Characterization of TiC and α-Ti coating on graphite prepared by Powder Immersion Reaction Assisted Coating (PIRAC) Oxidized at 1000ºC in Air

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Abstract. Study of the formation of TiC and α-Ti coating on graphite has been successfully carried out by means PIRAC method. Graphite blocks were immersed into a mixed of titanium powder containing 4 wt% iodine and then proceed at 1000ºC for 10 hours in argon atmosphere. Two different treatment of graphite blocks were carried out; with and without dispersion ZrO_2 in the graphite surface before heat treatment. Characterizations of coated surface were include X-ray diffraction for phase and crystalline analysis, SEM and EDX analysis to determine the topography and distribution of elements in coated film. For sample without ZrO_2, as a result of interaction between titanium and graphite, carbon diffusion occurred and TiC coated film were formed. Whereas sample with the dispersant of ZrO_2 on the graphite surface caused diffusion of carbon into the titanium did not occur, as a result α-Ti were formed. Oxidation test at 1000ºC in air showed that TiC and α-Ti coated film underwent oxidation. In both cases TiO_2 was observed as a results of oxidation.

1. Introduction

Graphite material perform very good heat resistance, up to 3700ºC before sublimate. The heat resistant properties (refractory) of graphite compatible to high temperature application such as for nuclear reactors and materials for rocket nozzle. However graphite is susceptible to oxidation at moderate temperatures (> 400ºC) in an environment containing oxygen or chlorine [1], and highly erodible (hardness 1-2 mho). Therefore, to reduce erosion aspect of graphite, coating process is necessity using a refractory material and resistance to scratches.

Refractory materials that may be used as a coating for graphite are B_4C, SiC, WC, TiC or ZrC. Methods of coating formation could be carried out through CVD (Chemical Vapor Deposition) [2], magnetron sputtering [3], evaporation [4] and PIRAC (Powder Immersion Reaction Assisted Coating) [5], [6]. There are disadvantages of such methods in particularly CVD performed a weak adhesion between the substrate and the coating [6]. The PIRAC methods with a diffusional process so that the substrate and the coating would have strong adhesion.

It has been reported that the PIRAC method was successfully carried out for TiC coating in a vacuum process with the addition of iodine into titanium powder [6]. Mechanism of diffusional process of TiC coating on the surface of graphite should be in two steps, first the metal was transferred from the powder onto the surface and react with carbon to form TiC, after that the coating growth governed by the diffusion of carbon towards the coating surface.

The vacuum processes for coating at high temperature is complicated process, to reduce this complication therefore the process should be carried out in inert gas atmosphere. It was reported that the formation of TiC coating optimally formed when processed in an argon atmosphere [7].

In this reports, PIRAC methods will be explored for graphite coatings, two treatments has been carried out; first, graphite immersed in a blended iodine and Ti powder, and secondly the surface of graphite was spreaded by ZrO_2 powder using starch binder to modify the nature of coating layer. Furthermore, the oxidation test at 1000ºC in the air on two coated samples will be reported.

2. Experimental

Graphite having density 2.09 to 2.23 g/cm^3 was shaped to form block (1x1x0.5 cm). Coating raw materials were metallic titanium powder >98% and iodine 'sublimated for analysis' were supplied by E. Merck. One part of sample was spreaded by powder ZrO_2 (Zirconium Oxide Purum Sigma-Aldrich GmbH-D30926) using starch solution. Both, were processed in a reactor tube made by 316 Stainless Steel in argon of 99.999% purity.

PIRAC process was carried out by immersing graphite into a mixture of titanium containing 4% iodine powder in the stainless steel reactor tube. Two different treatments were carried out; with and without dispersion ZrO_2 in the graphite surface before heat treatment. Sample without dispersion of ZrO_2 named sample A and sample with dispersion ZrO_2 named sample B. The process was carried out in argon atmosphere. The heat treatment in the tube-furnace were conducted at 950°C by holding time 10 hours. Oxidation test at 1000ºC in air on two coated samples for 20 minutes.

Characterizations of coated surface and after oxidation test were include X-ray diffraction of CuKα radiation for phase and crystalline analysis, SEM and EDX analysis using EVO MA 10 Carl Zeiss Microscopy to determine the topography and distribution of elements in coated film.

