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Letter

Development and characterization of composite Ni–Cr–C–CaF_2 laser cladding on γ-TiAl intermetallic alloy

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ABSTRACT

A process of laser cladding Ni–Cr–C–CaF_2 mixed powders to form a multifunctional composite coating on γ-TiAl substrate was carried out. The microstructure of the coating was examined using XRD, SEM and EDS. The coating has a unique microstructure consisting of primary dendrite or short-stick TiC and block Al_4C_3 carbides reinforcement as well as fine isolated spherical CaF_2 solid lubrication particles uniformly dispersed in the NiCrAlTi (γ) matrix. The average microhardness of the composite coatings is approximately HV 650 and it is 2-factor greater than that of the TiAl substrate.

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) [1–3]. According to the estimation by US NASA, 20–25% of the whole aero-engine materials would be TiAl alloys by the year 2020 [4]. Recently, significant efforts have been made on improving the room-temperature ductility and high-temperature oxidation resistance of TiAl alloys by alloy modifications, processing innovation and surface engineering [5–7]. But its utility is also restricted by the low surface hardness (about HV320) and wear resistance, especially low high-temperature wear resistance. For example, TiAl alloys are restricted to be used as elevated-temperature moving components (as high as 900 °C) such as turbine blades, in which tribological properties are critically important to the components in 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 [8].

In our previous study, the efforts of fabricating both wear and high-temperature oxidation resistant ceramic/cermet composite coatings on TiAl alloy with different constitution of Ni–Cr–C [9,10] and Ni–Cr–W–C [11] 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 the surface layer combines the excellent properties of the ductile γ-austenitic solid solution matrix and the very hard reinforced carbides of Cr_7C_3, TiC, W_2C, etc.

Although the above fabricated wear and high-temperature oxidation resistant composite coatings possess good wear resistance, it accelerates the wear process of the mating counterpart, i.e. the tribological compatibility or self-lubrication ability is bad, which is also deleterious and should be prohibited under many extreme operating conditions. Conducting effective lubrication for the contacting surface of the tribological moving components is effective measures for anti-friction and restrain wear. Fabricating a self-lubrication wear-resistant coating on a tribological component is one of the most efficient and economical ways to solve the problem, because the coating having the desired compositions and special physical properties can provide the tribological component with excellent self-lubrication, oxidation and wear resistant properties without limiting the bulk mechanical properties of the substrate structural materials.

CaF_2 is a well known and widely used solid lubricant. It has physical (i.e. it prevents adhesion), chemical (i.e. it enables tribo-chemical reactions) and microstructural (i.e. it has a lamellar structure with low shear strength) influences on the tribological contact of working surfaces. The mechanism behind its effective lubricating performance is understood to be easy shearing along the basal plane of the hexagonal crystalline structures. Also it is a useful

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addition in the production of self-lubricating ceramic composites, and is used in different anti-wear applications [12,13]. Moreover, its lower hardness and slip plane structure make CaF_2 easily softened and its chemical stability at elevated temperature makes it not easy to react with other elements such as TiC [14]. So it seems promising that γ-austenitic solid solution matrix composite coatings reinforced by high hardness carbides as well as solid lubricant CaF_2 are expected to possess good service properties under aggressive wear conditions. However, to the best knowledge of the authors, only very few literature are available concerned on the synthesis of the above similar self-lubrication and wear resistant composite coating on TiAl alloy by laser.

The present study is to explore the feasibility of fabricating high-temperature wear resistant and self-lubricating cermet composite coatings on TiAl alloys using Ni–Cr–C and CaF_2 mixed powders by laser cladding. Emphasis is placed on characterizing the microstructure and the evolution process of the laser clad composite coatings and investigating the wear behaviors. It is expected that this route can provide a novel way for synthesizing high-temperature self-lubricating wear resistant composite coatings on TiAl alloy and promote its commercial application.

2. Experimental procedures

The substrate material was a commercial titanium aluminides alloy Ti–44.5Al–0.9Cr–1.1V–2Nb (at.%) with a fully lamellar microstructure. Specimens of 8 mm × 10 mm × 40 mm were cut from the cast and homogenized ingots by electric discharge wire cutting machine for laser cladding.

