formed composite coatings. The wear mechanisms of the original TiAl alloy and laser clad composite coatings were investigated. The composite coating with an optimum compromise between constitution of NiCr–Cr_3C_2 precursor mixed powders as well as being processed under moderate scan speed exhibits the best wear resistance under dry sliding wear test conditions.

1. Introduction

TiAl-based ordered intermetallic alloys have been continuously developed as the promising high-temperature candidate structural materials due to the high melting point (>1450 °C), low density (up to 4 g/cm^3), high elastic modulus (160–180 GPa) and high creep strength (up to 900 °C) [1–4]. According to the estimation by US NASA, 20–25% of the whole aero-engine materials would be TiAl alloys by the year 2020 [5]. Recently, significant efforts have been made on improving the room-temperature ductility and high-temperature oxidation resistance by alloy modifications, processing innovation and surface engineering [6–8]. Some advanced TiAl alloys are now nearly maturing to the stage where it is possible to implement them in industrial applications. But its utility is also restricted by the low surface hardness (about HV320) and wear resistance, especially high-temperature wear resistance, when TiAl alloy using as elevated-temperature moving components (as high as 900 °C), for example, turbine blades, in which tribological properties are critically important to the components service life. Laser surface technology is preliminary verified to be an effective and economical method to solve the high-temperature wear problems, especially under the conditions of large loads and severe mechanical stress [9]. Reinforced carbides Cr_7C_3 and TiC possess both good high-temperature abrasive and erosive wear resistance because of their very high hardness, unique strong atomic bonds and high stability under high-temperature exposure [10–13]. So the high-temperature coatings reinforced by Cr_7C_3 and TiC carbides undoubtedly possess good high-temperature wear resistance. Simultaneously, there should exist continuous phase to play the critical role of firmly connecting and supporting the wear resistant phases so as to fully exert the wear resistant capabilities of the reinforced phases. The continuous phase should exhibit good combination properties including excellent high-temperature stability, oxidation resistance and good toughness. This is because high-temperature structure stability and oxidation resistance are prerequisites of the high-temperature coatings. As for good toughness, on the one hand, it could prevent cracking or delamination of the coatings during the high-temperature wear process and on the other hand, it could relieve the thermal stress during fabrication process. γ-austenitic solid solution is well known for its ductility and toughness, heat- and corrosion-resistant capabilities due to its compact face-centered-cubic crystal structure and super-saturation strengthening ability during the laser and other high energy beam induced non-equilibrium rapid melting and subsequent solidification process. It seems reasonable that γ-austenitic solid solution matrix composite coatings reinforced by Cr_7C_3 and TiC carbides are expected to possess good service properties under high-temperature and wear conditions.

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In our previous study [14], the efforts of fabricating both wear and high-temperature oxidation resistance ceramic/cermet composite coatings on TiAl alloy with different constitution of NiCr–Cr_3C_2 precursor mixed powders were made, the results show that it is a promising surface modification technique for TiAl alloy when applied as high as 1000 °C because it combines the excellent properties of the ductile γ-austenitic solid solution matrix and the very hard reinforced carbides of Cr_7C_3 and TiC.

As well known, surface microstructure and composition play a crucial role in determining surface dependent engineering properties like resistance to wear and corrosion, and it depend on constitution of the precursor mixed powders to a large extent. Also, laser processing parameters, especially the laser beam scan speed has remarkable influence on the resultant microstructure, and hence, the mechanical properties of the modified layers. Since γ-austenitic solid solution is the ductile and tough matrix, acting as the connecting and supporting continuous phase, and the reinforced carbides of Cr_7C_3 and TiC play the dominant role in resisting the intrusion caused by the micro rough peaks of the counter-part, so, their optimal volume fraction matching and dimension size and distribution of the composite are crucial to the microstructure and resultant properties. As a further step in obtaining high performance composite coatings on TiAl alloy with controllable microstructures and attendant properties, the effects of different constitution of the precursor mixed powders and laser beam scan speed on the clad coatings' microstructure, and resultant mechanical properties of the composite coatings are highlighted. The aim is to present some useful reference or guidance for the practical fabrication process.

2. Experimental procedures

The starting experimental material was a commercial titanium aluminides alloy Ti–48Al–2Cr–2Nb (at.%). The TiAl alloy was melted using high-purity charge materials by a vacuum magnetic-suspension induction skull-melting furnace (100 kW). After repeated melting for three times, each time for 15 min, ingots, 40 mm in diameter and 180 mm in length were cast. The as-cast ingots were vacuum-sealed in quartz tube and homogenized at 1360 °C for 2 h to produce a fully lamellar microstructure. Specimens of 8 mm × 10 mm × 40 mm for laser cladding were cut from the cast and homogenized ingots by electric discharge wire cutting machine.