3. Results and Discussions

3.1. Coating Formation

Figure 1 shows X-ray diffraction of coating formation. The only phase detected in sample A was TiC while α-Ti in sample B. TiC coating formation occurs involve Ti ion transport to reach the surface of graphite substrate. It was believe that Ti ion transport includes iodine reaction with Ti powder (TiI_4) before reaction with carbon to form TiC [6].

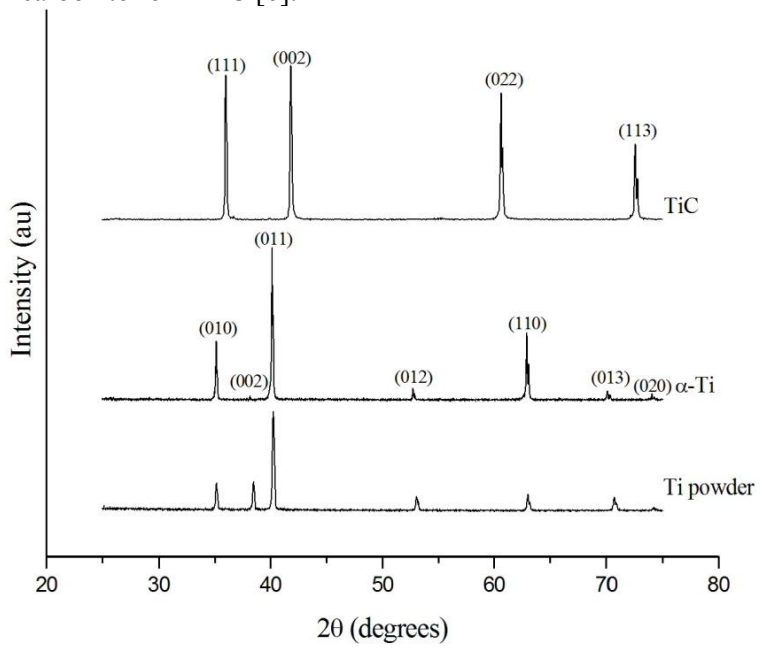


Figure 1. X-ray diffraction pattern and phase identification for coatings were formed.

For sample B, XRD pattern of coated layer compared to the initial Ti powder show equal pattern, except (002) reflection which was low intensity for coated layer. The possible cause for this mediocre intensity was vacancies of Ti ion due to Zr^{4+} dissolve in the lattice structure of titanium. The indication of Zr^{4+} dissolve in titanium was peak shift to smaller diffraction angle [8]. Rietveld refinement (Figure 2) was carried out for deeper analysis. The results of Rietveld refinement depicted in Table 1. It shows that bigger cell volume for Ti coated layer compared to Ti powder.

Table 1. Result of Rietveld refinement Ti powder and Ti coating.

Titanium	Lattice Parameters		Cell Volume	Figure of Merit	
	a=b (Å)	c (Å)		χ^2	R bragg factor
Powder	2.9510 (2)	4.6860 (3)	35.3425 (41)	1.37	0.04
Coating	2.9575(1)	4.7320(2)	35.8449 (27)	1.55	0.11

