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Microstructure and kinetics study on tantalum carbide coating produced on gray cast iron in situ

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ABSTRACT

Tantalum carbide (TaC) coatings were produced in this study on gray cast iron samples by a combination of casting and heat treatment at 1115–1155 °C. The microstructure and growth kinetics of TaC coatings were investigated. Scanning electron microscopy, transmission electron microscopy, and X-ray diffraction were conducted to analyze macrostructure and the thickness of layer, microstructure, and phase composition. Results show that TaC coating thickness ranges from 14.4 ± 1.59 to 354.3 ± 2.89 μm depending upon the treatment time and temperature. The presence of Ta, TaC, α-Fe, G (graphite), and Fe_3C phases on the iron matrix surface was detected. From the surface to the substrate, the TaC particles gradually increased from 100–300 nm to 1–2 μm at 1155 °C for different times. The kinetics of TaC coating in situ showed a parabolic relationship between carbide layer thickness and treatment time, and the activation energy for the process was 388.68 kJ/mol.

1. Introduction

Carbides of transition metals are promising ceramic materials, because these compounds exhibit unusual combinations of physical and chemical properties such as high hardness, high melting point, and good electrical and thermal conductivities [1]. Tantalum carbide (TaC) is a transition metal carbide of the VB group that has a NaCl type structure [1]. TaC has excellent physical and chemical properties, such as high melting point (3880 °C), excellent hardness and electrical conductivity, resistance to wear, chemical attack (only soluble in the mixture of nitric acid and hydrofluoric acid solution), and oxidation [2,3]. To date, this metal carbide has attracted more attention for its potential use as cutting tools, abrasive materials, large-scale or super large-scale integration, rocket nozzles, and scramjet components because of its excellent properties [4,5]. Xiong et al. [6] fabricated a new set of C/C composites in which the carbon fiber is reinforced by the tantalum carbide coating. The thickness of the TaC coating is only about 0.7 μm.

TaC has been synthesized in bulk by various methods. Teghil et al. [7] used femtosecond pulsed laser method to ablate a TaC target and to deposit thin films on silicon. Results show a nanostructure consisting of a large number of spherical particles, with a mean diameter of about 50 nm. And an ablation–deposition mechanism, related to the ejection of hot particles from the target, is proposed. Long et al. [8] used chemical vapor deposition in preparing TaC coatings on C/C composites. They found smooth and crack-free coatings produced at 1100 and 1200 °C, as well as at high microhardness. Other methods include spark plasma sintered [9,10], thin film solid-state reaction [11], chemical vapor infiltration [12], pressureless sintering [13], and casting–heat treatment reaction [14]. Meanwhile, in situ casting–heat treatment reaction technique possesses numerous advantages compared with other methods. This method is simple, cost effective, reliable, and can easily be controlled. In situ casting–heat treatment reaction technique can in situ synthesize reinforcement phase and has an excellent bonding strength between coating and substrate [14].

This study mainly aims to produce a thin layer of TaC on gray cast iron substrate via in situ casting–heat treatment technique and investigates the cross-section morphology and phase structure of the layer. The growth kinetics of carbide coating compounds obtained by casting–heat treatment process has not been studied yet. Considerable research has been carried out to investigate the mechanism of carbide coating formation, factors controlling growth rate, and influence of elements in the carbide coating. During carbide coating formation, the changes of growth rate constant K and diffusion activation energy Q are not clearly elucidated. Thus, the growth kinetics of TaC coatings produced by casting–heat treatment technique, which can predict and control coating formation, is calculated.

2. Experimental procedures

Gray cast iron (HT300), which consists wt% of 3.45 C, 0.56 Si, 0.268 Mn, 0.224 P, 0.024 S, and Fe as balance, was used as a substrate. Ta is

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the main chemical composition of a tantalum plate, and its mass fraction is 99.9%. The experimental processing procedure of the surface composites is described as follows. First, a tantalum plate was cut into 10 mm × 10 mm × 1 mm by a numerically controlled wire cut EDM machine (Suzhou Nutac Electro Mechanic Co. Ltd., China) and ultrasonically cleaned in ethyl alcohol for 10 min. Second, the tantalum plate was placed at the bottom of a graphite crucible, as shown in Fig. 1. Third, molten gray cast iron was produced in a medium-frequency induction furnace and poured into the graphite crucible at 1430 °C. The specimen was immediately covered with quartz sand to avoid crack generation and cooled to room temperature naturally. Finally, the specimen was removed from the graphite crucible, subjected to heat treatment at 1115–1155 °C for 5, 10, 20, and 30 min in a horizontal tube furnace with an argon gas flow rate of 5 ml/min, and cooled to room temperature by quenching in water.

The longitudinal section of the specimen was used further as a research object. The macrostructure of the specimens and the thickness of layer were examined using a scanning electron microscope (SEM, JSM-5800, JEOL, Japan). Meanwhile, the morphology and crystal structure of TaC particle were determined by a transmission electron microscope (TEM, JEM-3010, JEOL 2010, Japan) equipped with an energy-dispersive X-ray spectrometer (EDS). The X-ray diffraction (XRD) data were recorded on an X-ray diffractometer (PW 1730, Philips, Netherlands) with monochromated Cu K_α radiation at 40 kV and 40 mA within the 2θ range of 20°–90°. Before SEM analysis, one side of the prepared specimens was ground with emery paper, polished, and corroded with alcohol solution containing 4% of nitric acid (volume fraction). Thicknesses of TaC layer were determined from SEM micrographs on the basis of averages of measurements at 5 equally spaced locations, as illustrated in Fig. 2c. For each casting–heat treatment condition, such measurements were made and the averages and the standard deviations of these measurements were determined. The surface phases of specimen were directly detected by XRD.