Experiments of laser cladding of the TiAl alloy were conducted on a 5 kW CO_2 laser-materials processing systems with 4-axes computer numerical controlled (CNC) working station. Specimens were first sandblasted and then cleaned with ethyl alcohol and acetone and painted with black paint to increase the laser-materials absorption before laser cladding.

In order to examine the influence of the precursor constitution on the resultant microstructure and properties, mixed powders of different constitution of Ni–20wt.%Cr alloy and Cr_3C_2, in proportion (wt.%) of 20:80, 50:50, 80:20, respectively, were mixed and bounded with cellulose aether and then pre-placed on the specimen's surface in a thickness of about 1.5 mm. While the moderate NiCr–50% Cr_3C_2 precursor mixed alloy powder underwent laser beam traverse speed determined as 1.50 mm/s, 2.00 mm/s, 2.67 mm/s, respectively, so as to check the influence of laser beam scan speed on the microstructure and properties. The other fixed laser cladding experiment processing parameters, optimized from adequate number of preliminary trials for the formation of a defect free clad layer during the present efforts were: laser output power 2.8 kW, the beam of which was focused as a rectangular cross-section in the dimension of 1 mm × 18 mm, through a scanning rotating lens. All the specimens were heated on a carbon steel hot-plate heated by a 2 kW electric stove to be adequately dried before laser beam irradiation, the particle size of the NiCr, Cr_3C_2 powders ranges from 70 to 140 μm. The purity of the above powders was 97.0% and 98.0%, respectively. Since the width of the laser beam was larger than that of the specimen, the composite coatings were created by a single track. Two steel blocks were placed tightly at two sides of the TiAl specimen to absorb partial laser irradiated energy so as to avoid the marginal effect and possible plasma effect. A 4 l/min flow of argon gas was passed through the melt pool to provide a protective environment for the sake of avoiding the reaction between the molten metals and oxygen.

Metallographic samples and wear testing specimens were machined by electric discharging cutting, followed by mechanical milling and grinding to acquire the wear testing surface with roughness of 0.8 μm from the slight rough as-laser clad specimens. Metallographic samples of the composite coatings were prepared using standard mechanical polishing procedures and were etched in HF:HNO_3:H_2O water solution in volume ratio of 1:6:7. Microstructure of the coatings was characterized by optical microscopy (OM), scanning electron microscopy (SEM) and energy-dispersive spectrometer (EDS). The phases present in the surface layer were identified by X-ray diffraction (XRD) using Cu Kα radiation. The recorded intensities and peak positions were compared with Joint Committee on Powder Diffraction Standards (JCPDS) data. The hardness profile along the coating depth was measured by an automatic microhardness tester (HXD-1000B, Shanghai Optics Apparatus Ltd., China) with a testing load of 1.96 N and a dwelling time of 15 s. The values of hardness were averaged by at least five points of measurements.

The room-temperature dry sliding wear test was carried out on a MM-200 block-on-ring wear testing machine [14]. The load was 98 N. The hardened 0.45%C steel ring had a hardness of HRc55 and surface roughness of 0.8 μm was selected as the mating material because it is the most-widely used metallic materials as moving components. The sliding speed was 0.84 m/s. The complete wear test cycle was 60 min, resulting in a total wear sliding distance of 3.02×10^3 m. The wear weight loss was measured using a high accuracy photoelectric balance. The relative wear resistance (i.e. the ratio of wear weight loss of the original specimen to that of the laser clad specimen) was used to judge the wear resistance of the laser clad coatings. SEM was used to characterize the worn surface of the laser clad composite coatings and original TiAl alloy to assist in analyzing the wear mechanism.

3. Results and discussion

3.1. Microstructure

As a result of the direct laser beam irradiation, most of the preplaced mixed NiCr–Cr_3C_2 powders were melted, producing a laser clad Ni–Cr–C alloy molten pool on surface of the substrate and subsequently, leading to formation of the titanium carbide (TiC) and chromium carbide (Cr_7C_3) reinforced γ-NiCrAl/TiC/Cr_7C_3 composite coatings metallurgically bonded to the TiAl alloy substrate after solidification of the molten pool following the forward movement of the scanning laser beam. The TiC and Cr_7C_3 reinforcements are uniformly distributed in the ductile, heat- and corrosion-resistant γ-NiCrAl austenitic solid solution matrix. The X-ray diffraction (XRD) results and the phase constitutions formation mechanism had been discussed in our previous paper [14].