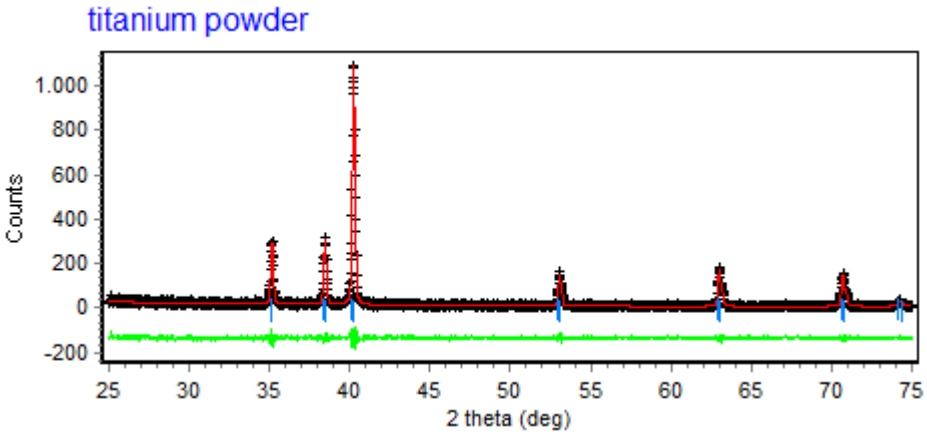
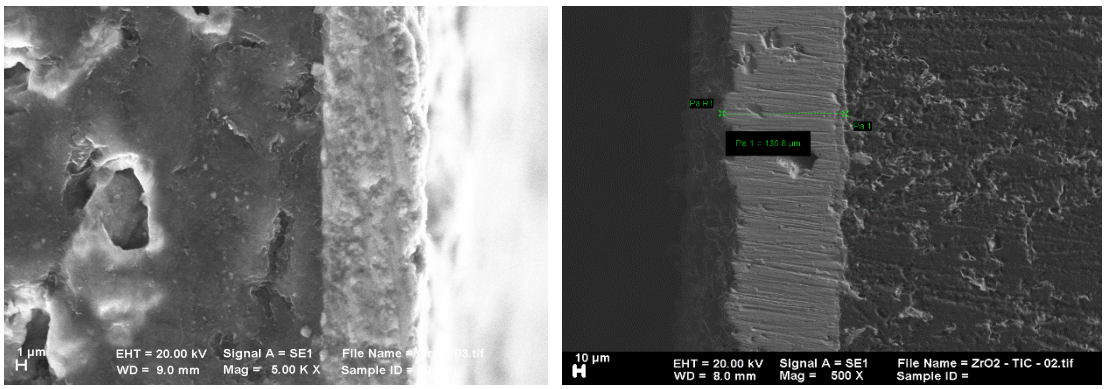


Figure 2. Rietveld refinement analysis for Ti powder.



(a.) (b.)

Figure 3. SEM image of coating: (a.) TiC (sample A), (b.) α-Ti (sample B).

SEM images (Figure 3) show that the thickness of coated layers are different, α-Ti layer (Sample B) growth faster then TiC layer (Sample A). The thickness of TiC layer is ~10 μm whereas α-Ti layer is ~100μm. SEM observation for sample B using magnification (Figure 4) and EDX analysis indicate that there is a thin layer between graphite and α-Ti layer (arrowed), while sample A did not. The formation of α-Ti layer should be thought follows, in this phase thin layer should blocked the carbon diffusion to reach Ti layer. This carbon diffusion mechanisme decelerate the formation of TiC layer. By contras for sample B, the coating layer growth rapidly compared to the sample A, because of unnecessary reaction involves carbon diffusion in the layer formation. EDX element mapping (Figure 5) shows that titanium difuse to the graphite porosity and yellow thin layer between Ti and carbon layer indicate blocking layer for carbon diffusion as mentioned in previous paragraph.

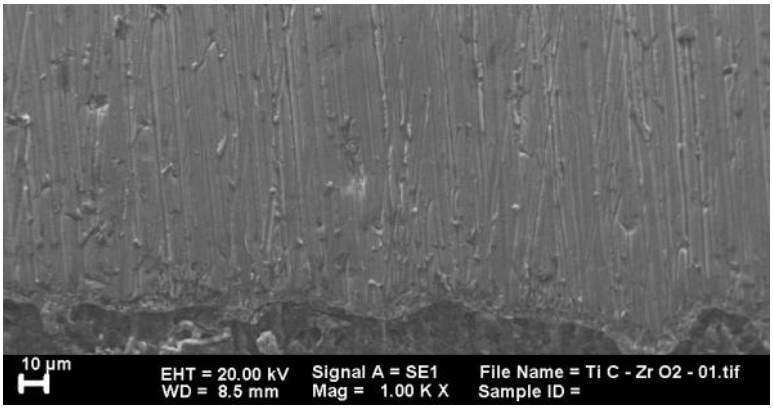


Figure 4. SEM of α-Ti coating with magnification: 1000×.

