

In Situ Preparation of Titanium Carbide Ceramic Layer on Grey Cast Iron

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In this article, we report the in situ synthesis of TiC ceramic layer between titanium plate and graphite phases in grey cast iron using heat treatment method. The microstructure of the compound region was characterized by X-ray diffraction (XRD) and scanning electron microscopy (SEM), and the kinetics of the TiC ceramic layer was analyzed. The results revealed that the as-prepared TiC samples were irregularly shaped particles with a size of 1 ~ 8 μm and gradient distribution on the surface of grey cast iron. The thickness of the reaction layers increased gradually as the incubation continued, which were 62, 81, 95 and 108 μm after incubation at 1164 °C for 1, 2, 3 and 4 hours, respectively. Also, it can be recognized that the layer thickness changes in a parabolic style with incubation duration. The formation process of TiC ceramic layer consists of diffusion and in situ reaction of carbon and titanium atoms.

Keywords: TiC, ceramic, in-situ reaction, microstructure, kinetics.

1. INTRODUCTION

Metal-based composites reinforced by ceramic particles have become a novel class of advanced materials that are widely applied in inexpensive wear resistant parts. Therefore, these materials have been intensively investigated during the past three decades [1]. The composites offer various advantages such as cost-effectiveness, good wear resistance, excellent mechanical properties, etc.

Titanium carbide (TiC) reinforced iron surface composite, which can provide great wear resistance for the substrate in a variety of working conditions, has gained increasing attention and become one of the hottest topics in the field of surface composites [2–4]. TiC with a Vickers hardness of 2895 ~ 3200 HV is one of the most promising reinforcing agents for the iron and steel matrix due to its availability, high melting point, high hardness and good thermodynamic stability. Most importantly, the TiC can be chemically wetted by the iron matrix. It has been shown that the wetting angle (θ) between TiC and molten iron is less than 50°, even at elevated temperatures or with pressure [5–6].

Methods that are commonly employed for the preparation of the TiC particle reinforced iron-based surface composite include accelerated electron beam irradiation [5, 7], GTAW multi-layers melting process [8], self-sustaining high-temperature synthesis (SHS) [6] and surface alloying using laser cladding [9]. However, these methods show several drawbacks such as imperfect surface quality, low precision, high content of gas, porosity and slag inclusion, resulting in limited capability of fabricating components with complex geometry, etc.

In situ reaction technology has been considered as one of the most promising methods for the preparation of iron-based composites in virtue of the fine size and thermodynamic stability of the ceramic particulates in the matrix and a strong interfacial bonding between the reinforcing agents and the matrix. In this article, an in situ process was developed for the fabrication of TiC ceramic layer on grey cast iron matrix and the phase evolution and microstructures were studied. One of the most promising advantages of the proposed process is the metallurgical bonding between ceramic layer and matrix as a result of in situ reaction. Other advantages include low cost, facile process and simple equipment.

2. EXPERIMENTAL DETAILS

For the in situ fabrication of TiC ceramic layer on grey cast iron, grey cast iron (HT 300) and titanium plates (thickness = 0.125 mm and purity = 99.779 %) were employed as carbon and titanium sources, respectively. The chemical composition of grey cast iron (wt.%) was: 3.45 C, 0.56 Si, 0.27 Mn, 0.224 P, 0.024 S.

Fig. 1 is a schematic diagram showing the fabrication procedures of TiC ceramic layer on grey cast iron. A grey cast iron block with a cube shape (10 mm \times 10 mm \times 10 mm) was prepared. The titanium plate (10 mm \times 10 mm \times 0.125 mm) was fixed to the cube. Afterwards, the specimen was heated to 1200 °C and kept for 20 min, followed by incubation at 1160 °C, an appropriate temperature that was chosen based on the partial dissolution temperature of the titanium plate determined by differential scanning calorimetry (DSC) [10]. The specimen was subjected to heat treatment at 1160 °C for different dwelling times (1, 2, 3, and 4 hours) in a horizontal tube furnace with a modest flow of argon and cooled down to room temperature naturally.

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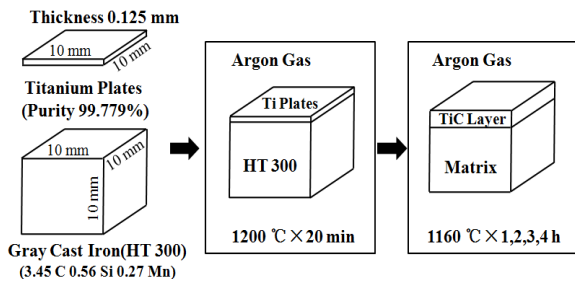


Fig. 1. Schematic diagram of fabrication procedures of TiC ceramic layer on grey cast iron

After polishing with diamond paste and etching with a 4 % Nital solution, the as-prepared specimens were characterized by scanning electron microscope (SEM; EVO-18 ZEISS, Germany). Then, the specimen was characterized by X-ray diffraction (XRD; PW 1730 Philips, The Netherlands) with monochromated Cu K_{α} radiation at 40 kV and 40 mA in the 2θ range of $10 \sim 90^{\circ}$.