Fig. 1 is the optical micrograph showing cross-section thickness of the laser clad composite coatings with NiCr–50%Cr_3C_2 precursor mixed powders under different laser beam scan speed, and Fig. 2 is the corresponding microstructure. Of course all the main phase constitutions of the clad coatings are similar, i.e. mainly

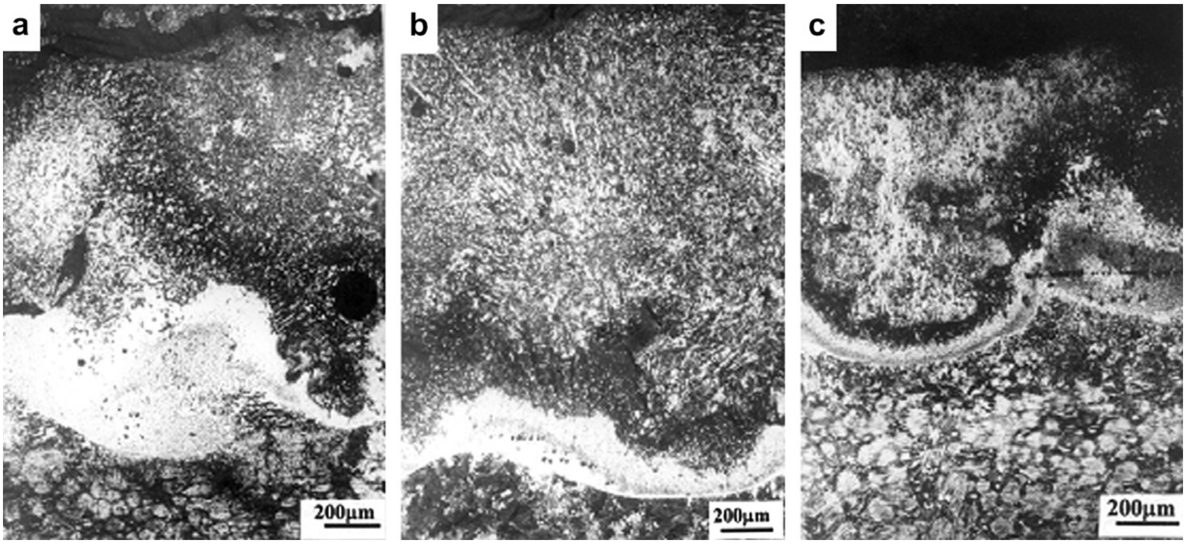

Fig. 1. Optical micrographs (OM) showing cross-section thickness of laser clad composite coatings on TiAl alloy as function of laser beam scan speed: (a) 1.50 mm/s; (b) 2.00 mm/s and (c) 2.67 mm/s. Fixed processing parameters: constitution of precursor mixed powders NiCr–50%Cr_3C_2, laser output power 2.8 kW, laser beam dimension 1 mm × 18 mm.

