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Formation of Two Types of Alumina/Intermetallic Composites based on the Reaction of Ilmenite and Aluminum

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A B S T R A C T

Ilmenite is a valuable industrial mineral containing Fe and Ti elements. Two composites with different morphology and composition were produced using the reaction of synthesized ilmenite and aluminum. The molar ratios of 1:2 and 1:8 were selected. The critical temperatures of each molar ratio were determined using the Differential Thermal Analysis (DTA). The heat treatment of the systems with different molar ratios was conducted at selected temperatures on the activated primary powders. It was specified that in the molar ratio of 1:2, at first, $FeTiO_3$ reacts with aluminum, which leads to the formation of Fe, TiO_2 and Al_2O_3. At higher temperatures, Fe reacts with TiO_2 and so spherical Fe_2Ti forms in the matrix of TiO_2 and Al_2O_3. It should be noted that in the molar ratio of 1:8, $FeAl_3$, $TiAl_3$ and Al_2O_3 form through the reaction of $FeTiO_3$ and aluminum, as a matter of fact, none of their products do not change at higher temperatures.

1. INTRODUCTION

Using ceramic reinforcement particles in the metal matrix increases the strength, hardness, wear resistance, high temperature strength and light weight. Although most research focused on light alloy composites which have the resistance to wearing, several studies have been carried out on this type of material. Typically, Al_2O_3, TiC, B_4C, VC, TiN_2, ZrO_2, and Si_3N_4 have been used to strengthen ferrous core composites [1, 2]. Titanium aluminides and iron aluminides/alumina composites are also the materials that have extraordinary features including high strength, low density and good oxidation resistance. Theses composites have been produced via several methods such as mechanical alloying [3, 4], thermal explosion [5], combustion synthesis [6] and in situ process [6-11] using TiO_2 and Al powders.

Moreover, Ilmenite as a valuable industrial mineral containing Fe and Ti has beenused to produce titanium or titania [12]. Ilmenite has been also applied to create some composites such as Al_2O_3/TiC-Fe composites, which are suitable for producing cutting tools [13, 14]. The reaction of ilmenite and aluminum has been studied by several researchers [15-18]. In all of these studies, due to the high proportion of aluminum, only the iron and titanium aluminides have been formed. Sleziona et al. [17] have reported that Ti can form using the molar ratio of 1:2 of ilmenite and aluminum,. The results of this study also confirmed that with a further increase in the aluminum content, the iron and titanium aluminides would be the dominant produced phases. The aluminum particle size factor has also been investigated by Azizov et al [22].

It should be mentioned that the molar ratio of aluminum and ilmenite was constant and the effect of long periods was not considered. However, in this study, two different molar ratios were taken into account and based on the detected critical temperatures of each molar ratio, heat treatment was performed for a long period.

According to the previous published study [14] and the thermodynamic calculations (which will be discussed in more details), it was found that at the molar ratios more than 1:3 of ilmenite to aluminum, the mechanism can change. This also is predictable based on the aforementioned studies. Thus, the molar ratios of 1:2 and 1:8 were chosen in which the aluminum content is less and more than what was needed for changing the mechanism, respectively. Thereupon, the novelty of this study is the formation of two types of alumina/intermetallic composites with a different structure and composition based on the reaction of ilmenite and aluminum. The effect of activating the

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primary powders on the time of the reactions was also investigated in current research

2. EXPERIMENTAL PROCEDURES

Ilmenite was synthesized using 3.78 g of Fe (99.5%, <10µm, from Merck company), 5.41 g TiO_2 (98%, <45 µm, prepared from Crimea Titan PJSC) and 10.81 g Fe_2O_3 (96.5%, <64 µm, from Crimea Titan PJSC company). The mixture was heat treated for 48h at 1100°C under an argon atmosphere to prepare pure ilmenite. Consequently, synthesized ilmenite was mixed with the aluminum (99.5%, 10 µm) containing molar ratios of 1:2 and 1:8. The combinations (blends) were mixed for 5h in a fast mill at 400 rpm within an alumina jar including 16 alumina balls of 2 cm diameter. The ball to powder ratio (BPR) was (5:1). This ratio was utilized to activate the primary powder for accelerating the reactions. The Differential Thermal Analysis (DTA; NETZSCH STA 409 PC/PG) was performed on the samples to determine the critical temperatures. According to the DTA results, the heat treatment the samples containing the molar ratios of 1:2 and 1:8 of ilmenite to aluminum was carried out at 740°C and 870°C up to 15h, respectively.

