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The Effect of Raw Material Ratio on the Formation Mechanism of Fe-TiC/Al_2O_3 Composite

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A B S T R A C T

Ilmenite, aluminum and graphite have been used to produce in-situ Al_2O_3/TiC–Fe composites. Al_2O_3/TiC-Fe composites are used as cutting tools for machining gray cast iron and steels. Very few publications can be found in the literature discussing the effect of aluminum and graphite molar ratio on the formation mechanism of Al_2O_3/TiC–Fe composites. Therefore, the present research is an effort to make this issue clear. To achieve this goal, in this research, at first, the mechanism of the Fe-TiC/Al_2O_3 composite formation from ilmenite, aluminum and graphite mixture with a molar ratio of 1:2:1 was clarified. Then the samples with different molar ratios of aluminum and graphite were prepared. Since interpreting the results of the system in which the molar ratios of aluminum and graphite have been changed simultaneously, was complicated, both of the aluminum and graphite new ratios were changed separately in this work. The samples were heat treated at 1300°C to make sure that all reactions are done. The final products were analyzed with XRD and SEM. It was found that the optimum molar ratio of ilmenite, aluminum and graphite mixture is 1:2:1 because undesired compounds were not detected in the products. Compared with the ratio of 1:2:1, increasing the aluminum content of the raw materials caused the $TiAl_3$ formation while insufficient aluminum did not allow the reactions to be completed. It was also found that using more graphite content, leads to the formation of Fe-C compounds while less graphite will result in uncompleted reaction.

1. INTRODUCTION

Recently, Al_2O_3/TiC–Fe composites have gained high importance as cutting tools [1]. Various methods can be used to produce these composites. Among which, the sintering of the ilmenite, aluminum and graphite mixture is economic because ilmenite is a cheap mineral consisting of iron and titanium. Furthermore, the temperature of the final produced products is lower compared with the other sintering methods [2-8].

Some researchers have investigated the formation mechanism of Al_2O_3/TiC–Fe composites. Zou et al. [9-11] proposed a mechanism based on the TiO_2-Al-C system. Tang et al. [2] investigated the foresaid system from 600 to 1400ºC, but the final product involves $MgAl_2O_4$ which could change the composite performance. To prevent such impurities, Khoshhal et al. [3] have used synthesized ilmenite instead of ilmenite concentrate to pursue the right trend of the reactions.

Tang et al. [2] also studied the effect of Al/C ratio on the reaction products. Since the Al/C ratio has changed simultaneously, interpreting the results was complicated. Thus, the aim of this study is the separate determination of the effect of aluminum and graphite molar ratio, and also the determination of the optimal ratio of the raw material stoichiometry.

To achieve this, some mixtures of $FeTiO_3$, Al and graphite powders with molar ratios of 1:2:0, 1:2:0.5, 1:2:1, 1:2:1.5, 1:0:1, 1:1:1 and 1:3:1 were prepared. The finally mixed and pressed samples were heat treated at 1300°C to obtain final products.

2. MATERIALS AND METHOD

Ilmenite was synthesized as stated in our previous publication to prevent the formation of undesirable products [3]. Synthesized ilmenite powder was sieved (170 mesh) and mixed with aluminum (Merck, 99.5 %,< 45µm) and graphite (Merck, 99.7%) powder with molar ratios of 1:2:0, 1:2:0.5, 1:2:1, 1:2:1.5, 1:0:1, 1:1:1, and 1:3:1.

The 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 was pressed in a mold under 3.44×10^6 Pa to obtain pellets of 1 cm in diameter and 5 mm in height. At the first step to clarify the mechanism

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of the system for the molar ratio of 1:2:1 (ilmenite: aluminum: graphite), the samples were heated at critical temperatures (according to the DTA analysis results in the previous study [3]) of 600, 720, 930 and 1070ºC.
The temperature where lower time is needed for the reactions to be completed was determined as 1300ºC. Finally, different molar ratios of ilmenite, aluminum and graphite samples were heat treated at 1300ºC to clarify the effect of changing the ratios of aluminum or graphite on the reaction mechanism.
To prevent the oxidation of the products, heat treatment was done under argon atmosphere. To do so, an induction furnace has been used as shown in Fig. 1. In addition to the furnace thermocouple, another thermocouple was used which was located near the samples to show the exact temperature.
XRD technique was used for the phase analysis of the products using a PHILIPS model PW 1800 machine with Cu-Kα radiation (λ = 1·54 Å) under a voltage and current of 40 kV and 30 mA, respectively.

Figure 1. The induction furnace used in this study.