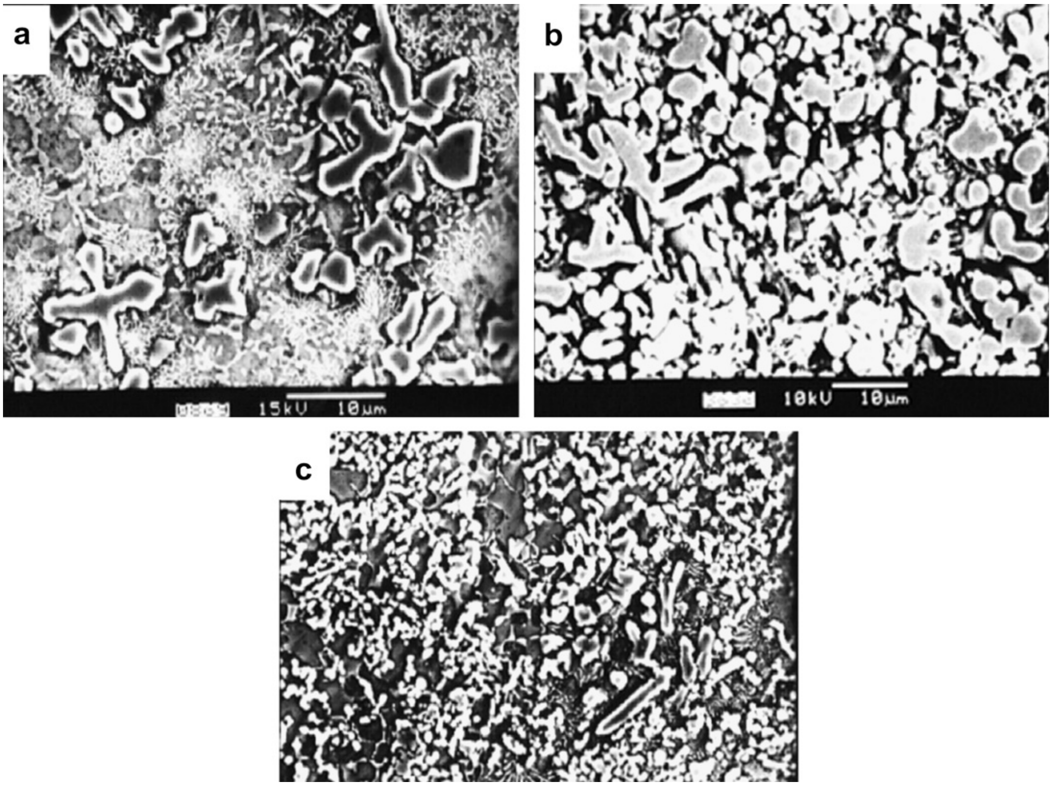

Fig. 2. Microstructure comparison of laser clad composite coatings on TiAl alloy as function of laser beamscan speed: (a) 1.50 mm/s; (b) 2.00 mm/s and (c) 2.67 mm/s. Fixed processing parameters: constitution of precursor mixed powders NiCr–50%Cr_3C_2, laser output power 2.8 kW, laser beam dimension 1 mm × 18 mm.

composed of the primary blocky hypereutectic Cr_7C_3 and the inter-primary lamellar or chrysanthemum-like γ/Cr_7C_3 eutectics plus some white dendritic or particulate phase TiC. Microstructure possesses its own characteristics due to the different absorbing heat and the subsequent cooling-rate resulted from the varied scan speed. The primary blocky Cr_7C_3 is coarse and the inter-primary lamellar or chrysanthemum-like γ/Cr_7C_3 has the notable eutectic characterization. TiC also exhibits well-developed dendritic shape, which implies the typical microstructure feature under the slowest scan speed, i.e. 1.50 mm/s, as shown in Fig. 2a. On the contrary, the primary phase is relatively fine, volume fraction of the inter-primary eutectics is decreasing and TiC demonstrates fine particulate shape, which indicates the microstructure under the highest scan speed, i.e. 2.67 mm/s, as can be seen in Fig. 2c. From the solidification and nucleation as well as growth mechanism points of view, it could be understood that when the laser beam scan speed is slow, the interaction time between laser beam and specimen is long, then the absorbed heat and the melted substrate was much more, induces the relatively higher concentration of TiAl in the molten pool. So the subsequent cooling-rate is slower and the growing time is longer under the same heat conduction conditions. Thus, led to the formation of coarse blocky primary Cr_7C_3 and the distinct inter-primary lamellar or chrysanthemum-like γ/Cr_7C_3 eutectics and the well-developed TiC dendritic. With the increasing of scan speed, both the interaction time and the absorbing energy of the specimen are reduced, resulting in the high-temperature gradient, cooling-rate and the subsequent fast nucleation rate and growing rate in the laser induced molten pool. At the same time, the melted substrate is less and the TiAl concentration is relatively lower. Therefore, the primary Cr_7C_3 is refined and the TiC demonstrates fine particulate form, the whole microstructure of the laser clad composite coating exhibited relative fine and uniform characteristics. It can be very clearly seen that laser beam scan speed exerts significant influence on the microstructure of the composite coatings by comparing Fig. 2a and c.

Fig. 3 is the typical microstructure of the laser clad composite coatings on TiAl alloy with different constitution of precursor mixed powders. For a given laser processing condition, as can be expected, the volume fraction of the reinforced carbides, i.e. Cr_7C_3 and TiC, increases with increase of Cr_3C_2 in the precursor mixed powders, while the volume fraction of the γ-NiCrAl solid solution matrix decreases with the increase of the Cr_3C_2. It shows that the microstructure and composition of the laser clad coatings are determined by the constitution of the precursor mixed powders to a large extent. Through careful examination, it is shown that the volume fraction of the reinforced Cr_7C_3 and TiC are not the simple linear relationship with the increasing content of the Cr_3C_2 in the precursor mixed powders, comparing Fig. 3a and c, it is clear that the increasing of the particulate phase TiC is more pronounced than that of coarse blocky hypereutectic Cr_7C_3, this is because the Gibbs energy formation of TiC (−184 kJ/mol) is very lower than that of the Cr_7C_3 (−26.0 kJ/mol), which implies its large affinity with C and the attendant comparative superiority under the C enriched environments.