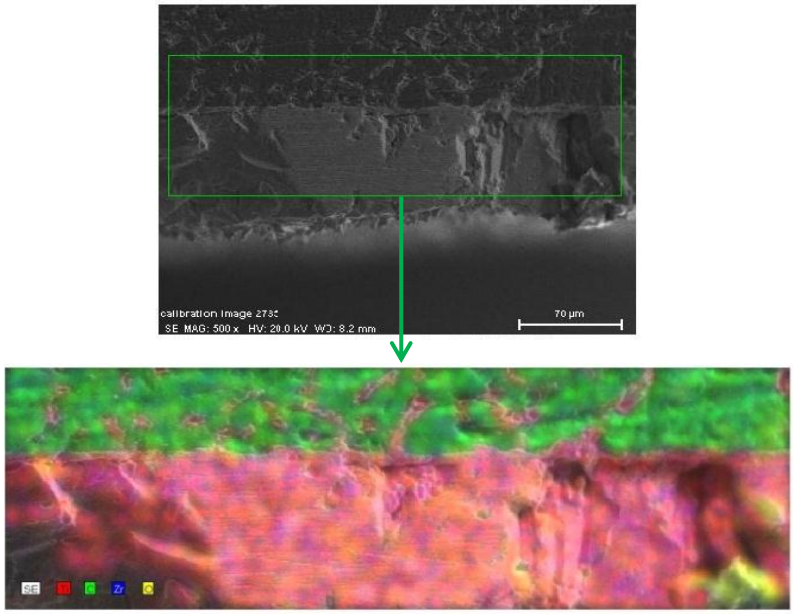


Figure 5. EDX element mapping for α-Ti layer.

3.2. Oxidation Test

Oxidation test at 1000ºC in air shows that TiC and α-Ti coated film underwent oxidation for 20 minutes. X-ray diffraction pattern and phase identification for both samples were TiO_2 (Figure 6). The reaction that may occur for TiC coating is

$$TiC_{(s)} + 2O_{2(g)} \rightarrow TiO_{2(s)} + CO_{2(g)}$$

Whereas for α-Ti coating, the reaction of Ti with oxygen that may occur is

$$Ti_{(s)} + O_{2(g)} \rightarrow TiO_{2(s)}.$$

Figure 6 shows peak shift between TiO_2 from sample A (TiC) and sample B (α-Ti). Based on Rietveld refinement analysis are shown in Table 2. TiO_2 from sample A has larger lattice parameter than sample B. Supposedly sample A, titanium release carbon ion and react with O_2 to form CO_2, then O_2 reacts with titanium to form TiO_2.

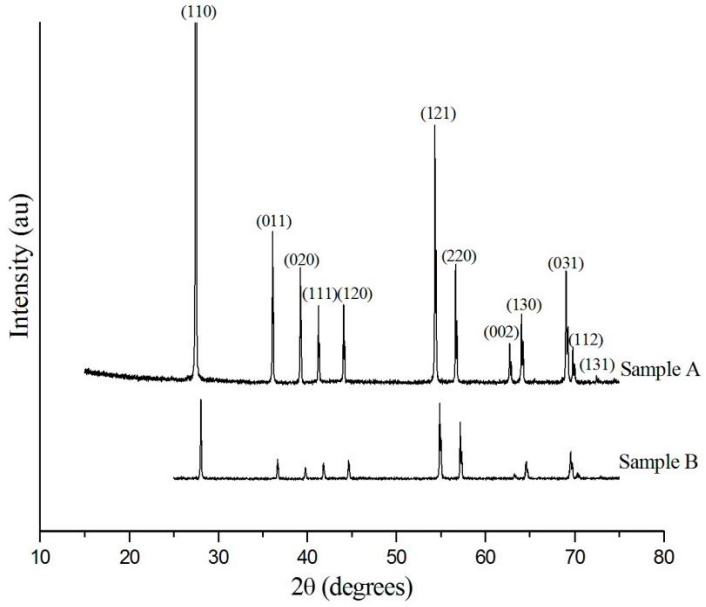


Figure 6. X-ray diffraction pattern of coated layer for sample A and sample B.

Table 2. Result of Rietveld refinement of coated layer for sample A and sample B.

Sample	Lattice Parameters		Cell Volume	Figure of Merit	
	a=b (Å)	c (Å)		χ^2	R bragg factor
A	4.5914 (1)	2.9589 (1)	62.3778 (32)	1.00	0.11
B	4.5884 (2)	2.9566 (2)	62.2478 (47)	1.54	0.04

4. Conclusions

It has been shown that coating layer TiC and Ti could be grown onto the surface of graphite by PIRAC method. As a result of interaction between titanium and graphite, carbon diffusion occurred and TiC coated film were formed. Whereas graphite with the dispersant of ZrO_2 on surface was α-Ti. The existence of thin layer between substrate and coated layer causes the diffusion of carbon into the titanium did not occur. Furthermore, oxidation test at 1000ºC in air for 20 minutes showed that TiC and α-Ti coated film underwent oxidation. As a result of oxidation, in both cases TiO_2 was observed.

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