3. RESULT AND DISCUSSION

In the first step of the experiments, the pure ilmenite was synthesized to prevent the unknown effects of impurities present in the ilmenite concentrate. According to Tang's research [23], the different impurities, such as Mg, can cause new products and change the reaction processes. The XRD analysis was used to show that the ilmenite has been successfully synthesized (see Fig.1.)

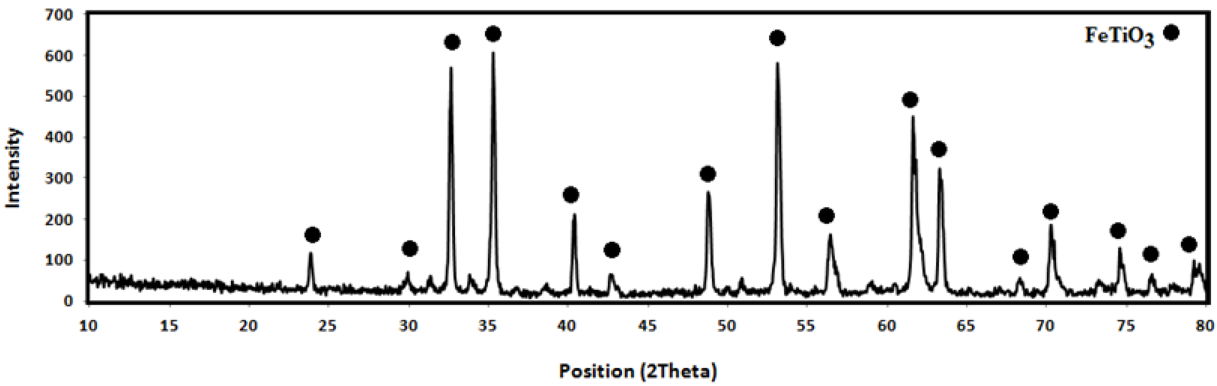


Figure 1. XRD analysis of the synthesized ilmenite

For the second step, Differential Thermal Analysis (DTA) has been performed on two molar ratios of 1:2 and 1:8 of ilmenite to aluminum. As can be seen, the increase in aluminum content leads to develop the endothermic peak of the aluminum melting (640ºC) and restrict the distance between the aluminum melting point and the peak of the molten aluminum reaction with the ilmenite. According to the DTA analysis results, the values of 740°C and 870°C were selected as the heat treatment temperatures in which aluminum melts and reacts with the ilmenite, respectively.

In addition, based on Fig. 2, the exothermic peak was shifted to the lower temperatures by increasing the aluminum content. The reason for this can be explained as follows: since increasing the aluminum heightens the adiabatic temperature, lots of generated energy can provide the activation energy of the reactions and help them to perform at lower temperatures.

Initially, before performing the heat treatment, the mechanical activation was applied on the primary powders for 5h in a fast mill at 400 rpm inside an alumina jar including 16 alumina balls of 2 cm diameter. To ensure that no reaction occurred between the raw materials during the activation process, XRD analysis was carried out at the ratio of 1:8 of ilmenite to aluminum (Fig. 3).

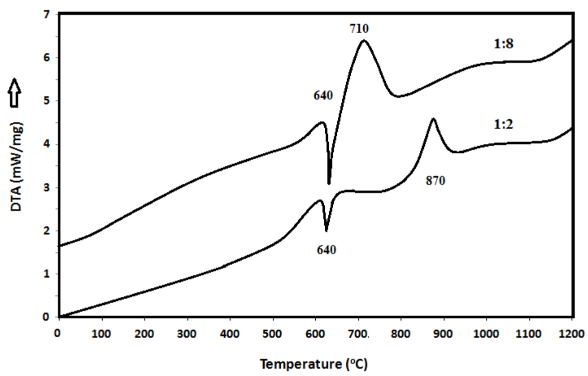


Figure 2. DTA results of the samples containing the molar ratios of 1:2 and 1:8 of $FeTiO_3$ to Al powder mixture

The molar ratio of 1:8 was chosen for the XRD analysis, because according to the DTA analysis, the reaction of ilmenite and aluminum in the molar ratio of 1:8 takes place at the lower temperatures, as the reactions are easier to perform in the ratio 1:8 in comparison with 1:2.

