ON THE REACTIONS IN ILMENITE, ALUMINUM AND GRAPHITE SYSTEM

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Abstract: *Al2O3/TiC composites are used as cutting tools for machining gray cast iron and steels. The addition of iron improves the toughness of Al2O3/TiC composites. Ilmenite, aluminum and graphite can be used to produce in-situ Al2O3/TiC–Fe composites. However, the formation mechanism and reaction sequences of this system are not clear enough. Therefore, the present research is designed to determine the reactions mechanism of the first step of reactions that may be occurred between raw materials.*
In this research, pure ilmenite was synthesized to eliminate the effects of impurities available in the natural ilmenite in the system. The milled and pressed samples, prepared from the synthesized ilmenite, aluminum and graphite mixture with a molar ratio of 1:2:1, were heat treated at 720°C for 48h. In addition, two samples one containing ilmenite and aluminum with a molar ratio of 1:2 and ilmenite and graphite with a molar ratio of 1:1 were heat treated at 720°C for 48h. The final products were analyzed with XRD. It was found that at 720°C, aluminum reacts with FeTiO3, forming Fe, TiO2 and Al2O3. Since the aluminum content used in the mixture was more than the stoichiometry for reaction of ilmenite and aluminum, some unreacted aluminum remains. Therefore, the residual aluminum reacts with the reduced Fe to form Fe2Al5.

Keywords: *Ilmenite, Aluminum and Graphite, First step mechanism*

1. INTRODUCTION

Lately, the interest in the use of Al2O3/TiC composites [1] as cutting tools for machining of gray cast iron and steels is growing due to the reason that they can machine with high cutting speeds and produce a good surface finish [2]. Composites with a Al_2O_3 matrix containing dispersed titanium carbide is mainly used and it is expected to be used more widely compared to pure Al2O3, as its toughness is increased by the addition of TiC [3]. Nevertheless, low toughness is their major deficiency. Addition of ductile metal such as Fe can improve the tensile stress and toughness of the final composites [4-7].

These composites can be produced by a number of methods, among them, the combustion synthesis method requires the least energy [8]. Moreover, ilmenite is a cheap mineral consisting of Iron and titanium. Furthermore, in-situ growth of TiC can greatly reduce the cost and environment pollution [3]. Therefore, the advantage of this project is to use cheap ilmenite as raw material for the in-situ synthesis of Fe-TiC/Al_2O_3 to simultaneously obtain a combination of the all mentioned benefits.

Based on equation 1, Fe, TiC and Al_2O_3 are produced in the form of a composite material by reaction between FeTiO3, Al and C:

$$FeTiO_3 + 2Al + C = Fe + TiC + Al_2O_3 \quad (Tad=2472.7°C) \qquad (1)$$

Fortunately, the adiabatic temperature of this system is higher than the Merzhanov index (Tad > 1800 K), therefore this system undergoes a self propagating high temperature synthesis reaction (SHS) [8].

Few research [9-13] have been performed using ilmenite as a raw material, for the synthesis of Al2O3-TiC/Fe composites. Tang et al [13] presented a relatively comprehensive research on this system, but there are some vague and contradictory notes on the work such as wrong identification of the present compound according the XRD analysis and therefore an incorrect proposed mechanism based on the wrong discussion. Zou et al [9-11] have investigated on

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the effect of some factors such as the graphite source, additives such as Mo and Cr and the preheating time on the FeTiO3-Al-C system. They have also proposed a mechanism based on the TiO_2-Al-C system. Accordingly, at first the ilmenite was reduced to different valent of titanium oxides and iron by molten aluminum, including TiO_2, Ti_3O_5, Ti_2O_3 and a number of Ti_xO_y phases. When the Ti/O ratio in the Ti-Al-O system comes to equilibrium and the residual aluminum combines with α-Fe, a Fe-Al solid solution is formed. However at this stage there is not anymore free aluminum to deoxidize the Ti_xO_y's, therefore, low valent titanium oxides react with C, and as a result TiC phase is formed. However Zou et al [9-11] did not mention the effect of the released Fe in the mechanism. Furthermore all of their claims were based on the final product and the intermediate steps, were not explicit to clarify the sequence of the reactions. Zargaran determined the effect of temperature, heating rate, pressure and the various molar ratios of $FeTiO_3$:Al:C on the formation of TiC. He proposed the optimum condition to produce the TiC. However the reaction mechanism was not determined. In another investigation [14-18], the conversion of TiO_2 to TiC has been considered [19, 20]. Also, there is no agreement on the type and the conversion steps of these titania sub oxides.