The mixtures of Ni14.4–Cr40–C5.6–$CaF_2$40 (wt.%) were used as the coating material, and were first mixed by using a QM-ISP04 series ball miller. The composite powders were then mixed with cellulose acetate, pasted onto the substrates and dried in an oven at 100 °C for 1 h. The thickness of the pastes was about 1.2 mm.

Experiments of laser cladding were conducted on a 5 kW CW CO_2 laser materials processing systems with 4-axes computer numerical controlled (CNC) working station. Relatively lower laser energy density was deliberately selected during laser cladding to avoid substantial thermal decomposition and vaporization of the CaF_2 powders during the laser cladding process based on our preliminary work and other studies [15,16]. The laser cladding parameters are: laser output power 2.0 kW, beam diameter 4.0 mm, beam traverse speed 10 mm/s. Argon gas was used to protect the surface from oxidation.

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-cladded 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 reference database for identifying was powder diffraction file (PDF). 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.

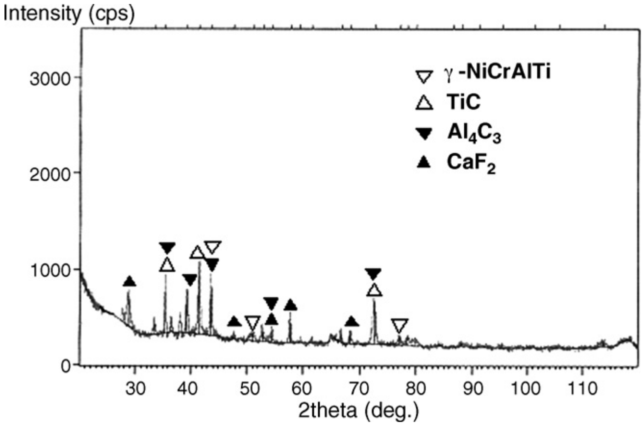

Fig. 1. X-ray diffraction pattern of the laser clad composite coating.

3. Results and discussion

As a result of the direct laser beam irradiation, most of the pre-placed mixed Ni–Cr–C–CaF_2 powders were melted with certain dilution of the substrate, producing a hybrid complex Ni–Cr–C–Ca–F–Ti–Al alloy molten pool on surface of the substrate and subsequently, leading to the formation of the rapid solidification composite coating. XRD analysis results, as shown in Fig. 1, indicated that the main phases of the coating include TiC and Al_4C_3 carbides, γ-NiCrAlTi matrix and CaF_2. Some cracks appeared near the surface and propagated to the middle bottom of the clad layer due to the high thermal stress and hard and brittle phases of TiC and Al_4C_3 carbides, but no network cracks occurred.

Fig. 2(a) is the typical microstructure of the laser clad composite coating (SEM), which can be more clearly seen in Fig. 3 with high magnification. Through careful examination, it showed that there were mainly four phases existed in the coating, as labeled in region A, B, C and D in Fig. 3. Area A possessed the grey blocky morphology and was enriched in Al and C by EDS analysis (see Table 1), while area B was the grey continuous matrix and its composition was Ni, Cr, Ti and Al, and their content was relatively even. Area C presented the white dendrite or short-stick morphology mostly and was enriched in Ti and C, while the isolated grey fine spheri-