As shown in Fig. 3, no reaction occurs during the activation process between the raw materials. Therefore, only the raw material peaks are detectable.

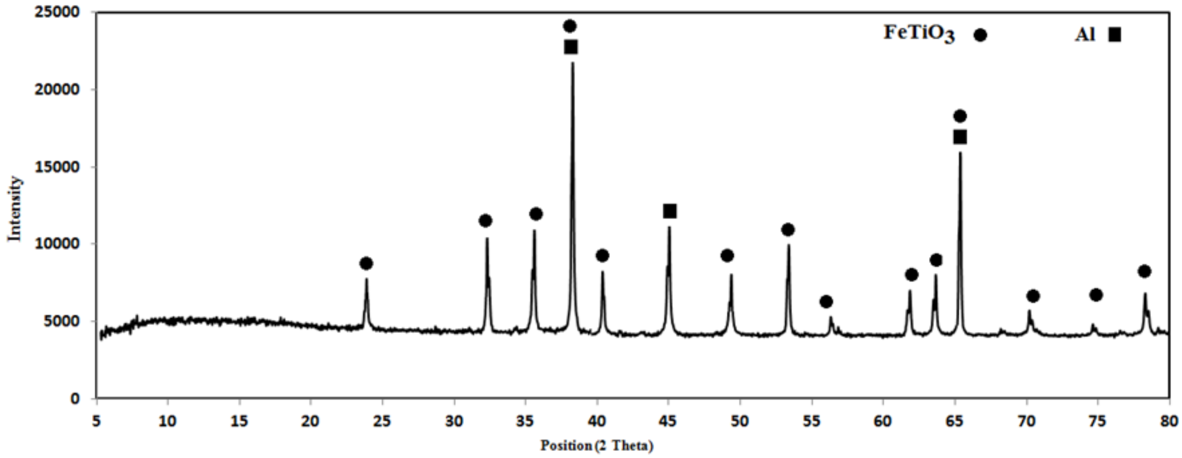
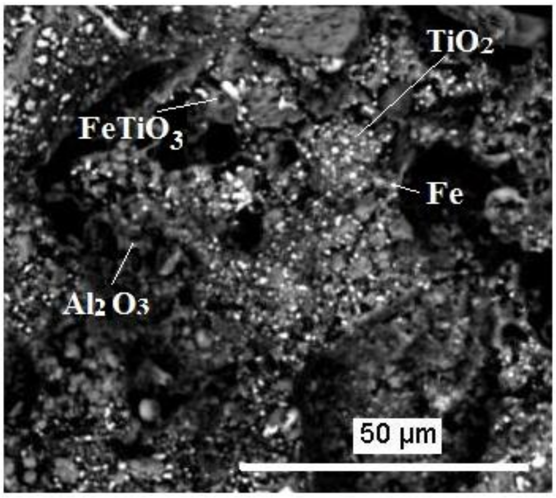
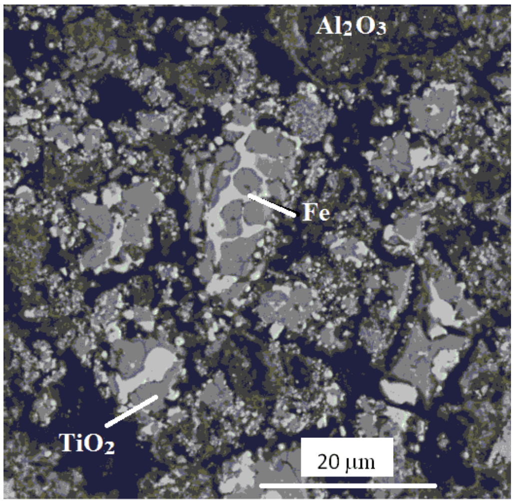


Figure 3. XRD analysis obtained from the sample containing the molar ratio of 1:8 of ilmenite to aluminum, activated for 5h in a fast mill at 400 rpm inside an alumina jar including 16 alumina balls of 2 cm diameter



(a)



(b)

The predicted composition	W%			A%		
	Al	Ti	Fe	Al	Ti	Fe
$FeTiO_3$	4.28	46.01	49.71	7.89	47.81	44.30
Fe	0	3	97.00	0	3.48	96.52
TiO_2	21.32	74.52	4.16	33.38	65.73	0.89
Al_2O_3	84.01	10.92	5.07	92.46	6.77	0.76