3.2. Microhardness

The variations of the microhardness of the laser clad composite coatings along depth direction as functions of constitution of the precursor mixed powders and the laser beam scan speed are plotted in Figs. 4 and 5, respectively. Because of the rapid solidified fine microstructure and the presence of large amounts of hard primary Cr_7C_3 and TiC carbides distributed in the γ/Cr_7C_3 eutectics matrix, the microhardness of the laser clad composite coatings are nearly three to five times higher than that of the substrate, TiAl alloy, which is about HV250–HV300, depends on the different constitution of the precursor mixed powders and their tendency to change along the depth is gradual. It is very obvious that the average microhardness of the composite coatings increases with the increases amount of the Cr_3C_2 content in the precursor mixed powders. The variational scan speed leads to a different hardness distribution of the coatings. The basic rule is that the hardness increases with the increase scan speed, especially under the highest scan speed, i.e. 2.67 mm/s, resulted in the maximum improvement in hardness (as high as HV1100) that is confined to a very shallow depth from the surface corresponding to the clad layer surface. This phenomenon conforms to the general rule of heat conduction and cooling crystal during laser induced melt pool and subsequent cooling solidification process. The reason is that the higher the scan

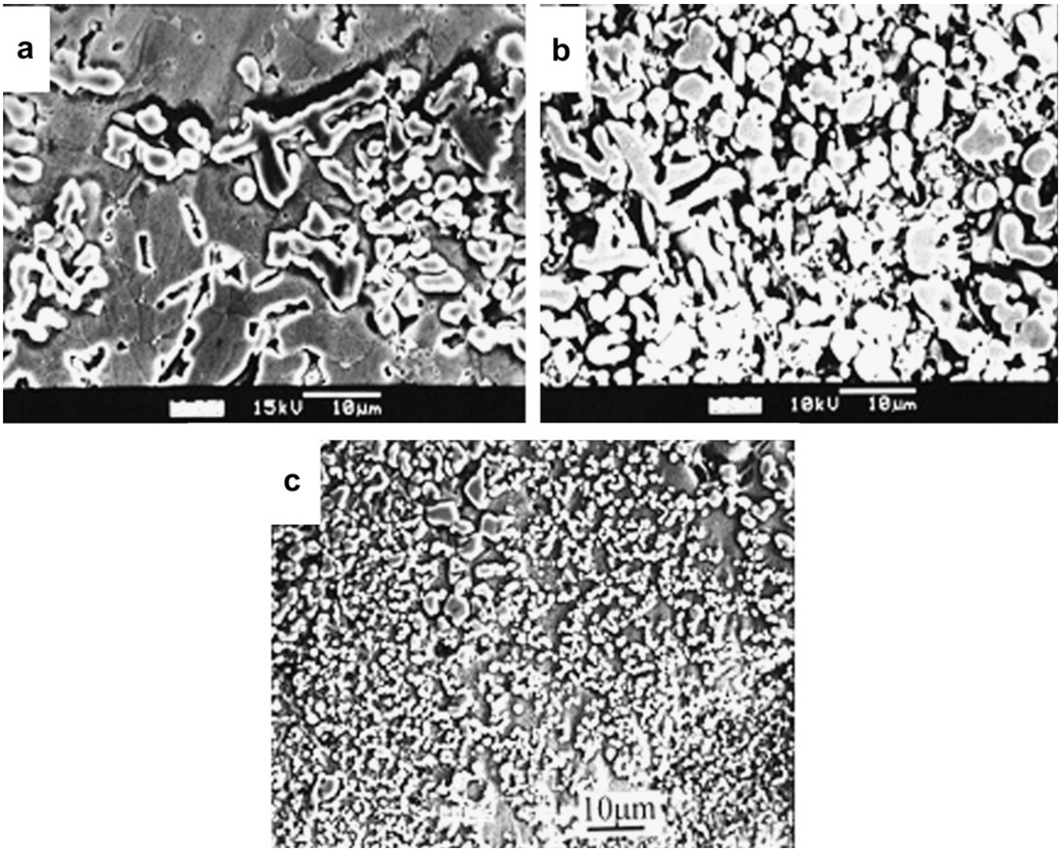

Fig. 3. Microstructure comparison of laser clad composite coatings on TiAl alloy as function of constitution of precursor mixed alloy powders: (a) NiCr–20%Cr_3C_2; (b) NiCr–50%Cr_3C_2 and (c) NiCr–80%Cr_3C_2. Fixed processing parameters: laser output power 2.8 kW, laser beam scan speed 2.00 mm/s and beam dimension 1 mm × 18 mm.