3. RESULT AND DISCUSSION

As described in the experimental section, for the first step, the mechanism of the reactions in the ratio of 1:2:1 (ilmenite: aluminum: graphite) system was determined. This ratio has been chosen according to the following reaction in which the Al_2O_3/TiC–Fe composites could be produced.

$$FeTiO_3 + 2Al + C = Fe + TiC + Al_2O_3 \quad (1)$$

To achieve this goal, temperatures of 600, 720, 930 and 1070ºC were used as the critical temperatures at which the reactions get started (according to the DTA analysis (previous work[3])). The XRD results of the samples with the ratio of 1:2:1 (ilmenite: aluminum: graphite) heat treated for 48h at 600, 700, 930 and 1070ºC are shown in Fig. 2. As can be seen, at 600°C, new compounds were not detected. At 720°C, ilmenite reacts with aluminum and Fe leading to formation of TiO_2 and Al_2O_3. This part of mechanism is in full agreement with Tang's study [2]. Tang investigated the mechanism of the $FeTiO_3$-Al-C system. Their results showed that new phases did not appear at 600°C after 0.5 h heat treatment. Tang also stated that at 700°C, ilmenite reacts with aluminum to produce Fe, TiO_2 and Al_2O_3. But there are some contradictions in the next step of the proposed mechanism. In Tang's work [2], titanium sub oxides such as Ti_4O_7 and Ti_3O_5 were found as a result of the reaction of the produced TiO_2 and remained Al, while ilmenite and Al disappeared. Tang also detected Fe_3C at 700°C which disappeared at higher temperatures. But in this work, it was found that the reaction at 700ºC continues with the reaction of the remaining aluminum and the produced Fe leading to the formation of Fe_2Al_5. This fact has been proved in the previous work [12]. Furthermore, no Fe_3C has been detected in the XRD results. This is logical according to the standard Gibbs free energy of Fe_3C formation at 700ºC. Because the standard Gibbs free energy of Fe_3C formation is positive [13]. By increasing the temperature up to 930°C, Fe_2Al_5 reacts with TiO_2 and FeAl forming Ti_2O_3. Finally, at 1070°C, FeAl reacts with Ti_2O_3 and graphite leading to TiC, Fe and Al_2O_3 production. On the other hand, after 48 h heat treating at 1070°C, the final products are obtained.
In Tang's study [2], it has been shown that TiC appeared at 1000°C based on the reaction of Ti_3O_5 and Ti_4O_7 and carbon. This process completes at 1300°C. $MgAl_2O_4$ was also detected in the final product of the Tang's study which confirmed the presence of impurities in the primary ilmenite. In comparison with other published works, the benefit of this work is the use of synthesized ilmenite to prevent the existence of the impurities and also perusing the exact route of the reactions.

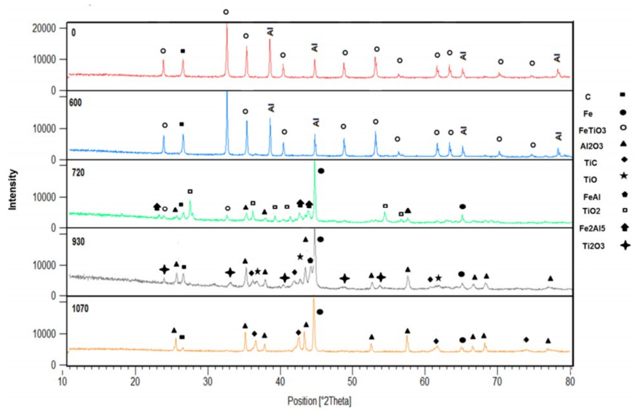


Figure 2. The XRD results for ilmenite, aluminum and graphite samples with the molar ratio of 1:2:1, heat treated for 48h at 600, 720, 930 and 1070ºC and the witness sample (0).

The goal of the second part of this work was to determine the temperature at which less time is needed to produce the final products (TiC, Fe and Al_2O_3). For this purpose, 1300°C was considered. It was shown that

4 hours is enough to complete the reactions at this temperature (Fig. 3). As can be seen in Fig. 3, the final products which have been produced at 1070°C after 48h were produced in a much shorter time (4h) at 1300°C. Based on these results, 4 hours and 1300°C were considered as the investigation temperature and time.

The mechanism which has been discussed before was proposed for the ratio of 1:2:1. Few researchers have studied the effect of aluminum or graphite ratio on the reaction mechanism. Tang et al. [2] have investigated the effect of the Al/C ratio on the reaction products, however, aluminum and carbon molar ratios have been changed simultaneously. Thereupon, the analysis of the results was complicated.

