Ti–Zr coating on graphite through powder immersion reaction-assisted coating (PIRAC) and its oxidation kinetics at $T = 1000^{\circ}\text{C}$

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Abstract. Coating of graphite with a metal alloy Ti–Zr was carried out on a block of graphite sample; the sample was initially dipped in ZrO_2 containing a natural starch solution and then proceeded to powder immersion reaction-assisted coating (PIRAC) after drying. Ti powder containing 4 wt% iodine was used as depositing material, and the process was carried out at $850\text{--}950^{\circ}\text{C}$ for 10 h. The characterizations include X-ray diffraction, scanning electron microscopy and the hardness test. The coating thickness is proportional to the temperature of the PIRAC process, while the percentage of Zr is inversely proportional to the temperature of PIRAC treatment. All the characterizations revealed that the coated layer was a Ti–Zr alloy with hexagonal crystalline symmetry similar to α -Ti. An oxidation kinetic assessment at 1000°C of uncoated graphite shows a burn-off mechanism, while for a coated sample reveals a reaction of Ti with oxygen produces TiO_2 ; the reaction kinetics obey a diffusional mechanism.

Keywords. Coating; graphite; Ti–Zr alloy; oxidation; diffusional mechanism.

1. Introduction

Graphite has always been known as a heat-resistant, lightweight and highly thermal-conductive material. High-temperature application frequently involves graphite, especially in the core of nuclear reactors, such as neutron moderators and reflectors which slows down fast neutrons [1,2] and is used in high-temperature structural application, such as turbine components [3]. The main disadvantage of graphite is its low hardness (27–61 HV); furthermore, the nuclear grade graphite IG-110 is susceptible to oxidation at moderate temperature (600°C) [4].

Many researchers take a conceded effort to enhance the weak characteristics of graphite through coating. Several methods have been explored, a few of these are as follows: pyrolytic carbon coating [1], pack cement process $\text{SiC}\text{--}\text{ZrO}_2$ coating [3], rf bias sputtering [5], chemical vapour deposition [6,7], vacuum plasma spraying process [8] and powder immersion reaction-assisted coating (PIRAC) [9,10]. The PIRAC process has been known as a diffusional process due to the strong adhesion between the coated materials and substrate; otherwise, complex shapes can be coated by this process. Yin *et al* [9] reported that the PIRAC method was successfully employed for TiC coating at very low partial pressure, not exceeding 10^{-5} Pa of N_2 and O_2 , and was followed by the addition of iodine into titanium powder as depositing material. The coating process involves

Ti atoms transported onto the graphite surface through dispersion and/or the evaporation–condensation process; because then only it reacts with carbon, the coating layer grows through carbon diffusion towards the coating surface. Furthermore, Wati *et al* [11] also demonstrated that TiC coating on graphite can be successfully achieved under atmospheric pressure of flowing argon through this procedure.

Ti–Zr alloy is known as implant material [12]. In addition, it can possibly be used as the coating material for graphite due to its high-temperature melting point, good corrosion resistance and categorized as a hard material [13]. Therefore, considering the advantage of the Ti–Zr alloy to improve the properties of graphite, the objective of this study was coating of graphite with the Ti–Zr alloy using the PIRAC method followed by the examination of its characteristics as well as the oxidation kinetics at 1000°C .

2. Experimental

A block of graphite with a density of $\approx 2.2\text{ g cm}^{-3}$ was cut into dimensions of $1 \times 1 \times 0.5\text{ cm}^3$ and then used in the design of substrate. Titanium powder ($>98\%$ purity), ZrO_2 powder ($>99\%$ purity) and iodine ‘sublimated for analysis’ were used as raw materials for the deposition process. Two samples were prepared for deposition: sample A being graphite as is

and sample B being graphite-dipped in a mixture of 10 ml natural starch solution and 1-g ZrO_2 powder. Samples were dried before being loaded into the reactor capsule made of stainless-steel high chrome ($\approx 16\%$) and completely filled with titanium powder comprising 4 wt% of iodine mixtures. Next, the sample was immersed in iodized titanium powder and afterward the capsule was closed tightly. The loading process was carried out in a glove box under a flowing argon atmosphere. All PIRAC processes were conducted under a flowing argon atmosphere in a tubular furnace: samples A and B at 900°C for 30 min and sample B at $850\text{--}950^\circ\text{C}$ for 10 h.