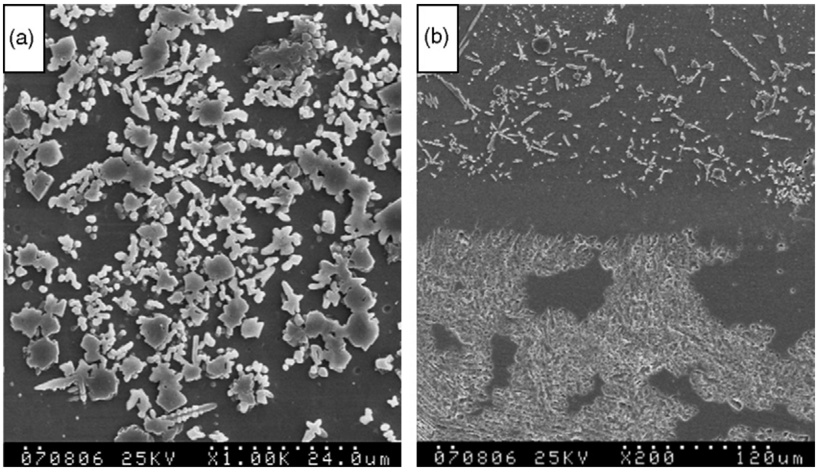

Fig. 2. Typical microstructure (a) and bonding zone (b) of the laser clad composite coatings on TiAl alloy.

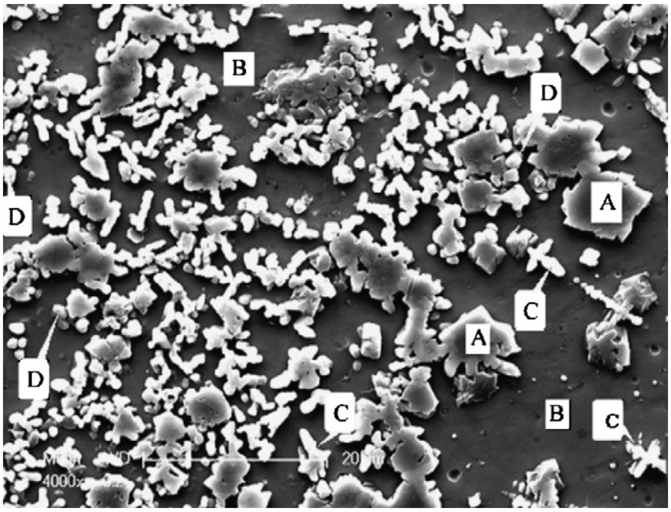

Fig. 3. Magnified SEM micrographs showing the clear typical microstructure of the composite coatings on TiAl alloys (areas A, B, C and D indicate the blocky grey, grey continuous matrix, white dendrite or short-stick and spherical particles, respectively).

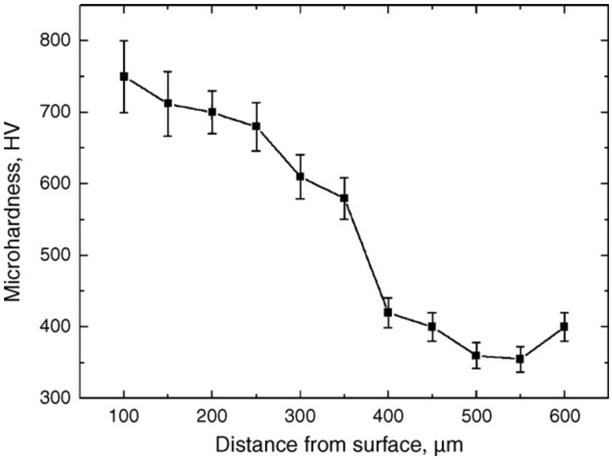

Fig. 4. Microhardness profiles of the laser clad composite coating as a function of the distance from the surface.

cal particles as marked by area D was enriched in Ca, F, Ti, Al, also including some Ni and Cr.