3. RESULTS AND DISCUSSION

3.1. Microstructure and phases

Fig. 2 shows the SEM micrographs of the reaction layer between the titanium plate and matrix after heat treatment at 1200°C for 20 min. The melting-point of the grey cast iron is about $1150 \sim 1200^{\circ}\text{C}$, according to the Fe-C equilibrium phase diagram. As a result, the grey cast iron surface was melted, and the reaction layer between the titanium plate and matrix was in form of particles. Despite of the minor variations, thickness of the reaction layer was approximately $25 \mu\text{m}$. The interface between the reaction layer and the matrix was clear and visible. Due to the cracks occurred in the interface of the reaction layer and the cast iron, the bonding strength between reaction layer and cast iron was lowered.

Fig. 3 shows the SEM micrographs of the microstructures of the reaction layers after heat treatment at 1160°C for different times. The thickness of the reaction layers, which were 62, 81, 95 and $108 \mu\text{m}$ for holding 1, 2, 3 and 4 hours, respectively, gradually increased with the incubation duration. The reaction layers were composed of dense particles and the density of the layers did not show significant change as the incubation continued. Besides, a significant change was observed in the microstructure of grey cast iron matrix. The graphite flakes in grey cast iron were consumed, leading to a mixture of pearlite and ferrite for the microstructure.

Phases presented in the reaction layer were characterized by X-ray diffraction and the result is shown

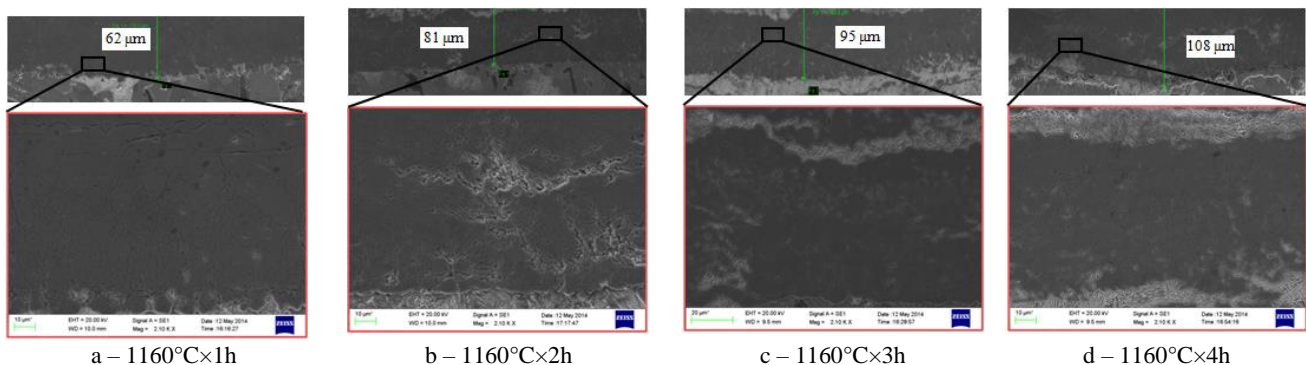


Fig. 3. SEM micrographs showing the overall microstructures of the reaction layers after heat treatment at 1160°C for different times

in Fig. 4. The XRD patterns of the reaction layer on grey cast iron were measured by taking the cross section of the sample as an example. In the specimen heat treated at 1160°C for 4 hours, peaks of α -Fe, TiC and graphite can be observed. Here, high α -Fe peaks indicate a large content of ferrite in the matrix and a small amount of graphite. Dense particles found in the specimens were identified as TiC. It can be concluded that the TiC particles were synthesized in situ between the titanium in titanium plate and the carbon in the graphite flakes. As the graphite flakes were consumed, and the matrix microstructure transferred to ferritic phase with graphite. Also, it's worth noting that no obvious pearlitic characteristic peaks are observed, while the reasons need further clarification.