(c)

Figure 4. Electron microscopic image for the sample with the molar ratio of 1:2 of ilmenite and aluminum heat treated for a) 6h and b) 15h at 740°C and C) EDX analysis results of the detected phases

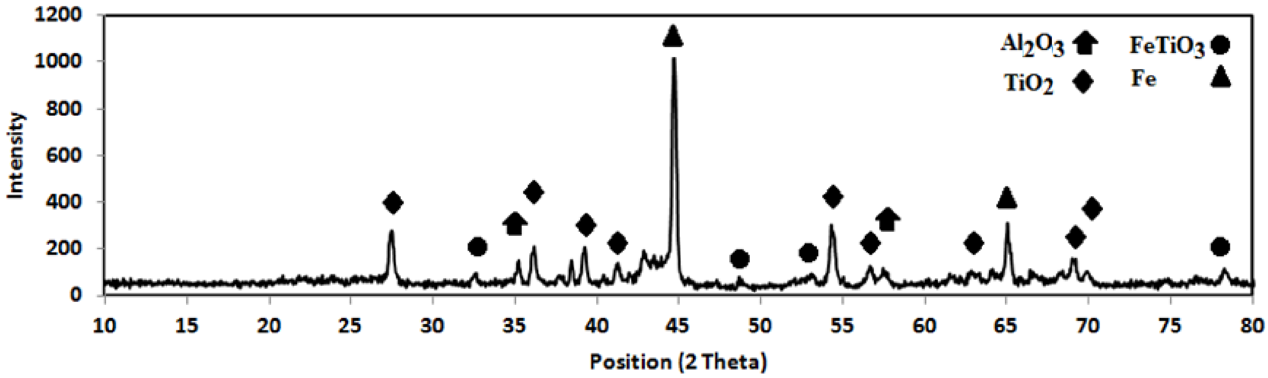
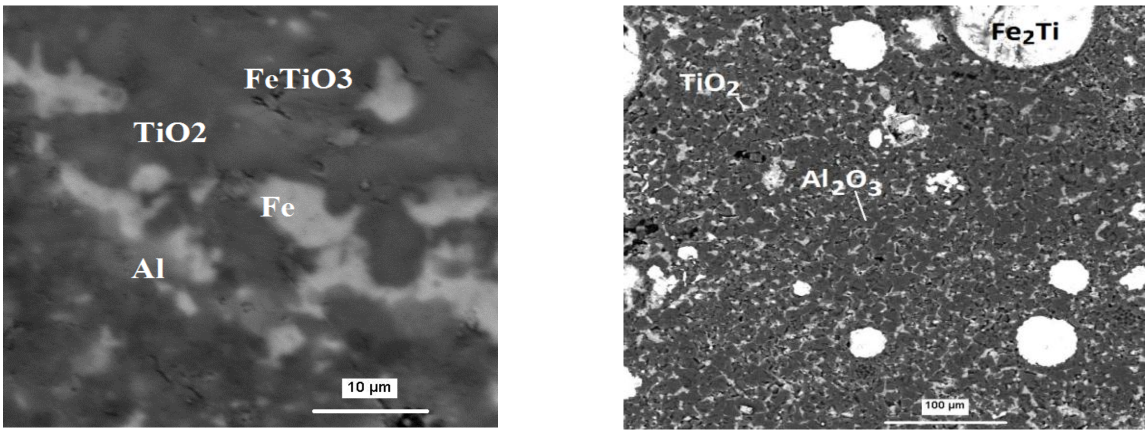


Figure 5. XRD analysis from the sample containing the molar ratio of 1:2 of ilmenite to aluminum, heat-treated at 740°C for 15 hours