The characterizations of the coated samples included X-ray diffraction (XRD) Philips X'Pert multi-purpose diffractometer using $\text{CuK}\alpha$ radiation. Data collected were analysed using (i) Match software for phase identification, (ii) Rietveld's refinement [14] for quantitative crystalline determination, (iii) scanning electron microscopy (SEM)/energy-dispersive X-ray (EDX) analysis for microstructure, (iv) element mapping by means of Carl Zeiss EVO MA10 and finally, Vickers micro-hardness Mitutoyo HM 211 for hardness. The oxidation test was carried out by quickly soaking the sample at 1000°C holding for 2 min under air and taking out of the furnace to cool down to room temperature. The mass was weighed before and after soaking, and this step was repeated up to 10 times.

3. Results and discussion

3.1 Mechanism of coating process

Figure 1 shows the XRD patterns of samples A and B that were subjected to PIRAC at 900°C for 30 min, which represent the early stage of coating reaction. It can be seen that sample A shows TiC pattern, while sample B shows a mixture of TiC and $\alpha\text{-Ti}$ type spectra. These data illustrate the mechanism of coating formation, sample A demonstrating the TiC layer formed by the reaction of Ti and C at the graphite surface at the initial moment, afterwards the carbon ion diffuses and passes through the TiC layer, it then reacts with titanium at the TiC–Ti interface. This conclusion was taken by considering that carbon, being a lighter element, is the more mobile ion than titanium. In sample B, amorphous carbon as a product of natural starch which was burnt out at the initial moment reacts with Ti similar to sample A, followed by a reaction occurring most likely at the TiC–Ti interface. After 30 min of holding time, the $\alpha\text{-Ti}$ type spectra were observed in the majority phase, than that of TiC in the minority phase, but no ZrO_2 peaks were detected. This signifies that the Ti deposition was faster than the TiC formation. The absence of ZrO_2 peaks in sample B should be considered during the PIRAC process under an ultra-high purity argon atmosphere; then, at a high temperature, the oxygen should leave ZrO_2 , creating an oxygen vacancy. Considering that the energy for oxygen vacancy formation is high i.e., $\approx 853.44 \text{ kJ mol}^{-1}$ when compared to 304 kJ mol^{-1} for Ti–Zr alloy formation [15,16], it is

Figure 1. XRD patterns of samples A and B for short dwell time (30 min) at 900°C .

reasonable to conclude that when oxygen vacates from ZrO_2 then the Ti–Zr alloy forms, the $\alpha\text{-Ti}$ type spectra presented in figure 1 correspond to the Ti–Zr alloy.

Figure 2 shows the XRD spectra of samples after the PIRAC treatment at different temperatures for 10 h of dwell time and Ti powder, as a reference, which was matched to $\alpha\text{-Ti}$. It can be seen that all coated layer spectra are similar to that of titanium powder spectra, and a similar crystalline symmetry to Ti powder (hexagonal closed packing—HCP) is used for analysis. However, the 900°C sample showed its highest peak for $2\theta \approx 63^\circ$, which was not the case for others; this phenomenon should be an effect of the preferred orientation of the $(\bar{1}20)$ reflection plane. It is important to note here that the position of XRD spectra peaks shifts, indicating that Zr dissolved in the Ti matrix of the coated layer to form the Ti–Zr alloy. The results of further analysis using Rietveld's refinement to quantitatively determine the lattice parameter and cell volume are presented in table 1. It shows that the cell volume is inversely proportional to the temperature of the PIRAC process, suggesting that the temperature of the PIRAC process has an effect on the Zr content in the coated layer.