Because the Gibbs standard free energy for formation of TiC (−221.75 kJ/mol) is much lower than that for Al_4C_3 formation (−121.34 kJ/mol) and that for Cr_7C_3 formation (−26.0 kJ/mol), which means Ti is more carbide-forming than Al and Cr. Considering TiC possess the highest melting point (3140 °C) than Al_4C_3 (about 2500 °C) and Cr_7C_3 (1565 °C), it is reasonable to deduce that TiC phase precipitated first from the molten pool in short-stick shape and some of them developed to dendrite due to the local preferential energy and composition undulation surroundings (C area in Fig. 3), then the Al_4C_3 blocky phase precipitated mostly in hexagonal blocks or platelets (A area in Fig. 3). Accompanying the formation of TiC and Al_4C_3, the residual molten pool was very poor in C, so most of the Cr could only be super-saturated in the Ni matrix in the laser induced non-equilibrium solidification process and formed the stable γ-NiCrTiAl solid solution, which is the ductile, heat- and corrosion-resistant matrix. This result is somewhat different from our previous study [9,10]. In the previous case, besides TiC, it was Cr_7C_3 rather than Al_4C_3 formed in the laser clad composite coating. Through detailed comparison and analysis, the main reason was the different composition, especially the Cr/C weight ratio of precursor mixed powders, mixed powders that resulted in the different carbides formation. The Cr/C weight ratio was about 8:1 ∼ 18:1 in our previous work and about 7:1 at this time in the precursor mixed powders. Relatively higher Cr/C weight ratio was beneficial for the formation of Cr_7C_3, while lower Cr/C weight ratio was beneficial for the formation of Al_4C_3 carbides in the Ni–Cr–C–Ti–Al molten pool. It can be seen that precursor composition has a deeper influence on the final microstructure of the pre-place laser clad composite coating. Similar phenomenon was also observed very recently by Luo et al. [17] that the microstructural characteristics of the Ni–Cr–Ti–Al clad coatings varied according to the composition of the coatings in diffusion bonding of laser surface modified gamma titanium aluminide alloy to nickel-base casting alloy. At last, the fine spherical particles, CaF_2, with the lowest melting point (1270 °C) and lower density (3.18 g/cm^3) than the metal matrix, precipitated solely within the primary short-stick or dendrite TiC and secondary Al_4C_3 grey block. It is likely that the melt immiscibility between carbides and metal matrix leads to phase separation during solidification of the cermet melt. Considering the 40% content of CaF_2 in the pre-placed mixed powders, it can be proposed that buoyancy, decomposition and vaporization of CaF_2 did occur to some extent because of its lower melting point, lower density and bad interfacial compatibility with the metal matrix.

A microhardness profile of the coating is shown in Fig. 4. There is an intergradation of microhardness in the interface between the coating and the substrate. The microhardness is in the range of HV 550–HV 750 in the coating zone, and in the range of HV 320–HV 360 in the substrate. The average hardness of the coating is approximately HV 650 and it is 2-factor improvement than that of TiAl substrate.

Since γ-NiCrTiAl solid solution is well known for its ductility and toughness, TiC and Al_4C_3 possess very high hardness, strong atomic bonds especially due to the fine size and uniform distribution, CaF_2 having layered crystal structure of cF12 is well known for its excellent self-lubricating properties at temperatures higher than approximately 600 °C when it undergoes the brittle to ductile transformation, forming a fully ductile phase with very low shear strength [15], this composite coating seems promising in the field of tribology and self-lubrication of TiAl alloys. Further investigations will be focused on the room and high-temperature wear and self-lubrication mechanisms of the laser clad composite coating and the quality control and optimization of the laser fabrication.

Table 1

Compositional analysis of the laser-cladded composite coating on TiAl alloy

Area	Composition (wt.%)						
	Ni	Cr	C	F	Ca	Ti	Al
Grey block (A)	0.53	1.42	17.30	10.93	0.28	17.10	52.44
Grey continuous matrix (B)	10.52	20.52	6.41	3.17	0.07	44.22	15.08
White dendrite or short-stick (C)	0.24	3.59	13.15	10.75	0.18	66.35	5.74
Spherical particles (D)	2.65	7.44	2.77	26.42	30.31	18.71	11.70

4. Conclusions

γ-TiC–Al_4C_3–CaF_2 metal matrix composite coatings was fabricated on γ-TiAl alloy by laser cladding with Ni14.4–Cr40–C5.6–$CaF_2$40 (wt.%) precursor powder mixtures. The laser-cladded composite coating has a unique microstructure consisting of primary dendrite or short-stick TiC and block Al_4C_3 carbides reinforcement as well as fine isolated spherical CaF_2 solid lubrication particles uniformly dispersed in the NiCrAlTi (γ) matrix. The average microhardness of the composite coatings is approximately HV 650 and it is 2-factor greater than that of the TiAl substrate.

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