J Mater Sci (2008) 43:1546–1551
DOI 10.1007/s10853-007-2350-y

Microstructure and wear properties of Fe–TiC surface composite coating by laser cladding

Shiyao Qu · Xinhong Wang · Min Zhang · Zengda Zou

Received: 15 August 2007 / Accepted: 27 November 2007 / Published online: 1 January 2008

Abstract AISI 1045 steel surface was alloyed with pre-placed ferrotitanium and graphite powders by using a 5-kW CO_2 laser. In situ TiC particles reinforced Fe-based surface composite coating was fabricated. The microstructure and wear properties were investigated by means of scanning electron microscopy, transmission electron microscopy, and X-ray diffraction, as well as dry sliding wear test. The results showed that TiC carbides with cubic or flower-like dendritic form were synthesized via in situ reaction between ferrotitanium and graphite in the molten pool during laser cladding process. The TiC carbides were distributed uniformly in the composite coating. The TiC/matrix interface was found to be free from cracks and deleterious phase. The coatings reinforced by TiC particles revealed higher wear resistance than that of the substrate.

Introduction

Ceramic particles reinforced Fe-based composite coatings find various tribological applications. TiC is a desired reinforcement in metal matrix composites (MMCs) due to its high hardness and high chemical stability. In recent years, TiC particles reinforced MMCs have received much attention in the world [1–3]. There are mainly two processing techniques available to produce reinforcement particles in the matrix of MMCs. One is mechanical mixing of the reinforcement externally [4–8]; the other is in situ formation of the reinforcement phase within the matrix. The former is based on the addition of the particulate reinforcement to the matrix materials. In this case, however, the shape and chemical composition of additives hardly remain unchanged due to the dissolution into metal liquid or metallurgical reactions with the environment resulting in the deterioration of the toughness and crack resistance of MMCs. The latter is realized through creating conditions favorable for reaction of elements to form the particles. It involves a chemical reaction resulting in the formation of a very fine and thermodynamically stable reinforcing ceramic phase within a metal matrix. The eminent advantage of this technology is that it eliminates interfacial incompatibility of matrix with reinforcements and, therefore, a stronger matrix-dispersion bond can be achieved.

Surface modification techniques, such as laser beam [9], plasma spraying [10], and flame spraying [11], have usually been used to produce surface composite coatings to improve the wear resistance of the component. Among those surface modification techniques, laser cladding is one of effective surface modification processes, which can make metal surface quickly melt and then rapidly solidify. In recent years, the in situ formation of TiC reinforcement in a laser molten pool has received much attention [12–14]. These researches indicated that TiC particles were formed by in situ reaction between pure titanium and graphite. However, there often exist some limits. Since pure titanium is an active element, it is easier to oxidize than ferrotitanium (Fe–Ti) alloy during laser cladding. Furthermore, compared to Fe–Ti alloy, pure titanium is expensive. Therefore, from both economic and applied points of view, Fe–Ti alloy has some potential advantages to synthesize TiC reinforcement.

S. Qu · X. Wang (✉) · Z. Zou
School of Materials Science and Engineering,
Shandong University, Jinan 250061, China
e-mail: xinhongwang@sdu.edu.cn

M. Zhang
School of Mechanical Engineering, Shandong University,
Jinan 250061, China

In the present investigation, an attempt has been made to fabricate TiC particles reinforced Fe-based surface composite coatings on an AISI 1045 steel substrate by laser cladding. TiC particles are synthesized by an in situ reaction of ferrotitanium alloy powder and graphite during the laser cladding process.

Experiment details

The powder mixtures of the coating alloy were prepared from ferrotitanium (Fe–Ti) alloy (200 mesh) and crystalline graphite (99.5% purity) (180 mesh) powders. The chemical composition of Fe–Ti in wt.% is: 40 Ti, Al less 6, balance Fe. The ratio of Fe–Ti alloy to graphite powder corresponded to that of stoichiometric TiC, that is, the ferrotitanium and graphite powders were combined in the desired molar ratio (mol_{Ti}:mol_C = 1:1). In order to obtain homogeneous distribution, the powders mixtures were first blended in a crucible for 0.5 h followed by ball milling at 300 rpm and a ball-to-powder weight ratio of 20:1 in a planetary ball mill for 1 h under argon protection condition.