Tang et al. [2] investigated the $FeTiO_3$–xAl –(4-3x/2)C system. It was understood that by increasing the Al content, the reduction process is accelerated. It was also mentioned that Fe_3C disappeared at higher temperatures for higher Al ratios. Tang also showed that for 0.5 mol Al, despite the absence of Al_2O_3, $MgAl_2O_4$ was produced. This can confirm the fact that $MgAl_2O_4$ has a great potential to be produced.

Based on the mentioned statement, it is going to be known whether the primary molar ratio can change the reaction mechanisms or not. On the other hand, the derivative purpose of this study is to draw attention on the effect of the raw materials molar ratio on the final products and the reaction mechanism. To do so, two series of samples were prepared. In the first group, graphite molar ratio was changed from 0 to 1.5, and in the other group, aluminum was increased from 0 to 3. In comparison with the research on the molar ratio (Tang study [2]), the advantage of this research is that the study of the aluminum and graphite molar ratio effects have been discussed separately.

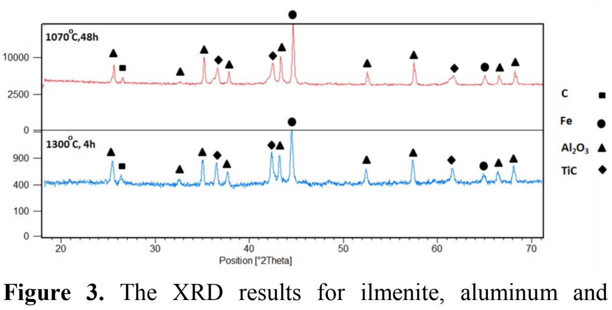


Figure 3. The XRD results for ilmenite, aluminum and graphite samples with a molar ratio of 1:2:1, heat treated for 48 h at 1070ºC and 4h at 1300ºC.

In following, at first, the effect of graphite molar ratio on the reaction mechanisms has been discussed.

3.1. The effect of graphite molar ratio on the reactions mechanism

To clarify the effect of graphite molar ratio on the reaction mechanism, a series of samples were prepared in which graphite molar ratio was changed from 0 to 1.5. As described in the experimental section, the ratios used were as 1:2:0, 1:2:0.5, 1:2:1, 1:2:1.5 (ilmenite: aluminum: graphite). In Fig. 4, the XRD results of the samples heat treated at 1300°C are shown.

Fig. 2a, illustrates the XRD result of the sample with the molar ratio of 1:2:0. Since no graphite exists in the sample, the final product is produced from the reaction of ilmenite and aluminum. TiO, Fe, Al_2O_3 and remained ilmenite are the produced compounds. To justify the TiO presence, the reactions mechanisms should be explored as follows:

According to Reaction 2 [3], ilmenite reacts with aluminum at the first step. Since the aluminum content is more than the needed level in Reaction 2, extra aluminum remains. The produced Fe reacts with aluminum and Fe_2Al_5 is formed (reaction 3 [3]). This reaction is discussed in details in the previous publications [12]. The Fe_2Al_5 reacts with TiO_2 to produce TiO (reaction 4 [3]). Subsequently, TiO can react with graphite in this step to form TiC (reaction 5 [3]), but due to the carbon absence, TiO remains unchanged at this ratio.

$$3FeTiO_3 + 2Al = 3Fe + 3TiO_2 + Al_2O_3 \quad (2)$$

$$2Fe + 5Al = Fe_2Al_5 \quad (3)$$

$$Fe_2Al_5 + 7.5TiO_2 = 2Fe + 2.5Al_2O_3 + 7.5TiO \quad (4)$$

$$TiO+C=TiC+CO(g) \quad (5)$$

The sample with the ratio of 1:2:0.5 contains less graphite than the ratio of 1:2:1. Therefore, Reaction 5 could not be completed. Furthermore, some of TiO remains while TiC is produced (Fig. 3b).

The next sample is the one with the molar ratio of 1:2:1 of ilmenite, aluminum and graphite for which the formation mechanism has been discussed previously. The final products of the sample are TiC, Al_2O_3 and Fe. These phases are the pre-set purpose in which Al_2O_3/TiC-Fe composite should be produced. In addition, no unintended compounds are present in the product (Fig. 3c). Since the effects of unknown compounds on the reaction mechanism are not clear and there are no unknown compounds in this ratio, therefore, this sample seems to be the optimum one. On the other hand, unknown compounds could affect the performance of the product. Accordingly, the ratio of 1:2:1 is the optimum sample.