The aim of this paper is to determine the mechanism of the first step of reactions occurring between ilmenite, aluminum and graphite. In the presented research by others [21-23], the ilmenite concentrate was used. Since the ilmenite concentrate consists of several impurities, and the effects of these impurities on the reactions are not clear, they may possibly change the reaction mechanisms. Furthermore Fe2+ and Fe3+ coexist in ilmenite concentrate, while in the synthesized ilmenite only Fe2+ is present. Therefore, to avoid confusion, pure ilmenite was synthesized and used in this study.

In this research, the milled and pressed samples, prepared from the synthesized ilmenite, aluminum and graphite mixture with a molar ratio of 1:2:1 (according to stoichiometery of equation 1), were heat treated at 720 °C for 48h. In addition, two samples one containing ilmenite and aluminum with a molar ratio of 1:2 and the other containing ilmenite and graphite with a molar ratio of 1:1 were heat treated at 720 °C for 48h to compare the result of ilmenite-aluminum sample and ilmenite-graphite sample with the result of ilmenite-aluminum-graphite sample. The final products were analyzed with XRD. It was found that at 720 °C (the first step of reactions in the ilmenite-aluminum and graphite system), aluminum reacts with $FeTiO_3$, forming Fe, TiO_2 and Al_2O_3. Then because of this fact that the aluminum content at the begging raw materials is more than needed for reaction of

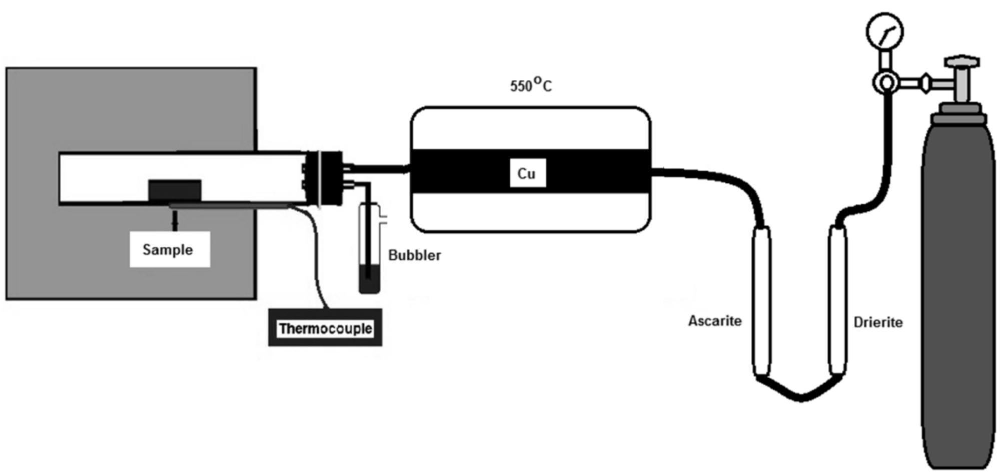

Fig. 1. The setup used for heat treatment of samples

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ilmenite and aluminum, some of the aluminum remains. Therefore the residual aluminum may react with the produced Fe and Fe_2Al_5 forms.

2. EXPERIMENTAL PROCEDURE

Ilmenite was synthesized as follows: 20 grams of the mixed powder with stoichiometric ratio of Fe, Fe_2O_3 and TiO_2 equal to 1:1:3 was pressed and heat treated for 48 h at 1100 °C under an inert argon atmosphere.

The prepared ilmenite powder was sieved (170 mesh) and mixed with aluminum (99.5%, <45μm) and graphite powder with a molar ratio of 1:2:1. Also, a powder mixture of aluminum and ilmenite with a molar ratio of 1:2 and a powder mixture of graphite and ilmenite with a molar ratio of 1:1 were prepared. Each powder mixture was milled for 10 min using a BPR (Ball Powder Ratio) of 5:1 at 400 rpm in a fast mill.