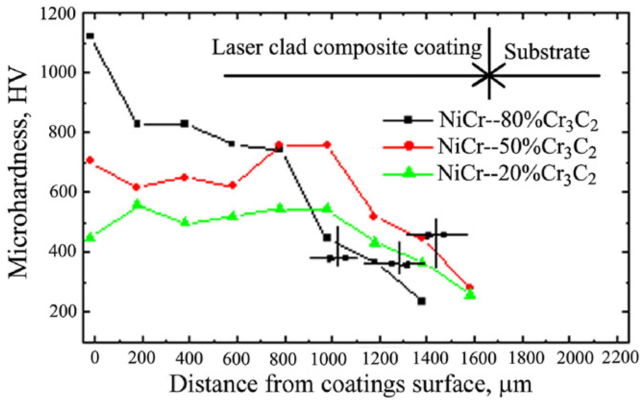

Fig. 4. Microhardness profiles of the laser clad composite coatings as functions of the constitution of NiCr–Cr_3C_2 precursor mixed powders. Fixed processing parameters: laser output power 2.8 kW, laser beam scan speed 2.00 mm/s and beam dimension 1 mm × 18 mm.

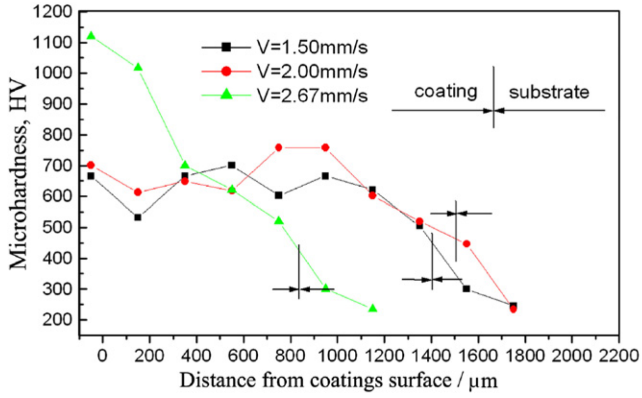

Fig. 5. Microhardness profiles of the laser clad composite coatings as functions of the laser scan speed. Fixed processing parameters: constitution of precursor mixed powders NiCr–50%Cr_3C_2, laser output power 2.8 kW, laser beam dimension 1 mm × 18 mm.

speed, the shorter the interaction time between the laser beam and materials, so the faster is the subsequent cooling-rate, the shorter the growing time of the formed Cr_7C_3 and TiC reinforcements, thus the fine and uniform microstructure, which is helpful for the increasing of hardness and roughness.

3.3. *Wear properties*

Based on the research results of Hawk and Alman [15], due to the inherent long-range ordered superstructure and the fairly good atomic bonding, all of the titanium–aluminide compounds (such as Ti_3Al, TiAl and $TiAl_3$) possess similar wear rates and are more resistant to abrasion than pure Ti and Ti-based alloys. So, it is comparatively harder to improve the wear resistance of TiAl alloy than Ti-based alloys, in which case, the conventional sliding wear resistance can be enhanced as much as more than 100 multiple as the results presented by Wang and Liu [16]. The room-temperature wear resistance of the laser clad composite coatings with reference to the TiAl alloy, calculated from the weight loss, is shown in Table 1, which indicated that under the normal load and sliding speed used in this study, the relative wear resistance of the laser clad composite coating with NiCr–50%Cr_3C_2 mixed powders is up to two times higher than that of the TiAl alloy. Morphology of the worn surface for the two kinds of coatings and the TiAl alloy are shown in Fig. 6. The TiAl alloy suffered several abrasive and adhesive wear, worn surface of the original TiAl alloy specimen is very rough, with typical adhesive wear features evidenced by numerous adhesive craters, deep ploughing grooves and serious plastic deformation characteristics, as shown in Fig. 5a. On the contrary, the worn surface of the laser clad composite coating is relatively smooth, there are only shallow grooves or slight scratches visible on the worn surface, as shown in Fig. 5b and c, no noticeable plastic deformation or adhesive wear occurred.

Table 1
Relative wear resistance of the laser clad composite coatings with reference to the original TiAl alloy under different precursor constitutions and processing speeds

Test materials	Relative wear resistance
Original TiAl alloy	1.00
Laser clad composite coating with NiCr–80%Cr_3C_2 precursor mixed powders (2.00 mm/s)	1.73
Laser clad composite coating with NiCr–50%Cr_3C_2 precursor mixed powders (2.00 mm/s)	1.90
Laser clad composite coating with NiCr–20%Cr_3C_2 precursor mixed powders (2.00 mm/s)	1.06
Laser clad composite coating under scanning speed of 1.50 mm/s (NiCr–50%Cr_3C_2)	1.68
Laser clad composite coating under scanning speed of 2.67 mm/s (NiCr–50%Cr_3C_2)	1.50