AISI 1045 medium carbon steel was used as substrate, whose nominal chemical composition in wt.% is: 0.43–0.50C, 0.50–0.80Mn, 0.17-0.37Si, P less 0.035, S less 0.035, Cr less 0.25, Ni less 0.3, Cu less 0.25, and balance Fe. The dimensions of the substrates are 100 × 15 × 10 mm^3, and the clad surfaces were ground to a surface finish of Ra = 0.3 mm. All specimens were rinsed with ethanol followed by acetone before laser cladding. The blended powders were mixed with a small amount of sodium silicate to keep the powders on the surface during laser cladding process. Then, the blended powders with sodium silicate were dried in hot air. Finally, the blended powders were pre-placed on the surface of the substrate, which were thoroughly cleaned, dried and finally rinsed by acetone, to give a thickness of about 1.0–1.2 mm.

Laser cladding was conducted with a 5 kW continuous wave CO_2 laser (model HL-T5000D, China) to produce a series of single clad tracks without overlap. The laser output power was 2.5 kW, the laser beam scanning velocity was 5 mm s^{-1}, and the diameter of the laser beam was fixed at 3 mm. In order to prevent the melted pool from oxidation, a shielding gas of pure argon was supplied through coaxial nozzle at 10 L min^{-1}.

Specimens for microstructural examination were prepared by sectioning the coatings in both the transverse and longitudinal directions. All specimens were etched with a solution of 3% nital. The microstructure and compositions were analyzed by using a scanning electron microscopy (SEM) and transmission electron microscopy (TEM). A type of Rigaku D/Max-rB X-ray diffractometer with Cu-$K\alpha$ radiation operated at 60 kV and 40 mA was used to analyze the coating phase structure. Micro hardness along the depth of the cross section was measured by using a Shimadzu HMV-2000 type micro Vickers. The load used was 200 g and loading time was set at 15 s. An average value of hardness was taken from five measurements.

A block-on-ring wear testing was carried out without lubrication at room temperature using a friction and wear tester. The ring material of the wear couple was W18Cr4V. Its hardness is 62 HRC. The outer radius of the circular test ring is 40 mm, and the width is 10 mm. The test specimens were machined to block with size of 35 × 6 × 8 mm^3. The wear conditions were a normal load of 49 N, a sliding speed of 0.84 m s^{-1} and a sliding distance of 1,008 m.

Results and discussion

Microstructure of the coating

Figure 1a–b shows the typical macrograph of the laser cladding coating from longitudinal directions and transverse cross section, respectively. From the macrograph of longitudinal direction, it can be seen that the coating is continuous, uniform profile, and free from cracks and porosity. Micrograph of the transition zone between the coating and the substrate is shown in Fig. 1c. It is found that the transition zone between the composite coating and the substrate is a thin band with the planar growth. Its thickness is about 20–30 μm. The transition zone reveals that α-Fe dendrites grow directionally and epitaxially from the substrate into the composite coating. These indicate that a good metallurgical bond is obtained between the composite coatings and the substrate. Fig. 1d shows the EDS analysis result of marked [A] dark dendrites growing in the interface region in Fig. 1c, it can be seen from Fig. 1d that besides [Fe], [Mn], and [Si] elements, some of [Ti] and [C] can be found. It indicates that some of coating materials dissolve into the transition zone and dark dendrites are TiC particles.

Figure 2 shows the XRD pattern of top surface of the composite coating. It reveals that the coating is mainly composed of α-Fe TiC phase and Fe_3C, which clearly confirms that the TiC particles were in situ synthesized by direct reaction between ferrotitanium (Fe-Ti) and graphite during laser cladding.

Figure 3 shows a typical microstructure of the composite coating. It can be seen that a large number of TiC carbides in the form of cubic or flower-like dendrite shape were distributed in the composite coating. It is well known that TiC-type MC carbide has both high melting point (3,200°C) and a lager negative free energy of formation ($\Delta G^\circ = -186\,606 + 13.22\,T$ J/mol) in the Fe–Ti–C system. TiC might precipitate from the liquid as the primary phase and grow freely as a dendrite. When the temperature of the residual