The mixed and milled powder systems were pressed in a mold under 500 Psi to obtain pellets with a diameter of 1 cm and 5 mm height. The pellets were finally heat treated at 720 °C for 48 h. To prevent the oxidation of the products, heat treatment was done under argon atmosphere. The used setup is shown in figure 1. Argon gas was passed through heated pure Cu wool at 550 °C to eliminate any O_2 present in the argon gas. Ascarite and Drierite were also used to eliminate the CO_2 and H_2O present in the argon gas as impurities, respectively.

XRD technique was used for the phase analysis of the products using a PHILIPS model PW 1800 machine with CuKα radiation (λ = 1.54 Å) under a voltage and current of 40 kV and 30 mA, respectively.

3. RESULTS AND DISCUSSIONS

As was mentioned before, three samples, namely, ilmenite-aluminum-graphite, ilmenite-aluminum and ilmenite-graphite were investigated which their results will be discussed here.

According to figure 2, the XRD pattern of the sample of ilmenite-aluminum-graphite with a molar ratio of 1:2:1, heat treated at 720 °C for 48 hours shows that Fe, Al_2O_3, TiO_2, Fe_2Al_5 and remained graphite are detected in the final product of reactions.

The XRD pattern of the sample of ilmenite-aluminum with the molar ratio of 1:2, heat treated at 720°C for 48 hours was shown in figure 3. It shows that Fe, Al2O3, TiO_2 and Fe2Al5 are the final product of the reaction of raw material at this temperature. These compounds are similar to final product of the sample of ilmenite-aluminum-graphite with the molar ratio of 1:2:1, heat treated at 720 °C for 48 hours.

In figure 4, The XRD pattern of the sample of ilmenite-graphite with the molar ratio of 1:1, heat treated at 720 °C for 48 hours was shown. As can be seen there is very few amount of Fe and TiO_2 as the reaction products between raw materials, but there are lots of remained $FeTiO_3$ in the

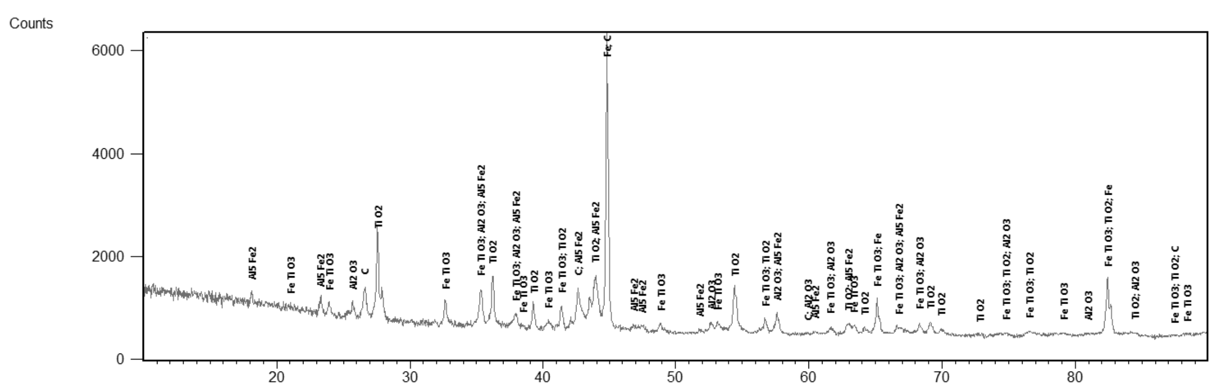

Fig. 2. The XRD pattern of the milled and pressed sample with an ilmenite, aluminum and graphite ratio of 1:2:1 heat treated for 48h at 720 °C

