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In situ synthesis and hardness of TiC/Ti_5Si_3 composites on Ti-5Al-2.5Sn substrates by gas tungsten arc welding

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Abstract: TiC/Ti_5Si_3 composites were fabricated on Ti-5Al-2.5Sn substrates by gas tungsten arc welding (GTAW). Identification of the phases was performed using X-ray diffraction (XRD). The microstructures were analyzed using scanning electron microscopy (SEM) combined with energy-dispersive X-ray spectrometry (EDS) and optical microscopy (OM). The Vickers hardness was measured with a micro-hardness tester. The TiC/Ti_5Si_3 composites were obtained in a double-layer track, and the Vickers hardness of the track increased by two to three times compared with the Ti-5Al-2.5Sn substrate.

Keywords: titanium alloys; surface modification; gas tungsten arc welding (GTAW); microstructure; hardness

1. Introduction

Hardness is regarded as an assessment of wear resistance. Light metals such as titanium alloys have been widely used due to their high strength, specific modulus, low density, and good corrosion resistance [1]. However, titanium alloys cannot fully satisfy the requirements of industry because of the relatively low shear strength and hardness value [2]. To circumvent these shortcomings, various techniques such as surface coating [3] and surface nitriding [4] have been used to improve the surface hardness and wear durability of titanium alloys. In addition, titanium matrix composites reinforced by the particulates have been extensively studied in the past decades [5-9]. In particular, TiC and Ti_5Si_3 have attracted increasing attention due to high hardness, high modulus, high temperature strength, and heat stability [10-11]. Meanwhile, TiC/Ti_5Si_3 composites have a potential to be used as reinforced particles for surface modification. However, scientific information about TiC/Ti_5Si_3 composites applied to surface modification is very limited except the preparation of bulk-form TiC/Ti_5Si_3 composites [12-14].

The performance of titanium-based composite materials enables them to be used for structural parts of rockets, aero engines, turbojet engines, and bio-implant applications [15-16]. Their performance can be enhanced by modifying the physical properties through several approaches. However, most of technologies can only produce thin surface layers, e.g., the laser nitriding layer [1, 17]. Furthermore, laser cladding or electron beam radiation processes are limited by several factors, such as costly manufacturing procedures, vacuum chambers, and expensive initial investments [18-19]. To improve the ability of bearing high loads and obtain high hardness and thick surface alloying layers, new attempt has been made by using gas tungsten arc welding (GTAW) to prepare Fe-based surface composite coatings [20]. GTAW process has the characteristics of processing precision, flexibility in operation, simultaneous melting, and rapid solidification. Compared with

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laser and electron beam processing, it can prepare a wider and thicker molten layer. However, there are few studies on the formation of ceramic reinforced particles via in situ reaction using GTAW process for surface modification of titanium alloys [21].

In this study, TiC/Ti_5Si_3 composites were fabricated on Ti-5Al-2.5Sn substrates by GTAW process. TiC/Ti_5Si_3 composite particles were synthesized by in situ reactions of compacts forming from the element powder of Ti, Si, and C during GTAW process rather than TiC and Ti_5Si_3 particles being directly added into the molten pool.

2. Materials and methods

The materials used were the commercial powders of Ti (99.6% purity, ~1.45 μm), Si (99.5% purity, ~10 μm), and C (99% purity, ~15 μm) powders. The powder mixture was prepared with Ti:Si:C (molar ratio) = 6:3:4 and then mixed by ball-milling for 2 h to ensure homogeneity. The mixed powders were mixed with a few drops of sodium silicate, as a binder, and then put in a self-designed mold of stainless steel and pressed into cylindrical compacts (8 mm in diameter and 150 mm in length) under 300 MPa. The compacts as welding wires were deposited on the surface of Ti-5Al-2.5Sn alloys by GTAW process to form composite layers. The parameters of processing were set as the direct-current supply (I) of about 300 A, the voltage (U) of 20 V, the travel speed (v) of 1.5 $mm\cdot s^{-1}$, the nonconsumable W electrode with 4 mm in diameter, and the pure argon flow rate of 0.3 $L\cdot s^{-1}$. The arc length was about 3 mm.