In figure 3, the SEM observation on a cross-section of the coated layer of three different temperatures of the PIRAC process is presented. It can be seen that the thickness of the coated layer was formed proportionally to the temperature; therefore, a high-temperature process (950°C) resulted in a thicker layer, while a lower temperature process (850°C) resulted in a thinner layer. The percentage of Zr content in the Zr–Ti alloy could be estimated by measuring the coated layer thickness and assuming that Zr atoms are equally distributed in the Ti-coated layer matrix. The thinner coated layer with the higher Zr content is presented in table 2. Accordingly, this result confirms the earlier conclusion of XRD analysis regarding the Zr content that the coated layer thickened as the increasing temperature of the PIRAC process induced smaller Zr content in the coated layer, and, therefore, the cell volume of Ti–Zr

Figure 2. XRD pattern and phase identification for coatings of sample B for 10 h sintering.

becomes smaller due to the fact that the radius of Zr is larger than that of Ti (atomic numbers of Zr = 40 and Ti = 22). We assume that coated layer growth obeys the Arrhenius equation:

$$t = A \exp\left(\frac{-Q}{RT}\right), \quad (1)$$

where t is the coated layer thickness, A the constant, Q the activation energy, R the gas constant and T the temperature in Kelvin. Taking a plot of $\log t$ vs. $1/T$ (figure 4), one can deduce the activation energy as $Q = 22.3 \text{ kJ mol}^{-1}$.

Further detailed observation of the SEM image shows the existence of an interfacial layer between the graphite substrate and coated layer of Ti–Zr (figure 5, SE image, arrow), it seems that this layer has a different nature presented in the previous XRD discussion. In depth analysis was carried out

by EDX element mapping to determine the distribution of elements on the interfacial layer. It showed that red (C) and blue (Ti) colours are signposted by the interfacial layer, indicating that titanium compound TiC—supposed to be amorphous—present in the interfacial layer acts as a limiting layer for carbon diffusion towards the TiC–Ti reaction surface. As a consequence, Ti–Zr formation dominated the coating growth. Furthermore, EDX element mapping using $\text{CK}\alpha$, $\text{TiK}\alpha$ and $\text{ZrL}\alpha$ shows that the coated layer is dominated by a blue colour representing Ti. Moreover, purple dots can be seen spreading mainly on the coated layer, indicating Zr content. The purple dots are also seen in minor quantity on the graphite substrate. Based on this analysis, the Ti–Zr alloy is a typical coating compound, and this conclusion reinforces the XRD analysis given previously.

Besides XRD and SEM characterizations, hardness measurement was carried out to verify the mechanical properties of the coated layer. The measurement was accomplished in the 900°C sample using a mass load of 0.2 kg $\approx 1.96 \text{ N}$ force of indentation; this gave a hardness of 282 HV $\approx 2.766 \text{ GPa}$. Literature data [17] show that the hardness of Ti–10Zr = 266 HV increased up to Ti–40Zr = 350 HV. In this measurement, the indentation produces 5.89 μm indent depth. Considering that the layer thickness of the sample was 91 μm on an average, the measured hardness fits well among the characteristics of Ti–Zr.

3.2 Oxidation kinetics at 1000°C in air

The analysis described earlier, shows that the nature of the coated layer of sample B is similar to that of the Ti–Zr alloy; the following oxidation kinetics analysis is therefore, reasonably carried out in one of the prepared samples. Figure 6a shows the XRD pattern of the oxidized surface and figure 6b shows a cross-section of a back-scattered SEM image of sample B (950°C) after oxidation test has been completed. The

Table 1. Lattice parameter and cell volume for different temperature treatments determined through Rietveld's refinement.

Sample	Lattice parameter ($\text{\AA}$)		Cell volume ($\text{\AA}^3$)	Reliability factor
	$a = b$	c		
Ti powder	29,506 (4)	46,855 (6)	35,327 (7)	$R_p = 14.07$ $R_{wp} = 9.45$ $GOF = 0.05$
950°C	29,515 (1)	46,895 (4)	35,379 (3)	$R_p = 17.18$ $R_{wp} = 11.83$ $GOF = 0.07$
900°C	29,540 (4)	47,043 (2)	35,551 (2)	$R_p = 24.15$ $R_{wp} = 20.91$ $GOF = 0.03$
850°C	29,561 (2)	47,251 (3)	35,758 (4)	$R_p = 16.34$ $R_{wp} = 17.26$ $GOF = 0.01$

Figure 3. SEM micrographs of coated (cross-section) sample B: (a) 850, (b) 900 and (c) 950°C for 10 h sintering.