The XRD result of the sample with the molar ratio of 1:2:1.5 of ilmenite, aluminum and graphite is shown in Fig.3d. With regard to the Fig. 3d, together with the desired compounds, $Fe_{1.88}C_{0.12}$ is formed. The reason of this is that extra graphite can react with the produced Fe which forms $Fe_{1.88}C_{0.12}$. Reduction of the Fe peak intensity in comparison with the previous samples also confirms the accuracy of this claim.

In following, the effect of aluminum molar ratio on the reaction mechanisms is discussed.

3.2. The effect of aluminum molar ratio on the reaction mechanism

As described in the experimental part of this study, to understand the effect of the aluminum molar ratio, a series of samples were prepared in which the aluminum molar ratio was changed from 0 to 3. The ratios were used as 1:0:1, 1:1:1, 1:2:1, and 1:3:1(ilmenite: aluminum: graphite). In Fig. 5, the XRD results of the samples heat treated at 1300°C for 4h are shown. The results are discussed as follows:

The sample with the molar ratio of 1:0:1 does not have any aluminum. As can be observed in Fig. 5a, if aluminum does not exist in the system, Ti_3O_5 and Fe will be the final products. The reason can be explained in this manner:

$FeTiO_3$ reacts with graphite which formes Ti_3O_5, Fe and CO_2 (g) as presented in Reaction 6. CO_2 leaves the system and cannot be detected by XRD analysis. What matters here is that TiC is not formed in this sample. It was discussed before by several researchers who have proved the fact that TiC is not producible by the reaction of TiO and C at temperatures lower than 1000°C [14-21]. This confirms the advantage of the using of aluminum, ilmenite and graphite system to have TiC at temperatures lower than the 1000°C.

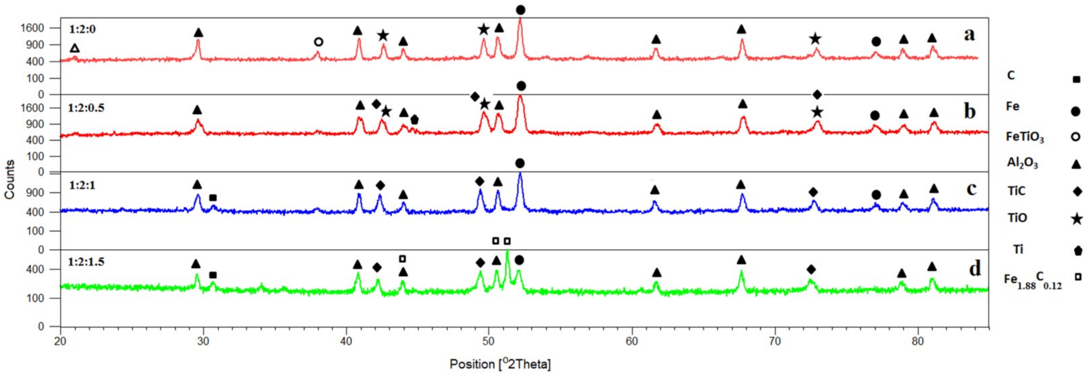


Figure 4. XRD Results for samples with molar ratios of a) 1:2:0, b) 1:2:0.5, c) 1:2:1and d) 1:2:1.5 heat treated at 1300°C for 4h.

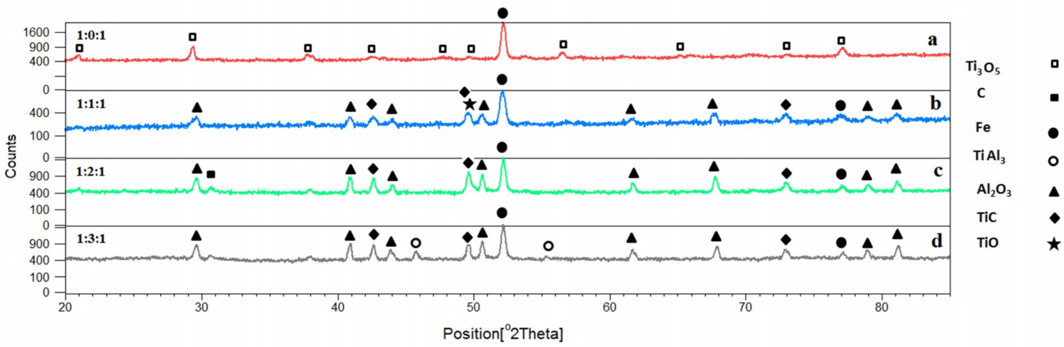


Figure 5. XRD results for samples with molar ratios of a) 1:0:1, b) 1:1:1, c) 1:2:1and d) 1:3:1 heat treated at 1300°C.