In the samples containing a molar ratio of 1:2, initially iron, titania and alumina forms as a result of the ilmenite - aluminum reaction (reaction 1 [24], Figs. 4(a) and (c)). Up to 15 hours, the iron phase increases (Fig. 4(b)). XRD results illustrates that

$$3FeTiO_3 + 2Al = 3Fe + 3TiO_2 + 3Al_2O_3 \quad (1)$$

iron, titania and alumina are the principal phases in the sample containing the molar ratio of 1:2, which has been heat treated for 15h at 740ºC. (see Fig. 5)
By increasing the temperature to 840ºC, after a short time (6h), the obtained products are similar to those appeare in XRD analysis shown in Fig. 5(a)(i.e. iron, titania and alumina). Nevertheless, after 15h, the structure suddenly changes and circular particles appear (see Fig. 5(b)). The XRD results and EDX analysis, respectively shown in Fig. 7 and Fig. 6(c), indicate that these spherical particles are Fe_2Ti. In the previous study [24], no activation was conducted on the primary powders and they only were mixed for 10 min. However, in the current study, the powders were activated for 5h. Comparing this results with the previous one [24] shows that the activation of the primary powder results in the formation of Fe_2Ti in the shorter time, which relates to the higher working temperature.



(a) (b)

	W%					A%				
The predicted composition	**Al**	**Si**	**Ti**	**Fe**	**Au**	**Al**	**Si**	**Ti**	**Fe**	**Au**
Fe_2Ti	**11.96**	**2.61**	**26.61**	**55.72**	**3.11**	**21.06**	**4.41**	**26.39**	**47.39**	**0.75**

(c)

Figure 6. Electron microscopic image for the sample with the molar ratio of 1:2 of ilmenite and aluminum heat treated for a) 6h and b) 15h at 870°C and the EDX analysis results from spherical particles

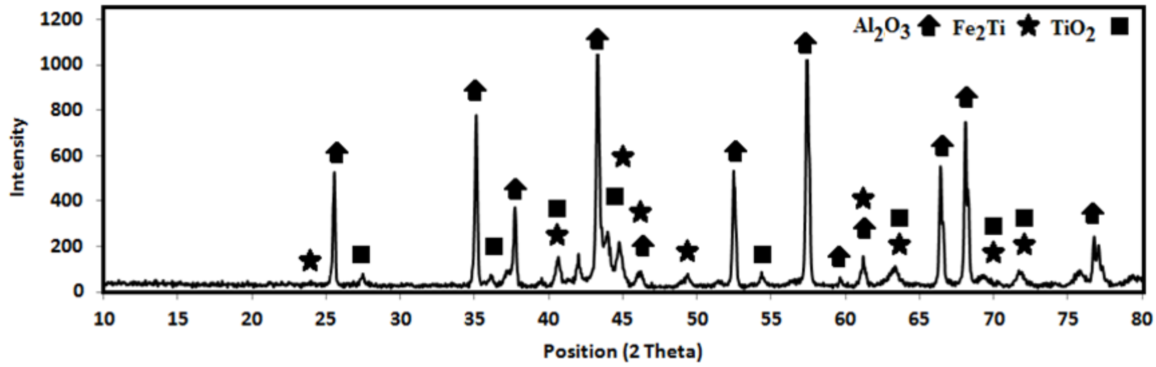
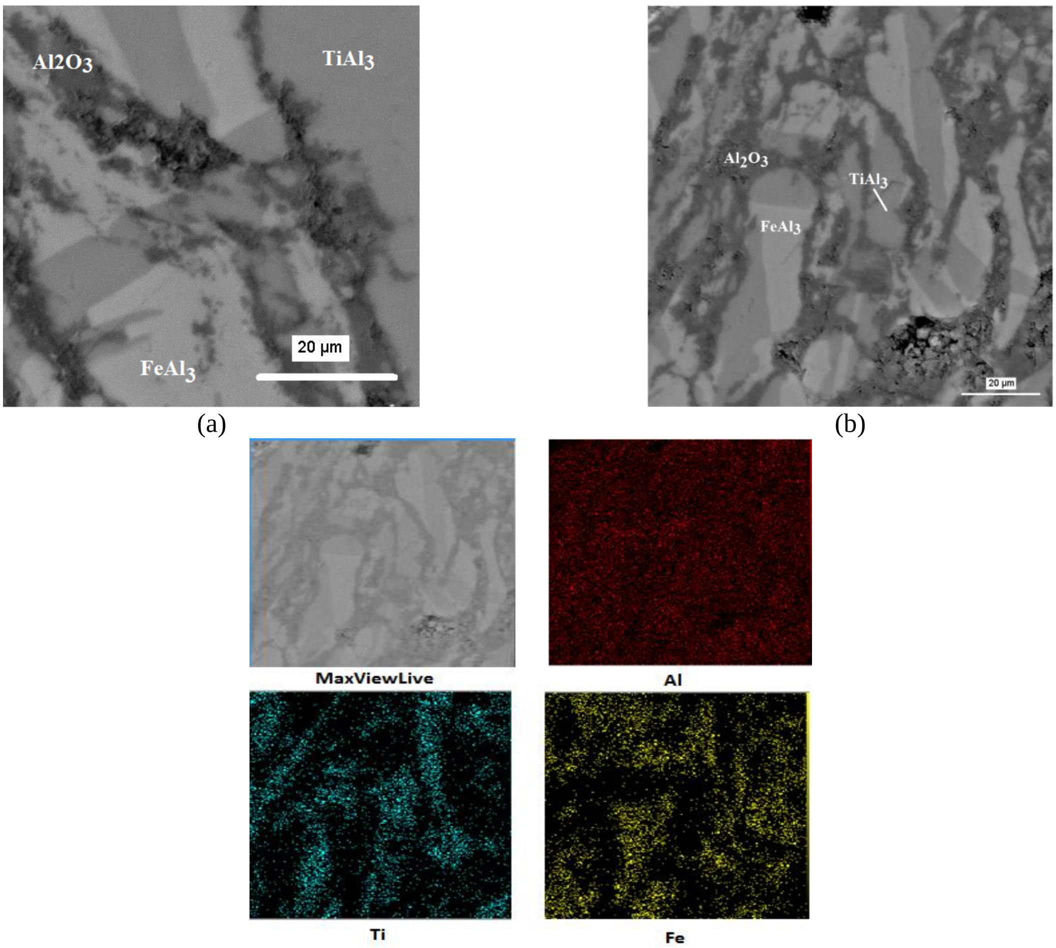