The higher wear resistance of the composite coatings and the above experiment phenomena could be explained as follows. In the laser clad composite coating, the hard and wear-resistant primary coarse Cr_7C_3 blocks and TiC particles are uniformly dispersed in the ductile and tough γ/Cr_7C_3 eutectic matrix. This 'tailor-made' microstructure of the laser clad carbides reinforced composite coating provides the coating with good wear resistance, especially under dry sliding wear conditions. First, the strong atomic bonds inherent to the Cr_7C_3 and TiC carbide phases provide the coatings with excellent resistance to metallic adhesion during wear tests. Second, the very high hardness of the reinforced carbide phases prevents the laser clad coatings from wear by severe micro-cutting and plowing. Third, the ductile and tough γ/Cr_7C_3 eutectic matrix could play the very important role of firmly connecting and supporting the hard phases and preventing the reinforced wear resistant phases and the coating as a whole from wear removal by mechanisms such as micro-fracturing and fragmentation. Thus the reinforced carbides can fully exert their wear resisting abilities. Finally, the non-equilibrium solidified homogeneous fine microstructure imparts to the coatings a good combination of high strength and toughness, which in turn provides the coatings with good resistance to spalling and delamination. As a result, the laser clad coatings show improved wear resistant capability. Naturally, with the increasing of the volume fraction of the reinforcing phases of Cr_7C_3 and TiC, the wear resistance of the laser clad coatings against the abrasive and adhesive wear is enhanced.

However, when the volume fraction of the pre-placed mixed powders surpasses a critical value, the ductility of the laser clad coating is considerably decreased. Thus the higher hardness, more brittle 80%Cr_3C_2 containing coating is more prone to fracture-related wear modes, such as spalling and carbide fracture removal and hence, the decreasing of the wear resistance. This analysis and deduction could be further substantiated and validated by the illustration of micro-pores formation on the worn surface of the composite coating with NiCr–80%Cr_3C_2 precursor mixed powders, which possesses the highest Cr_3C_2 content. The formation mechanism of the micro-pores is clearly explained in detail and can be found in our previous work [17]. Fig. 7 shows the SEM micrograph of the fracture surface of the partial spallation. From this SEM micrograph, typical cleavage and river shape pattern can be clearly seen, which implies the dominant trans-granular

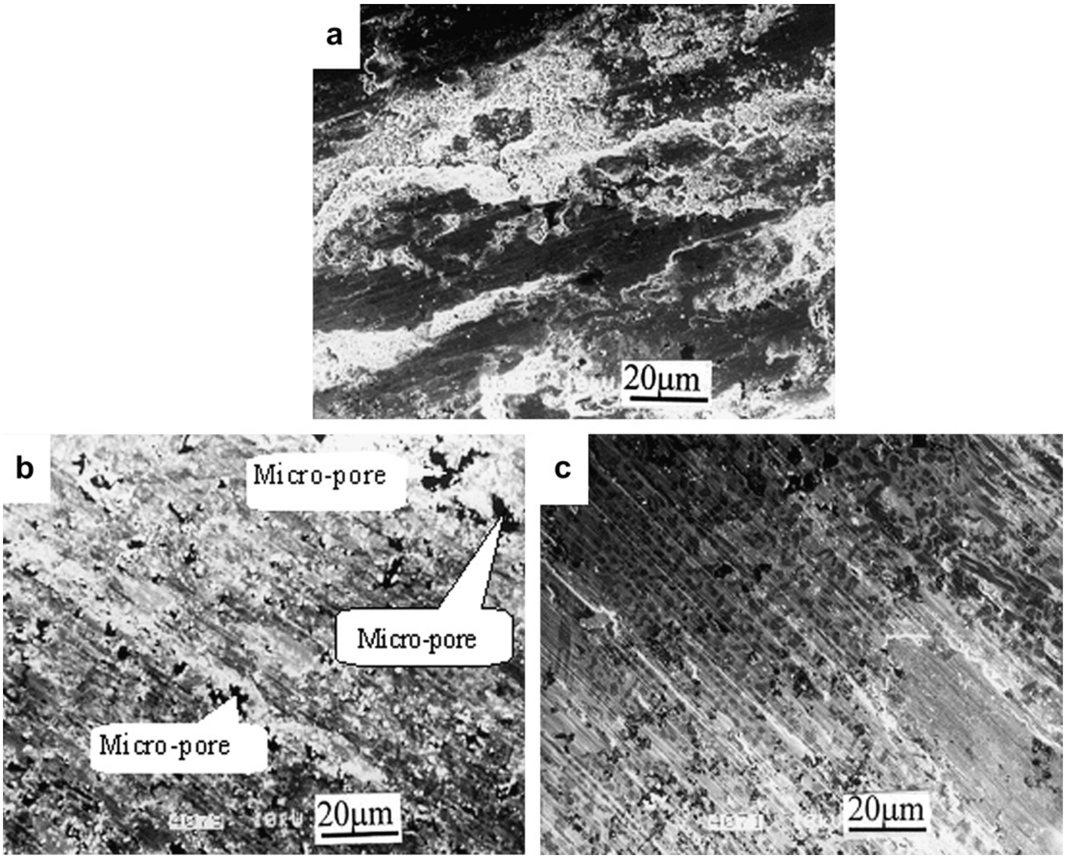

Fig. 6. Worn morphologies of: (a) the original TiAl alloy and the laser clad composite coatings with (b) NiCr–80%Cr_3C_2 and (c) NiCr–50%Cr_3C_2 precursor mixed powders.