In a work reported by Tang et al. [22], Ti_3O_5 and Ti_4O_7 were detected as the transient phases during the conversion process of TiO_2 to TiC. Zou et al. [9] also detected Ti_2O_3, Ti_3O_5 and TiO as transient sub oxides of TiO_2. The result of this study shows that if there is not any aluminum, the Ti_3O_5 can be identified as titanium sub oxide.

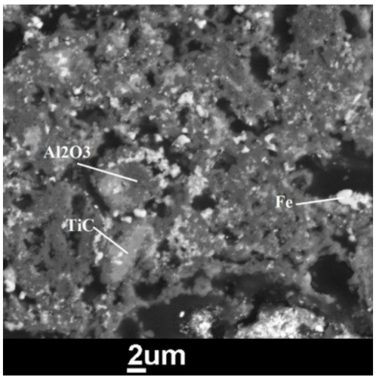
The aluminum content of the sample with a molar ratio of 1:1:1 of ilmenite, aluminum and graphite is less than 1:2:1, therefore in addition to the final desirable phases (Fe, Al_2O_3 and TiC), the products of previous stage such as TiO remains up to this temperature (Fig 5b).

As mentioned previously, the sample with a molar ratio of 1:2:1 of ilmenite, aluminum and graphite entails the best result. As can be seen in Fig. 5c, no undesirable phase was detected. The sample has the optimum molar ratio of raw materials which has been discussed before.

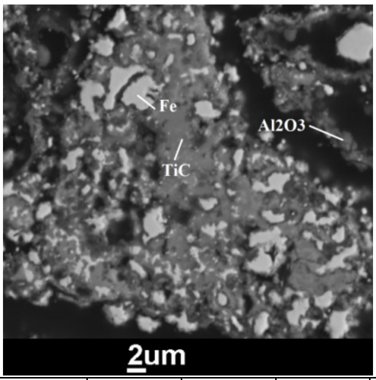
The sample with the molar ratio of 1:3:1 has extra aluminum content compared with the ratio of 1:2:1, which causes the formation of $TiAl_3$. This result seems reasonable, according to the previous study, in which the proportion of aluminum was more, where $TiAl_3$ was formed as the product of ilmenite and aluminum reaction [23].

As discussed before, the best results were obtained for the sample with a molar ratio of 1:2:1 where no more undesirable phase was detected. To study the microscopic image, SEM analysis equipped with EDS was used as shown in Fig. 6. With regards to Fig. 5; Fe, TiC and Al_2O_3 are the final products as was predicted before.

$$3FeTiO_3 + 2C = Ti_3O_5 + 3Fe + 2CO_2(g) \quad (6)$$



	Fe	Ti	Al	O	C
Fe	92,99	3,42	1,87	-	-
TiC	0,27	42,48	9,01	0,6	47,56
Al_2O_3	0,73	2,70	35,51	59,97	1,04



	Fe	Ti	Al	O	C
Fe	92,04	3,98	2,56	-	-
TiC	0,52	50,37	1,86	1,80	45,23
Al_2O_3	0,69	3,74	35,51	59,97	0,04

Figure 6. SEM images and DSC results of the samples with molar ratios of 1:2:1 heat treated at 1300°C.

4. CONCLUSION

The formation mechanism of Fe-TiC/Al_2O_3 composite from ilmenite, aluminum and graphite mixture with a molar ratio of 1:2:1 was clarified. It was found that at 720°C ilmenite reacts with aluminum and Fe forming TiO_2 and Al_2O_3. Then the reaction of the remained aluminum and the produced Fe leads to the formation of Fe_2Al_5. By increasing the temperature up to 930°C, Fe_2Al_5 reacts with TiO_2 and FeAl and Ti_2O_3 is formed. Finally, at 1070°C, FeAl reacts with Ti_2O_3 and graphite leading to the formation of TiC, Fe and Al_2O_3.

Then to determine the effect of aluminum and graphite molar ratio on the reaction mechanism the samples with the different molar ratios of aluminum and graphite were prepared and heat treated for 4h at 1300ºC. Since the simultaneous interpreting of the results with changing of aluminum and graphite ratio was complicated, the study of aluminum and graphite ratio was done separately. In this work, the results show that the best sample was the sample with the molar ratio of 1:2:1 (ilmenite: aluminum: graphite) because it contains pre-set phases such as Fe, TiC and Al_2O_3 and it does not have any undesirable phases such as Fe-C compounds or Ti-Al phases. It was also found that the ilmenite, aluminum and graphite system is sensitive to the raw material proportion. The results show that increasing the aluminum or graphite content more than Reaction 1 will produce undesired phases such as $TiAl_3$ or $Fe_{1.88}C_{0.12}$. It was also stated that using less aluminum or graphite will not complete the reaction.

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