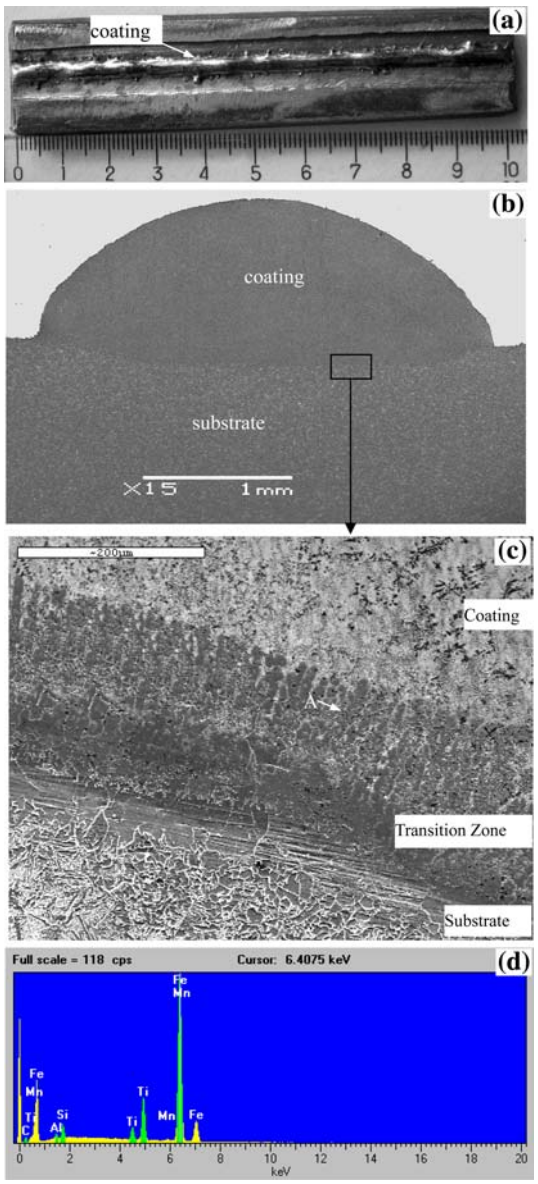

Fig. 1 Morphology of the laser cladding coating (**a**) macrograph of longitudinal directions; (**b**) macrograph of transverse cross section; (**c**) microstructure of the bonding region between the coating and the substrate; and (**d**) EDS of marked A in (**c**)

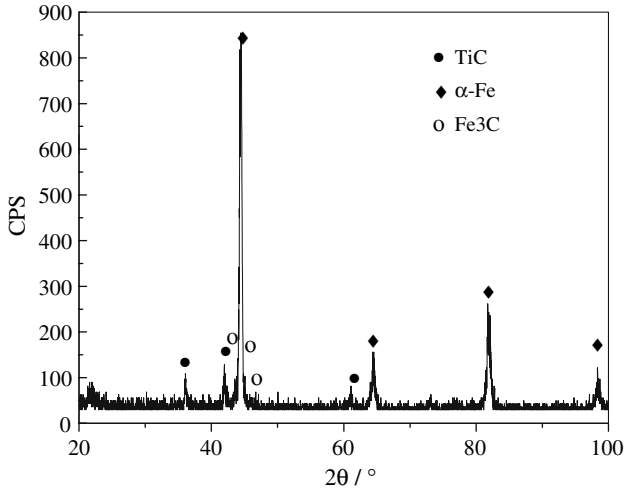

Fig. 2 XRD pattern of the composite coating

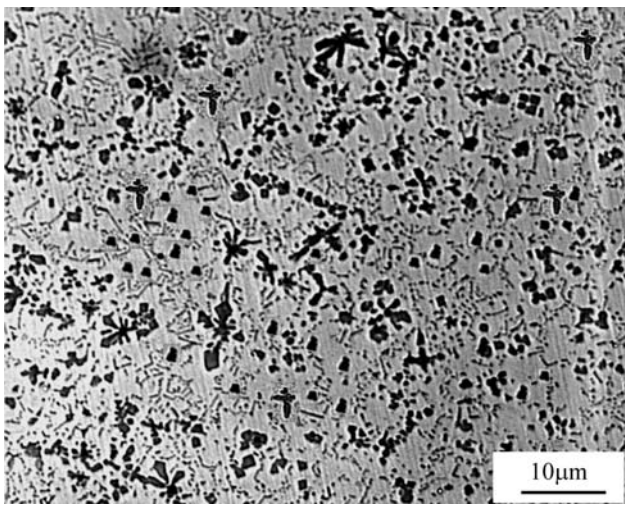

Fig. 3 Microstructure of the coating

liquid decreases, γ-Fe precipitates following the solidification of TiC. And then, γ-Fe changes to the α-Fe. Although some areas show more TiC particles than others, in general, the distribution of TiC particles is uniform in the matrix. Hence, these TiC particles act as reinforcement and are expected to improve the wear properties of the composite coatings.