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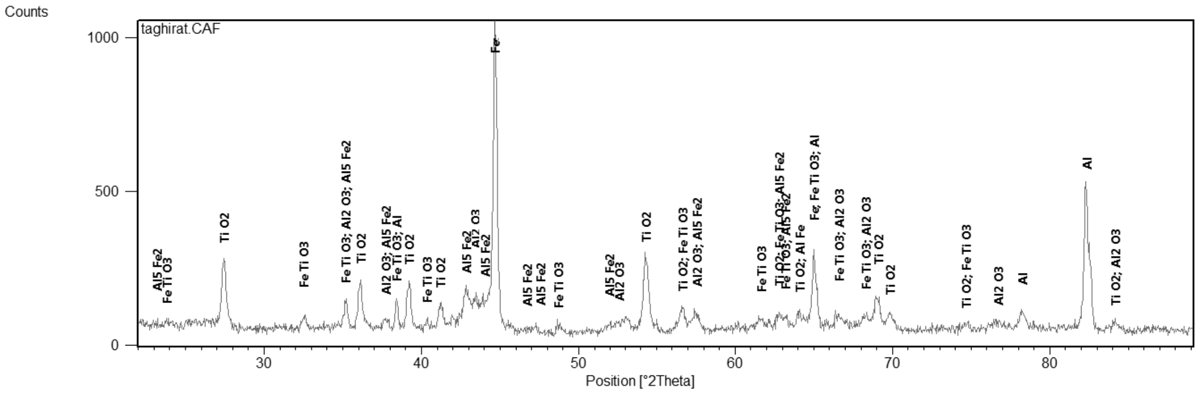

Fig. 3. The XRD pattern of the milled and pressed sample with an ilmenite: aluminum ratio of 1:2 heat treated for 48h at 720 °C.

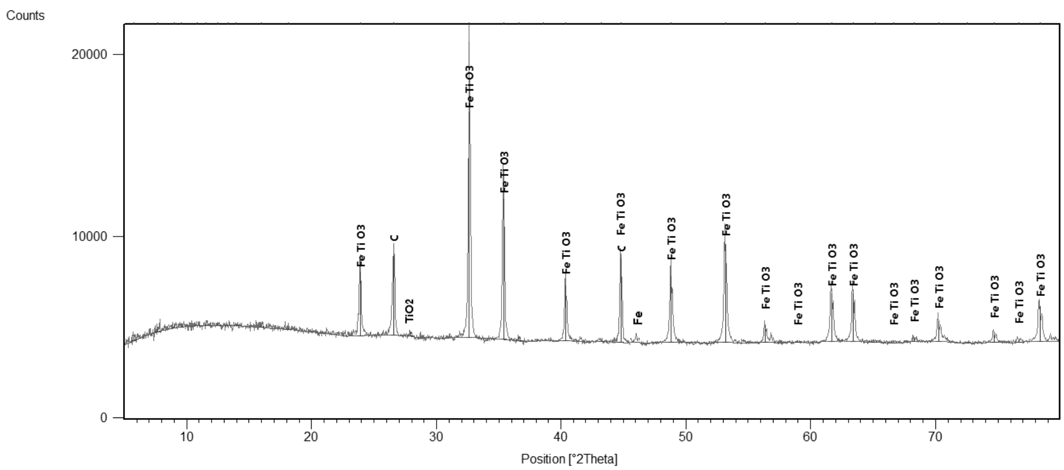

Fig. 4. The XRD pattern of the milled and pressed sample with an ilmenite: graphite ratio of 1:1 heat treated for 48 h at 720°C.

sample. Based on the XRD result, it seems that the reaction between ilmenite and graphite at this temperature is negligible.

The similarity in the XRD pattern of ilmenite-aluminum-graphite and ilmenite-aluminum samples confirms that despite the presence of graphite in ilmenite-aluminum-graphite system, ilmenite reacts with aluminum after melting of aluminum. The existence of Al_2O_3 in the ilmenite-aluminum-graphite system sample heat treated for 48h at 720 °C, clarify that Al reacts with ilmenite which contains oxygen and Al_2O_3 is formed. In addition graphite in this sample remained unreacted up to 48 hours heat treatment at 720 °C. It shows that graphite doesn't react with the either ilmenite or aluminum, so it remained unchanged.