3. Results and discussion

3.1. Organizational structure of TaC coatings

The average coating thicknesses and standard deviations for the TaC coating layers are given in Table 1 for different treatment temperatures and times. The typical microstructures of the cross-section of TaC-coated gray cast iron with different treatment times at 1155 °C are shown in Fig. 2. The coatings produced for 5 min (Fig. 2a) and 10 min (Fig. 2b) had 40.1 and 194.9 μm thicknesses, respectively. After heat treatment for 20 min (Fig. 2c) and 30 min (Fig. 2d), the thickness of the coating was more than 200 μm, which was much higher than those of the coatings produced for 5 and 10 min. Higher coating thickness is attributed to the higher reaction rate at longer time during the casting–heat treatment.

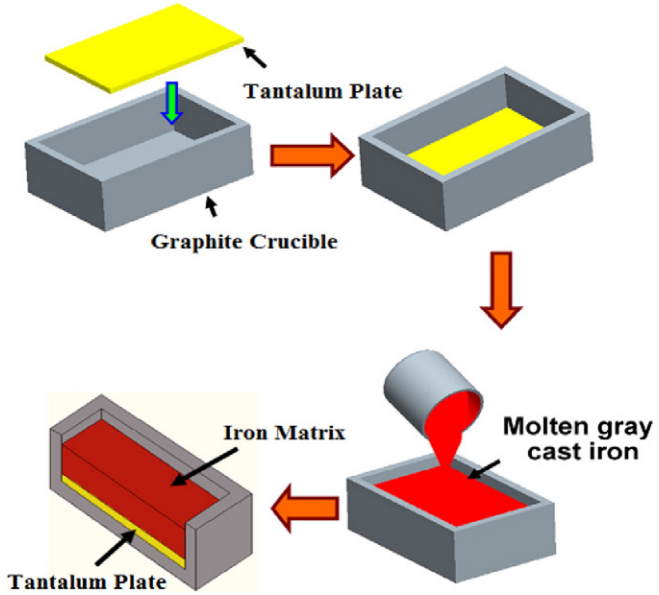

Fig. 1. Schematic illustration of experimental process.

Fig. 3 presents the XRD analysis of the casting–heat treatment reaction technique coating on the gray cast iron obtained at 1155 °C for different treatment times. The presence of graphite (G), Ta, TaC, Fe_3C, and α-Fe in the composition with 5–30 min heat treatment was detected. The tantalum diffraction peaks lowered and TaC diffraction peaks rose with increasing treatment time. Thus, the phenomenon confirms that most tantalum atoms are consumed by reacting with graphite in the matrix after treatment at 1155 °C for 30 min. TaC-dominated metal matrix composites can be obtained under the current conditions [24].

Fig. 4a and b shows the enlarged pictures of regions A and B, respectively. The grain size gradually increased from those near the top surface of the compound layer to the substrate. The particles were tightly closed together, and the reaction was uniform; the particle size was within 100–300 nm. The particles grew and into formed squares, with size within 1–3 μm can be seen in Fig. 4b. The increase of the grain size near substrate is probably induced by the poor tantalum atom supply to the reaction front because of the long diffusion distance of tantalum atoms and larger tantalum atomic size, resistance of formed coating to Ta and C atom diffusion, and consequently the low nucleation density, which may cause particle growth [23]. Due to small size and interstitial diffusion way of C atoms, the C atom diffusion rate was fast compared with Ta atom diffusion rate in TaC coating; therefore, Ta and C elements were found in large number near the Ta plate, and the nucleation rate was higher, consequently leading to small TaC particle size.

Fig. 5 shows the TEM micrographs, EDS, and the corresponding selected area diffraction (SAD) patterns of the TaC coating. The TaC coating consists of a large amount of nano-sized grains, which are in the order of tens of nanometers to hundreds of nanometers. Equiaxed grains with an average size of 200 nm are observed in the TaC coating. The EDS result exhibits that the equiaxed grains contain Fe, Ta, and C, and the SAD pattern (inserted image in Fig. 5) of these equiaxed grains is indexed to TaC.

3.2. Formation and mechanism of TaC coatings

Considering thermodynamic calculations, Zhong et al. [24] considered the possible reactions between Fe–C and Ta–C in this system. The reaction equations are as follows:

$$\mathrm{Ta(s)} + \mathrm{C(s)} = \mathrm{TaC(s)}\Delta G_1 = -142.250 - 4.3188T \quad (1)$$

$$2\mathrm{Ta(s)} + \mathrm{C(s)} = \mathrm{Ta_2C(s)}\Delta G_2 = -200.800 + 9.0602T \quad (2)$$

$$3\mathrm{Fe}(\gamma) + \mathrm{C(s)} = \mathrm{Fe_3C(s)}\Delta G_3 = -23.173 - 0.0188T(727 - 1727\ ^\circ\mathrm{C}). \quad (3)$$

The Gibbs free energies of TaC and Ta_2C were $\Delta G_1 = -6309.50 < 0$ and $\Delta G_2 = 12737.17 > 0$ at 1428 K, respectively. Therefore, Ta_2C did not meet the necessary thermodynamic conditions. The coatings could not find the Ta_2C phase.

In coating growth, four simultaneous processes occurred, namely, combined, diffusion, in situ reaction, and again-diffusion. Fig. 6 shows a schematic of an in situ reaction coating process on an iron matrix. After casting progressed and cooled to room temperature naturally, the tantalum plate and iron matrix exhibited bonding points (Fig. 6a). High temperature provides energy. The graphite carbon atoms move to the surface of the tantalum plate under heat treatment by diffusion, and a [TaC] forms on the surface [24]. When the [TaC] concentration