Surface alloying was carried out using welding wires as filled materials by GTAW to produce a single track (Fig. 1(a)) and a double-layer track (Fig. 1(b)). The double-layer track means that the second layer is on the top of the first track. Specimens for microstructure examination were prepared by cutting sections transversely to the GTAW surface alloyed tracks. Specimens with dimensions of 10 mm × 10 mm × 10 mm were then mounted in bakelite, grounded, and polished along the top surface and cross-section of the tracks, respectively. Specimens a and b denote the deposited single- and double-layer tracks, respectively. For specimen b, the second deposition layer was carried out when the first deposition layer cooled to room temperature. All specimens were etched with a solution of $HNO_3/HF/2H_2O$. With the help of X-ray diffraction (XRD), scanning electron microscopy (SEM), and optical microscopy (OM), the phase compositions and microstructures of the products were analyzed and observed. Vickers microhardness measurements were made on a microhardness tester equipped with a Vickers diamond pyramid indenter. The measurements were made along the depth of the cross-sections of the GTAW alloyed tracks. A load of 1.96 N was applied on the indenter and the loading time was set at 15 s. An average value of hardness was taken from five measurements.

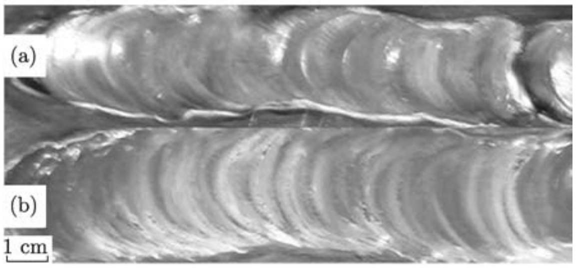

Fig. 1. Top views of GTAW surface deposition tracks: (a) single track; (b) double-layer track.

3. Results and discussion

3.1. Microstructure

Fig. 1 shows the surface morphology of the alloyed tracks. It can be seen that the deposition tracks gave smooth rippled surface patterns and no cracks were found on the surface. It indicates that GTAW process used in this study successfully produced surface alloyed tracks with the thickness of about 2.0-2.5 mm.

There are two almost orthogonal angle variants within the heat-affected zone (Fig. 2). Such transformation products have typical features of α′-Ti martensite. This was reported by various investigators in the rapidly quenched titanium alloys [22]. During rapid cooling, α′-Ti was formed by β-Ti → α′-Ti reaction within the heat-affected zone. Fig. 2 shows that the microstructures of the tracks observed on transverse sections are dendrite morphologies, and they form excellent metallurgical bonding to the substrate material.

The XRD patterns of the composite tracks are shown in Fig. 3. It can be seen that, besides TiC and α′-Ti diffraction peaks, Ti_5Si_3 diffraction peaks cannot be seen, but an unknown weak peak is found near 36° (2θ) as shown in Fig. 3(a). This unknown weak peak is attributed to SiC phase. In Fig. 3(b), the presence of TiC and Ti_5Si_3 diffraction peaks can be clearly seen, indicating the formation of TiC and Ti_5Si_3 particles. However, no Si and C peaks could be observed after GTAW deposition process, indicating that the reactions were complete.

Fig. 4 shows the micrographs of the composite tracks by back-scattered electron microscopy combined with energy-dispersive X-ray spectrometry (EDS). There are three different color regions in Fig. 4(a) marked by spots 1-3, respectively. Meanwhile, it is clearly seen that there are two phases in Fig. 4(b). Cobblestone-like and dendrite

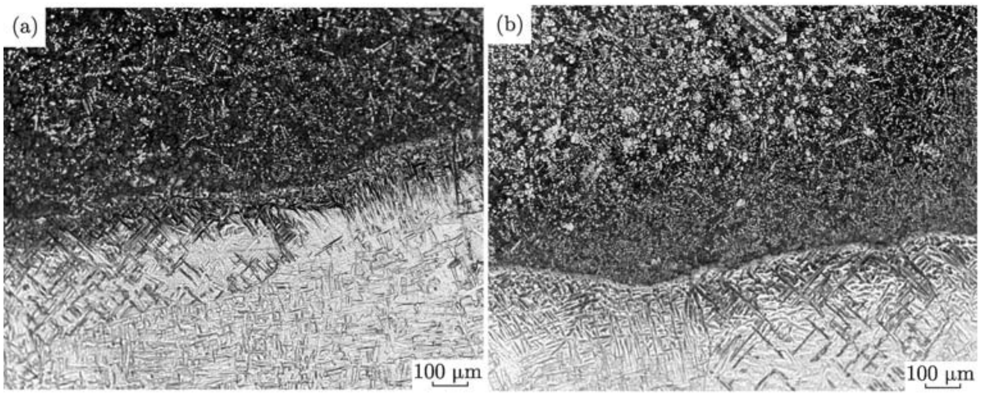

Fig. 2. OM micrographs of the interface between the ceramic layer and substrate: (a) single track; (b) double-layer track.