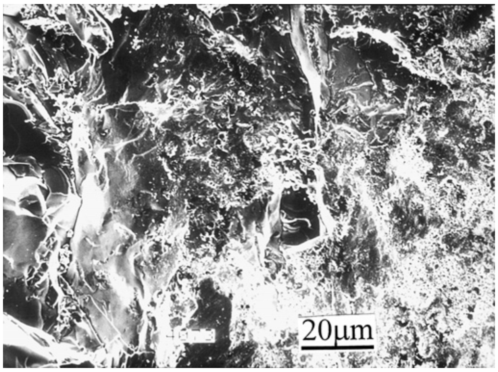

Fig. 7. Fracture surface of the laser clad composite coating with NiCr–80%Cr_3C_2 precursor mixed powders showing the cleavage and river shape pattern.

fracture mode, i.e. the typical brittle fracture mechanism. The inferior wear behavior to the clad with NiCr–20%Cr_3C_2 is evidently because of a comparatively lower hardness of the formed clad coating.

Meanwhile, testing results also show that the laser clad composite coating under moderate scan speed, i.e. 2.00 mm/s, resulted in the highest relative wear resistance. Our result presented here has some difference with the variation trend of Tian et al. [18], which indicated a lower scanning speed resulted in lower weight loss of the coatings, i.e. better wear resistance. But in that case, only two scanning speeds were employed and processed under relatively lower laser energy density (maximum 47.75 W/mm^2 S) and the resultant thickness of the coatings was relatively thin (0.7–1.0 mm). Generally, wear resistance is related to the surface hardness to a large extent, with the increasing of scan speed, the microstructure is defined and the hardness increases, so the wear resistance increases with the increasing scan speed within the lower scan speed range. Further increasing of the scan speed, the reinforced phases, i.e. Cr_7C_3 and TiC exhibit more fine and uniform distribution, which could increase the hardness undoubtedly. But no higher wear resistance occurs at this time. Our research work [19] also indicated that if the dimension of the reinforcements that exert the dominant role in resist wear was over-refined, the excellent wear-resistant abilities of withstanding shear cut from microroughen peak of the mating counter-part steel could not be fully brought into play. Other author's results [20,21] also implied that the coarser particulate size had better dry sliding wear resistance, especially under the wear conditions governed by micro shear cut. So, it is reasonable to conclude that over-refined microstructure is of course beneficial to the increasing hardness and toughness according to the generally accepted Hall–Petch relationship, but is not helpful to improve wear resistance by all means. Therefore, the wear resistance of the clad coating under the highest scan speed is lower than that of the moderate, despite its highest hardness and toughness. Similar to the result of the coating clad with NiCr–20%Cr_3C_2, too low hardness always accompanies inferior wear resistance as verified again this time, the coating formed under the slowest scan speed, i.e. 1.50 mm/s, shows the comparatively inferior wear resistance due to the relatively lower average microhardness.

4. Conclusions

Influences of precursor constitution and processing speed on microstructure and wear behavior during laser clad composite coatings on γ-TiAl intermetallic alloy were investigated. Both the constitution of the precursor mixed powders and the laser beam scan speed have remarkable influences on the microstructure, hardness and dry sliding wear behavior of the composite coatings. With the increasing of the constitution of Cr_3C_2 in the precursor mixed powders, the volume fraction of the hard Cr_7C_3 and TiC carbides increases, and hence, the enhanced microhardness and brittleness of the composite coating. With the increasing of laser beam scan speed, the microstructure of the laser clad composite coatings becomes refined and the microhardness increases, the thickness of the clad coating decreases. The dry sliding wear mechanism of the laser clad composite coatings are mainly micro-cutting, slight adhesive transfer, fragmentation and spalling of the reinforcing phases resulting from partial cracking, while the wear mechanism of the original TiAl alloy shows adhesion and, ploughing plastic deformation and delamination. It is demonstrated that the composite coating with an optimum compromise between volume fraction of the hard Cr_7C_3 and TiC carbides and the ductile γ/Cr_7C_3 dendrite matrix (i.e. the optimum compromise between the constitution of NiCr–Cr_3C_2 precursor mixed powders) as well as being processed under moderate scan speed exhibits the best wear resistance under dry sliding wear conditions.

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