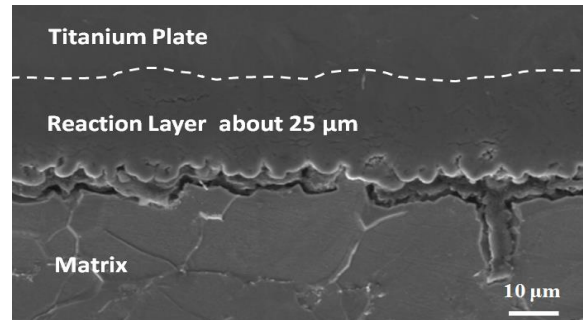


Fig. 2. SEM micrographs of the reaction layer between titanium plate and grey cast iron matrix after heat treatment at 1200°C for 20 min

The reaction on the titanium plate was realized by the heat diffusion of carbon and titanium atoms. The original interface between the titanium plate and the grey cast iron was eliminated while no defects were resulted. An Image Statistical Analysis about all the distribution of the dimensions in the different zones was performed [11]. The particle size after 4 h was also obtained by the Image Statistical Analysis. The TiC particles synthesized in situ are irregularly shaped, with a size of $1 \sim 8 \mu\text{m}$ and gradient distribution on the surface of grey cast iron. Additionally, the size of TiC particles increased from the interface to the composite surface, while pearlite and ferrite could be observed at the vicinity of the reaction boundary. From what has been discussed above, the titanium carbide ceramic layer on grey cast iron, which was prepared by in situ, has several characteristics. Firstly, the thickness of the titanium carbide ceramic layer on grey cast iron is $25 \sim 108 \mu\text{m}$, and the distribution of TiC particles on the matrix is dense and the density of the layer did not show significant change with the different times.

Secondly, the titanium carbide particle size is 1 ~ 8 μm and it increased from the interface to the surface. Thirdly, the micro-hardness of the titanium carbide ceramic layer is about 1400 HV_{0.05}, and shows excellent wear resistance. Sahoo C. K. et al [12] produced TiC reinforced steel composite layer by laser scanning over the preplaced TiC powder on AISI 304 steel substrate. The thickness of the composite layer was about 150 μm , and the particle size of TiC is 10 ~ 14 μm . The distribution of TiC particle is uneven, and the volume fraction of particle is lower. Beside, the micro-hardness of the layer is 800 ~ 1200 HV_{0.05} with different process, while the value in our study is about 1400 HV_{0.05} due to higher TiC volume fraction. Emamian A. et al [13] prepared Fe-TiC composite coating on AISI 1030 carbon steel by laser cladding. Dendritic TiC distributed in iron matrix, and the volume fraction of TiC is only 20 ~ 33 %, and the particle size is 2 ~ 10 μm , which is similar to our work. Onuoha C. C. et al [14] developed a family of nove TiC-304L stainless steel composite. The cermets exhibit high hardness, which increase with TiC content, exhibiting a maximum value in excess of ~ 2500 HV₁ with just 5 % steel binder content. The TiC particle size is about 7 μm , and volume fraction is 70 ~ 95 %, which is the reason to excellent wear resistance.

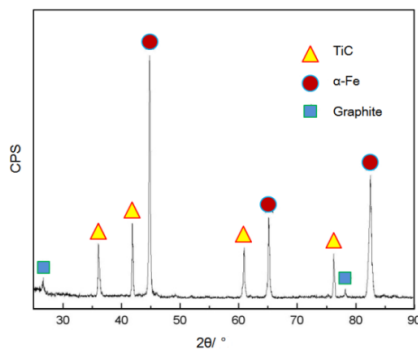


Fig. 4. XRD pattern of the specimen heat treated at 1160 °C for 4 h after heating at 1200 °C for 20 min

3.2. Kinetics of the TiC ceramic layer

The thickness of the TiC ceramic layer fabricated in situ depends on heat incubation temperature and duration. The classic relation between thickness of reaction layer (d) and heat treatment time (t) is:

$$d = Kt^{0.5} + b_0, \quad (1)$$

where b_0 is the initial thickness of the reaction layer and K is the growth rate constant depending on the processing temperature. The correlation between growth rate constant

(K) and processing temperature (T) can be expressed by an Arrhenius equation [15] as follows:

$$K = K_0 \exp\left(-\frac{Q}{RT}\right), \quad (2)$$

where K_0 is a pre-exponential constant, Q is the activation energy ($\text{J}\cdot\text{mol}^{-1}$) and R is the gas constant ($\text{J}\cdot\text{mol}^{-1}\text{K}^{-1}$).

If the kinetics of TiC layer progress for the periods between 1 and 4 hours is considered, it can also be recognized that the layer thickness changed in a parabolic style with time as seen in Fig. 5. Calculated K values derived from the slopes of the plots of the TiC layer treatment were $6.61 \times 10^{-7} \text{ m}\cdot\text{s}^{-0.5}$ at a processing temperature of 1160 °C.