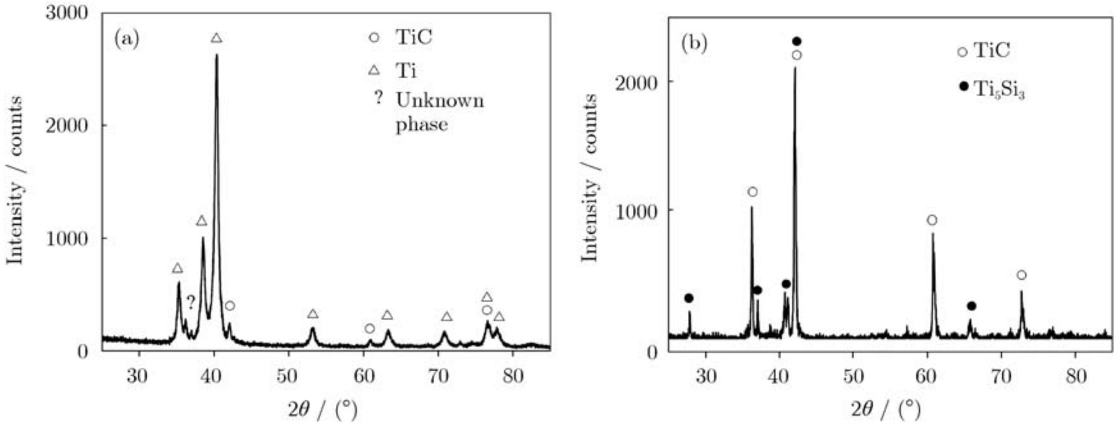

Fig. 3. XRD patterns of the composite coatings: (a) single track; (b) double-layer track.

microstructures (spot 1) and lath-shaped microstructures (spot 2) are found in Fig. 4(b). Figs. 4(b1) and 4(b2) show the EDS spectra of spots 1 and 2 marked in Fig. 4(b), respectively. The atomic ratios (Ti:C = 46.44:53.56 and Ti:Si = 60.94:39.06) are very close to the stoichiometric composition of TiC and Ti_5Si_3, respectively. Therefore, the cobblestone-like and dendrite microstructures are TiC phase and the lath-shaped microstructures are Ti_5Si_3 phases. At the same time, Figs. 4(a1)-4(a3) show the EDS spectra of spots 1-3 marked in Fig. 4(a), respectively, which show that the atomic ratios are Ti:C = 57.17:42.83, Ti:Si:Al = 89.31:2.10:8.59, and Ti:Si:Al = 69.49:26.69:3.82. Therefore, the dark stone-like microstructures are TiC phase, the gray block-like microstructures are mainly the α′-Ti solid solution with a small amount of Si, and the light small dot-like microstructures are the solid solution of Ti, Si, and Al.

3.2. Synthesized mechanism of TiC and Ti_5Si_3 by GTAW process

Different deposition layers could produce different compositions in the tracks by GTAW process. The substrate alloys react with the compact wire materials in the molten pool during depositing the single track, which leads to the super-abundance of Ti due to the dilution of the substrate. Unreacted Ti rapidly solidifies after melting to form α′-Ti phase (Fig. 3(a) and Fig. 4(a)). According to Li *et al.*'s report [23], silicon will evaporate in the conditions of high temperature; therefore, besides the evaporation part of Si, one of the residual parts forms a solution with the α′-Ti and Al, and the other forms a small amount of SiC. From Fig. 4(a), it is concluded that TiC particles are the precipitated phases from the substrate alloy. Therefore, the formation of TiC belongs to the precipitation mechanism in the single track. However, the compact wire materials react with themselves under GTAW heating sources during depositing the second layer in the double-layer track, and at the same time, the bottom layer is reheated and melted. The melting liquid materials including the bottom layer materials and the filling materials form a molten pool. The complex reactions occur in the liquid state. A TiC/Ti_5Si_3 composite is the ultimate product seen from Fig. 4(b). However, α′-Ti phase disappears. This attributes to the transformation of α′-Ti → β-Ti during reheating which is endothermic transformation, but it does not affect the heat energy maintaining the liquid pool