Figure 4a shows a typical TEM micrograph of TiC particles in the coating. Selected area electron diffraction shows that the TiC has an fcc crystalline structure (as shown in Fig. 4b). Results of the selected area diffraction pattern in the [111] direction show that the carbide has NaCl crystal structure. Figure 4c presents the phase interface between the TiC and the matrix. It is noted that the interface remains clean and free from deleterious phases of Fe_2Ti and Fe_3C. Because of the high cooling speed and solidification during laser cladding, the interface reaction between TiC and the melting alloy is restrained. Therefore, the TiC-matrix has a strong interface bond.

Microhardness

Microhardness profile along the cross section of the composite coating is illustrated in Fig. 5. Compared to the substrate, the microhardness of the coating increases significantly, which is attributed to the presence of reinforcements in the composite coating, the microhardness within the coating gradually increases from the bottom to the top surface of the coating. It is noted that there is no sudden change of the microhardness

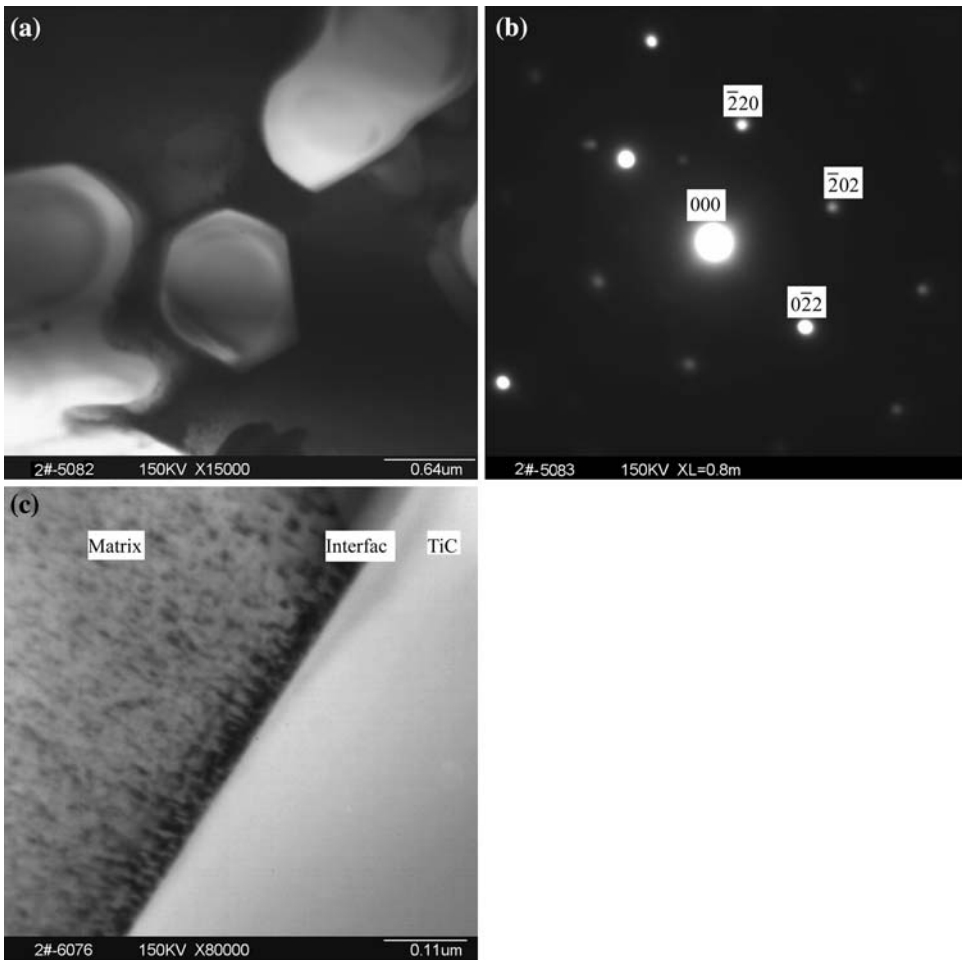

Fig. 4 TEM micrograph of TiC particles in the coating: (**a**) TiC morphology; (**b**) electron diffraction of TiC; and (**c**) interface morphology of TiC and matrix

across the whole coating, which indicated an absence of a sharp demarcation in materials properties across the interface. This distribution may be attributed to the differential-density-driver. Compared to the Fe-based alloy, the relatively lower density of TiC (4.94 g/cm^3) tended to segregate it to the upper regions in the coating, which causes a gradient distribution on a macroscale. Sometimes it was unavoidable to make indentions close to the TiC particles, the result of which was a much higher hardness. This resulted in some fluctuations on the hardness curves, despite that an average of five measurements was taken.