Table 2. Thickness of coated layer and Zr contents for different temperature treatments.

Temperature treatment (°C)	Coated layer thickness (μm)	Zr contents in coated layer (%)
850	81.6 ± 4.3	15 ± 0.8
900	91.2 ± 1.8	11 ± 0.2
950	129.8 ± 6.7	4 ± 0.2

Figure 4. Arrhenius plot of log of coated layer thickness against $1/T$.

phase identification by means of XRD shows that the pattern was appropriate to TiO_2 and there is no other phase pattern identified. Therefore, it would be correct to assume that in this layer, the oxidation reaction took place as shown below:

Figure 5. EDX element mapping for coated layer sample B (950°C).

Besides, the back-scattered SEM image shows different contrasting lamellae which are assumed to be oxidized layers for outer lamella and un-oxidized one for inner lamella. In equation (2), a sign of mass gain was given when Ti–Zr was oxidized. Therefore, the kinetics of oxidation can be elaborated.

Figure 6. Oxidation test for sample B (950°C) after completed 10×2 min soaking in air at 1000°C. (a) XRD pattern of coated layer surface matches to TiO_2 . (b) Back-scattered SEM image of coated cross-section surface.

Experimental data, figure 7a, show that for uncoated graphite, linear weight loss is detected as a result of burning of surface carbon to form CO_2 gas. In contrast, the coated graphite shows a non-linear mass gain, as is predicted by equation (2). Recalling the first Fick's law for oxygen diffusion:

$$J = -D \frac{dC}{dx}, \quad (3)$$

where J is the oxygen flux, D the oxygen diffusion coefficient and dC/dx the oxygen concentration gradient along dx . The oxygen flux J must be equal to the reaction rate, assuming that $dm = \rho A dx$ can then be deduced as a quadratic equation:

$$\frac{m^2}{K} + \frac{m}{L} - t = 0, \quad (4)$$

where $K = \frac{2DC_{\text{ox}}^0}{N} (\rho A)^2$ and $L = \frac{k_R C_{\text{ox}}^0 C_{\text{Ti}}^0}{N} (\rho A)$. Here, C_{ox}^0 is the oxygen concentration in the surface and C_{Ti}^0 is the titanium concentration at the reaction interface of Ti– TiO_2 . The solution for positive m can then be obtained as:

$$m = \left[\frac{K^2}{4L^2} + Kt \right]^{1/2} - \frac{K}{2L}, \quad (5)$$

Figure 7. Oxidation kinetics at 1000°C in air. (a) Plot of mass loss of uncoated graphite and mass gain of coated graphite sample B (950°C) against cumulative soaking time at 1000°C in air. (b) Replot of mass gain sample B (950°C) showed in (a) against the square root of soaking time $t^{1/2}$.

and finally, for long oxidation process (equation (5)), then becomes

$$m \approx (Kt)^{1/2} + C, \quad (6)$$

where C is a constant. Figure 7b shows the plot of mass gain against the square root of cumulative oxygenation soaking time $t^{1/2}$, the data are appropriate to equation (6) as $m = 0.7604t^{1/2} + 0.8154$. This means that oxidation mechanism obeys diffusion mechanism.

4. Conclusion

The metal alloy Ti–Zr was successfully coated on graphite by the PIRAC process of Ti powder containing 4 wt% iodine under an ultrahigh purity argon atmosphere. XRD, SEM and hardness examination gave evidence to verify that the coated

layer exhibits the hexagonal crystalline symmetry of the α -Ti type structure. Coated layer thickness is proportional to the temperature of the PIRAC process; however, Zr percentage in the coated layer is inversely proportional to the temperature *via* coated layer thickness. An oxidation kinetic test in air at 1000°C showed that an uncoated sample lost its mass due to a burns-off mechanism, while a coated sample showed the diffusional mechanism of oxidation producing TiO₂ on the Ti–Zr alloy.

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