4. THERMODYNAMIC ANALYSIS

To understand the possible reactions in this system, the HSC software was used [24]. As can be seen in figure 5, the reaction of $FeTiO_3$ and Al has the least standard Gibb's free energy; thereupon this reaction can be occurred easier than the others. Therefore, at the first step of ilmenite, aluminum and graphite system reactions, ilmenite reacts with aluminum and Fe,

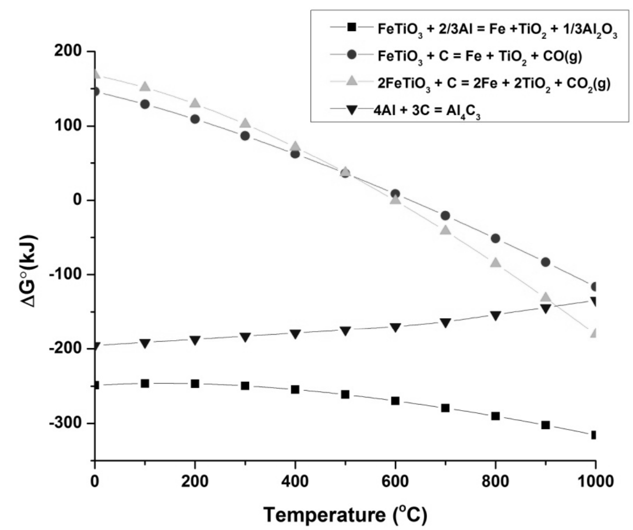

Fig. 5. The standard Gibb's free energy of reactions may occur between materials used in the mixture calculated with HSC software

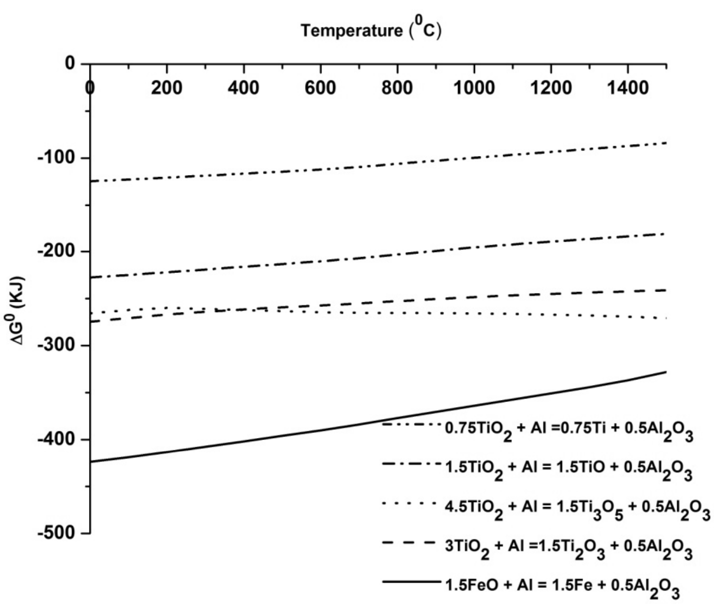

Fig. 6. The standard Gibb's free energy of FeO and TiO_2 by Al calculated with HSC software

TiO_2 and Al_2O_3 form. The amount of aluminum required to react with ilmenite is 2/3 of ilmenite molar ratio. The amount of aluminum used in raw materials is more than this ratio; therefore, after reaction of ilmente with the aluminum, some unreacted aluminum remains. This aluminum may react with Fe (the production of ilmenite and aluminum reactions) and Fe_2Al_5 forms.

As was discussed earlier, it was shown that the FeO was reduced to Fe but the TiO_2 remained unchanged. To address this result, Figure 6 could be useful. As can be seen in Figure 6, the reaction of FeO and aluminum has the least Gibb's free energy; therefore, FeO can be reduced easily by aluminum while TiO_2 remains unchanged.

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5. CONCLUSION

As a conclusion, the first mechanism step of reactions in the ilmenite, aluminum and graphite system to produce Al_2O_3/TiC-Fe composites were discussed. It seems that the first reaction may occur in this system after the melting of aluminum. At this step ilmenite reacts with aluminum to form Fe, TiO_2 and Al_2O_3. Because the aluminum content at the begging raw materials is more than needed for reaction of ilmenite and aluminum, some of the aluminum remains. The residual aluminum may react with the produced Fe and Fe_2Al_5 forms.

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