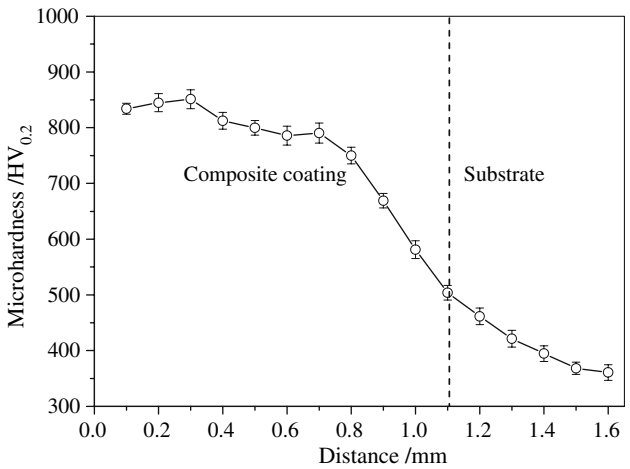

Fig. 5 Microhardness profile along the cross section of the composite coating

Wear resistance

Figure 6 shows the wear volume loss of the TiC particles reinforced composite coating and the substrate. Compared with the substrate, the composite coating has high wear resistance. The increased wear resistance of the composite coating is mainly attributed to the reinforcement of TiC carbides. When metallic surfaces are in contact during dry sliding wear, the local temperature at the contact points of the surface is high, and the hardness near these points quickly decreases. As a result, serious plastic deformation, local contact-welding between the contacting asperities, and materials transfer lead to serious material removal from the friction surface. However, due to the high hardness of TiC, the composite coating has the capability to

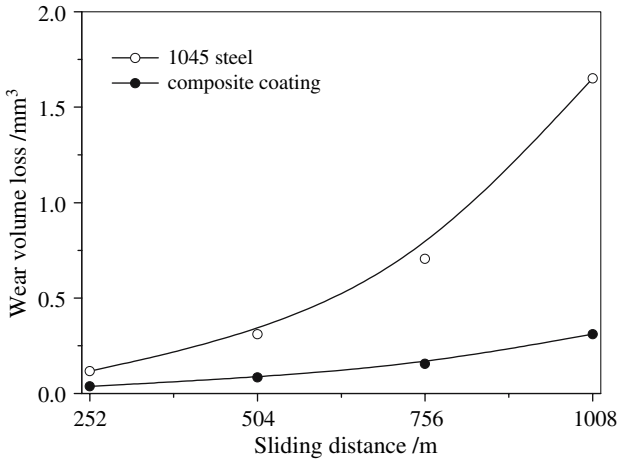

Fig. 6 Wear volume loss of the coating and the substrate

resist micro-cutting, micro-plowing, and repeated surface plastic deformation. Thus, the composite coating exhibits excellent abrasive wear resistance.