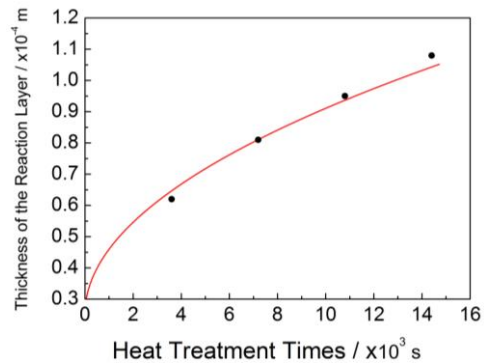


Fig. 5. Thickness of the reaction layer with different heat treatment times

3.3. Formation process of TiC ceramic layer

Based on the microstructure and kinetics process, a schematic diagram of TiC ceramic layer on grey cast iron was depicted, as shown in Fig. 6. The formation of TiC ceramic layer consists of diffusion and in situ reaction of carbon and titanium atoms and the whole process may be divided into three main stages:

First stage: Metallurgical bonding between titanium plate and grey cast iron (heat treatment at 1200 °C for 20 min). Due to the good wettability, titanium plate and grey cast iron is metallurgically bonded at a heat treatment temperature is 1200 °C. On one hand, solid solution of titanium diffused into the ferrite in the form of displacement solution at temperatures above the austenitizing temperature. On the other hand, carbon atoms were extracted from graphite flakes at 1200 °C. In consequence, concentration gradients of titanium atoms and carbon atoms were observed at the interface between titanium plate and grey cast iron (Fig. 6 a).

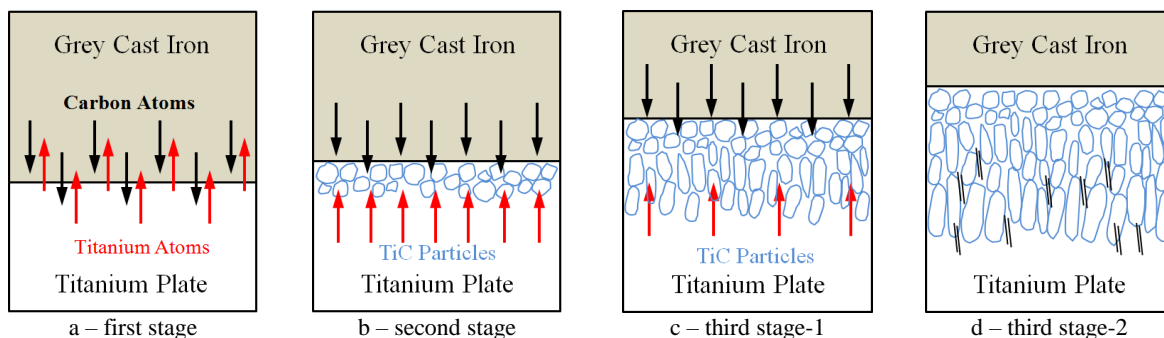


Fig. 6. Reaction process model of the TiC ceramic layer on grey cast iron

Second stage: Formation of small TiC particles. Carbon atoms in the grey cast iron were interstitial ones due to their small atomic radii and the diffusion rate was high. It diffused to the interface firstly, followed by reaction with titanium solid solution in ferrite as follow:



where Eq. 3 is the in situ reaction process, and Eq. 4 is the nucleation process of TiC. Due to the large quantity of nuclei formed, the reaction system was dominated by particle nucleation. Moreover, the growth of TiC grain was inhibited by the high atomic concentration of carbon. Therefore, the grain size of TiC at this stage was relatively small (Fig. 6 b).

Third stage: Formation of big size TiC particle and diffusion of TiC. After heat treatment at 1200 °C for 20 min, heat incubation temperature was reduced to 1160 °C, and the grey cast iron was in molten state. The diffusion rate decreased due to the formation of TiC reaction layer. Meanwhile, titanium plate and grey cast iron were segregated by the reaction layer, and the solid solution of titanium into the ferrite was interdicted. Concentrations of carbon and titanium atoms at the interface decreased drastically and the particle size of TiC increased because of the reduced inhibitory effect from carbon atomic concentration (Fig. 6 c). After heating halting, unreacted carbon atoms in the matrix transform to cementite, and microstructure of the matrix are pearlite and ferritic (Fig. 6 d).

In summary, the forming process of TiC layer can be simplified as “diffusion and in situ reaction”, including transportation of carbon atoms to the reaction sites by diffusion and synthesis of TiC by in situ reaction.

4. CONCLUSIONS

Using a novel in situ process, the synthesis of a TiC ceramic layer on grey cast iron can be facile. The synthesized TiC was irregularly shaped particles with a size of 1 ~ 8 μm and gradient distribution on the surface of grey cast iron. The thickness of the reaction layers increased gradually with the holding times. Also, it can be recognized that the layer thickness changed in a parabolic style with times. The formation process of TiC ceramic layer consists of diffusion and in situ reaction of carbon and titanium atoms.

Acknowledgments

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