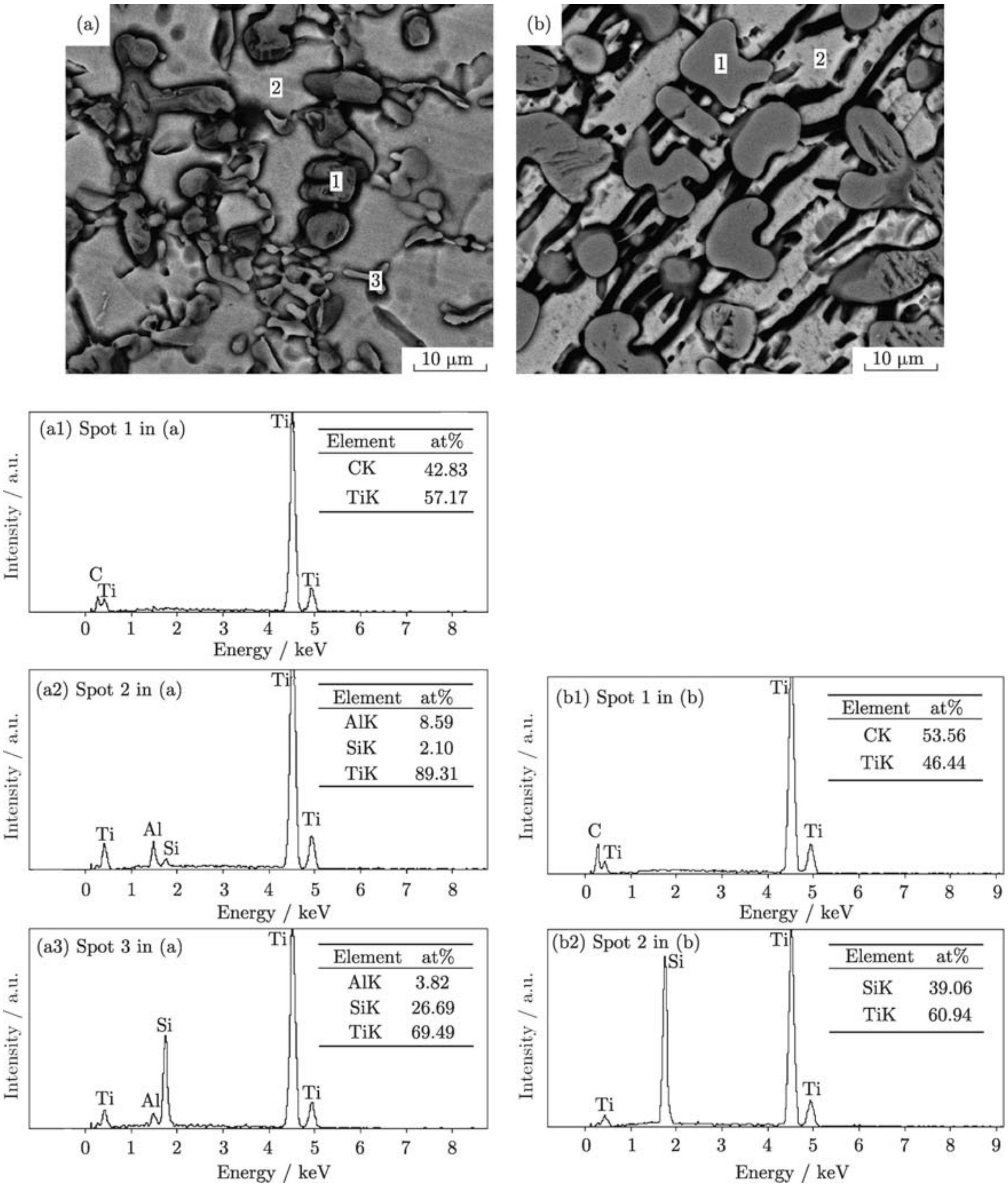

Fig. 4. SEM micrographs of the composite tracks and corresponding EDS spectra: (a) single track; (b) double-layer track.

state due to high arc heat. β-Ti reacts with Si and C in the melting pool to form Ti_5Si_3 and TiC. TiC particles are grown by means of the coalescence and precipitation mechanisms on the boundaries of Ti_5Si_3 phase in the double-layer track. From Fig. 4(b), it can be seen that the particles between TiC and Ti_5Si_3 have clear interfaces and TiC phase is embedded uniformly in the intermetallic compound of Ti_5Si_3, which prevents Ti_5Si_3 brittle phase from growing up. This is the cause why the cracks are not found on the surfaces of the alloyed tracks.