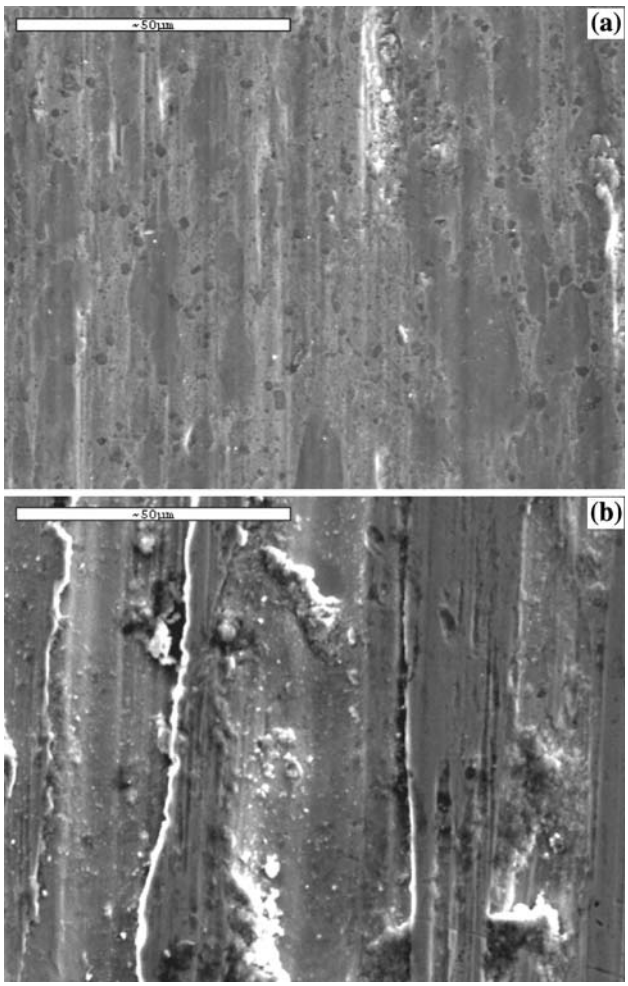

Fig. 7 Wear scar of the composite coatings and 1045 steel under a normal load of 49 N, a sliding speed of 0.84 m s^{-1} and sliding distance of 1,008 m: (**a**) composite coating; and (**b**) 1045 steel

Figure 7a–b shows the wear scar of the composite coating and substrate, respectively. It indicates that there is a mild wear with fine scratches for the composite coating. For 1045 steel, plastic deformation is observed inside it, indicating that wear could proceed mainly from an adhesion mechanism. However, wear tracks of composite coatings were mainly surface deformation and damage in the form of longitudinal grooves extending parallel to the sliding direction. As mentioned earlier, TiC particles in the Fe-based matrix are formed in an in situ manner, which improves the bonding strength between the TiC particles and Fe-based matrix interface. As a result the hard TiC particles are not easily pulled out from the matrix during wear sliding. Therefore, the composite coating is found to possess a much higher resistance to plastic deformation and scoring, which increases the resistance to plastic deformation and removal of the edges of grooves during subsequent passes.

Conclusions

(1) In situ TiC particles reinforced Fe-based surface composite coating has been produced on mild carbon steel using laser cladding. The continuous and defect-free coating was obtained.
(2) TiC particles were synthesized by direct in situ reaction of ferrotitanium and graphite. The morphology of TiC is mainly cubic or flower-like form. The interface of TiC and matrix is found to remain clean and free from deleterious phase.
(3) The coating reveals higher microhardness in comparison with the substrate. Sliding wear tests show that the composite coating possesses good wear resistance properties due to the presence of in situ synthesized TiC particles.

Acknowledgement This research was supported by the Development Program of Shandong Province (06GG3203009).

References

1. Chong PH, Man HC, Yue TM (2002) Surf Coat Technol 154:268
2. Dubourg L, Ursescu D, Hlawka F, Cornet A (2005) Wear 258:1745
3. Abkowitz S, Abkowitz SM, Fisher H, Schwartz PJ (2004) Adv Mater Process 162:82
4. Saidi A, Chrysanthou A, Wood JV, Kellie JLF (1994) J Mater Sci 29:4993
5. Qi X, Aust E, Eigen N, Gartner F, Klassen T, Bormann R (2006) Adv Eng Mater 8:427
6. Clyne TW, Mason JF (1987) Metall Trans A 19:1519
7. Kattamis TZ, Suganuma T (1991) Mater Sci Eng A 128:241
8. Wa Y, Lavernia EJ (1992) Metall Trans A 23:2923

9. Park H, Nakata K, Tomida S (2000) J Mater Sci 35(3):747
10. Schulz U, Peters M, Bach F-W, Tegeder G (2003) Mater Sci Eng A 362(1–2):61
11. Li ZW, Liu CS, Huang JH, Yin S (2003) J Mater Sci Technol 19(2):161
12. Yang S, Zhong M-L, Liu W-J (2002) J Aeronaut Mater 22:26 (in Chinese)
13. Wu X, Hong Y (2000) Acta Metall Sin 36:282 (in Chinese)
14. Singh A, Dahotre NB (2004) J Mater Sci 39:4553
15. Knacke KO, Hesselmann K (1991) Thermo-chemical properties of inorganic substances, 2nd edn. Springer-Verlag, New York
16. Lu WJ, Zhang XN, Zhang D, Wu RJ, Bian YJ, Fang PW (1999) Acta Metall Sin 35:536