During GTAW process, the matters taking part in reactions are mainly Ti, Si, and C. In the Ti-Si-C system,

$$\Delta G_T^{\ominus} = \Delta H_{298}^{\ominus} - T\Delta S_{298}^{\ominus} \tag{1}$$

$$\Delta H_{298}^{\ominus} = \sum\left(n_i \Delta H_{i,\mathrm{f},298}^{\ominus}\right)_{\mathrm{resultant}} - \sum\left(n_i \Delta H_{i,\mathrm{f},298}^{\ominus}\right)_{\mathrm{reactant}} \tag{2}$$

$$\Delta S_{298}^{\ominus} = \sum \left(n_i S_{i,298}^{\ominus}\right)_{\text{resultant}} - \sum \left(n_i S_{i,298}^{\ominus}\right)_{\text{reactant}} \quad (3)$$

where T is the temperature, n is the number of moles, $\Delta G_T^{\ominus}$ is the standard Gibbs free energy at T, $\Delta H_{298}^{\ominus}$ is the standard enthalpy at 298 K, $\Delta S_{298}^{\ominus}$ is the standard entropy at 298 K, $\Delta H_{i,\text{f},298}^{\ominus}$ is the standard mole enthalpy of the matter i participating in reaction at 298 K, $S_{i,298}^{\ominus}$ is the standard mole entropy of the matter i participating in reaction at 298 K. The data of $\Delta H_i^{\ominus}$ and $S_i^{\ominus}$ are obtained from Ref. [24].

The possible reactions for TiC and Ti_5Si_3 are as follows:

$$\text{Ti} + \text{C} \rightarrow \text{TiC},$$

$$\Delta G(1900^\circ\text{C}) = -157.7 \text{ kJ}\cdot\text{mol}^{-1} \quad (4)$$

$$5\text{Ti} + 3\text{S} \rightarrow \text{Ti}_5\text{Si}_3,$$

$$\Delta G(1900^\circ\text{C}) = -597.2\text{kJ} \cdot \text{mol}^{-1} \quad (5)$$

In reactions (4) and (5), TiC and Ti_5Si_3 phases form when the temperature is lower than 1900°C because of the large reduction of Gibbs free energy. In GTAW process, the temperature of the molten pool is ~1600-1900°C, which favors to the formation of TiC and Ti_5Si_3. Therefore, TiC and Ti_5Si_3 might precipitate from the liquid and grow freely.

3.3. Microhardness

The microhardness of specimens was measured along the depth of the cross-sections of the GTAW surface alloyed tracks. It is noted that the Vickers hardness scatters in a range as shown in Fig. 5. The microhardness values of the GTAW surface alloyed tracks are shown to be ~3-4 times that of the Ti-5Al-2.5Sn substrate (2.0 GPa). It is noted that the hardness of the heat-affected zone consisting of martensitic structure is slightly higher than that of the substrate. The microhardness values of the GTAW surface alloyed tracks show that the hardness of the double-layer track is higher than that of the single track. This can be attributed to the increasing volume fraction of the Ti_5Si_3 structure [25]. Another phenomenon is observed that the microhardness increases first and then decreases in the double-layer tracks with different compositions between the top and bottom layers. This behavior could be attributed to the different compositions along the depth of the track. The fraction of Ti_5Si_3 on the top layer is higher than that of the lower layer.

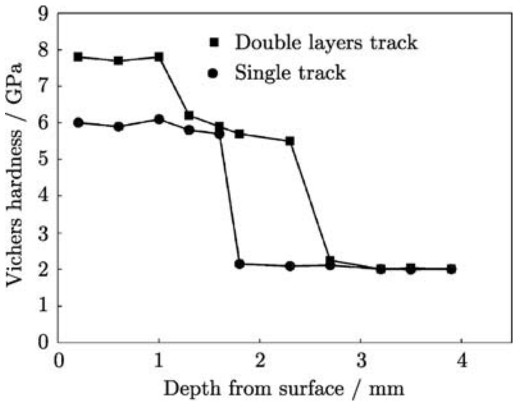

Fig. 5. Microhardness profile of surface alloyed tracks.

4. Conclusions

A surface alloyed track was fabricated on a Ti-5Al-2.5Sn substrate using GTAW process. The thickness of the track is about 2.0-2.5 mm and the micro Vickers hardness of 7.4 GPa can be obtained by depositing a double-layer track (~3-4 times that of substrate material). The microstructure of the top surface of the double-layer alloyed track consists of TiC and Ti_5Si_3 phases. During high-temperature liquid-state reactions, the precipitation mechanism is the main mechanism in the single track, but precipitation combined with coalescence and α′-Ti → β-Ti transformation are the main mechanisms in the double-layer track. Overall, these results suggest that GTAW bonding is an energy efficient and economical alternative for the surface modification of Ti-5Al-2.5Sn ductile substrates.

Acknowledgements

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