Figure 7. XRD result from the sample containing the molar ratio of 1:2 of ilmenite to aluminum, heat-treated at 870°C for 15h

Reaction 2 [24] demonstrates how Fe_2Ti forms through the raw materials:

$$FeTiO_3+1.3335Al=0.5Fe_2Ti+0.5TiO_2+0.6665Al_2O_3 \quad (2)$$

By increasing the aluminum content in the raw materials, the ratio of aluminum to ilmenite reaches 1:8, where even after 2h, $TiAl_3$, $FeAl_3$ and Al_2O_3 phases form. The type of these phases does not change even after 15 hours (see Fig. 8). This suggests that increasing the amount of aluminum in the system enlarges the forming tendency of titanium aluminide and iron aluminide. The production of these compounds is also confirmed by means of XRD analysis. (see Fig. 9)



(c)

Figure 8. Electron microscopic image for the samples with the molar ratio of 1:8 of ilmenite and aluminum heat treated for a) 2h, b) 15h at 740°C, (c) Elemental distribution map of the samples b

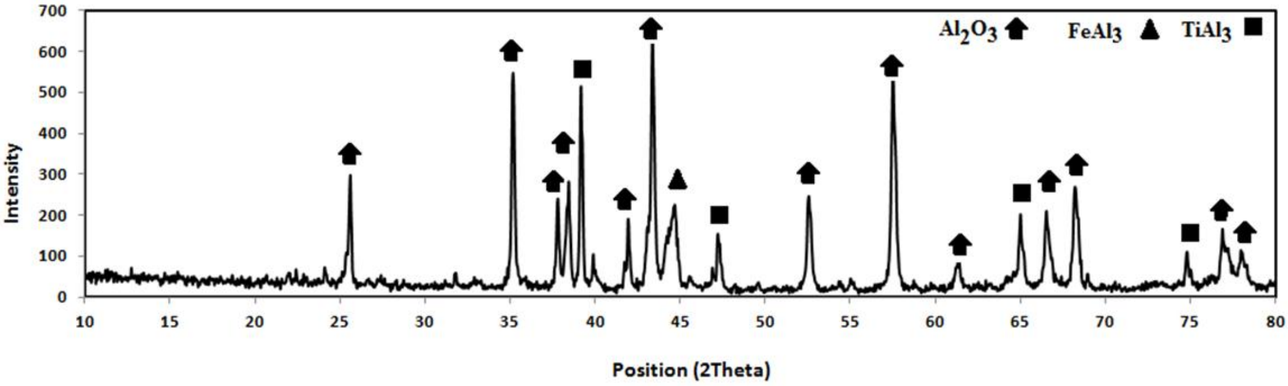
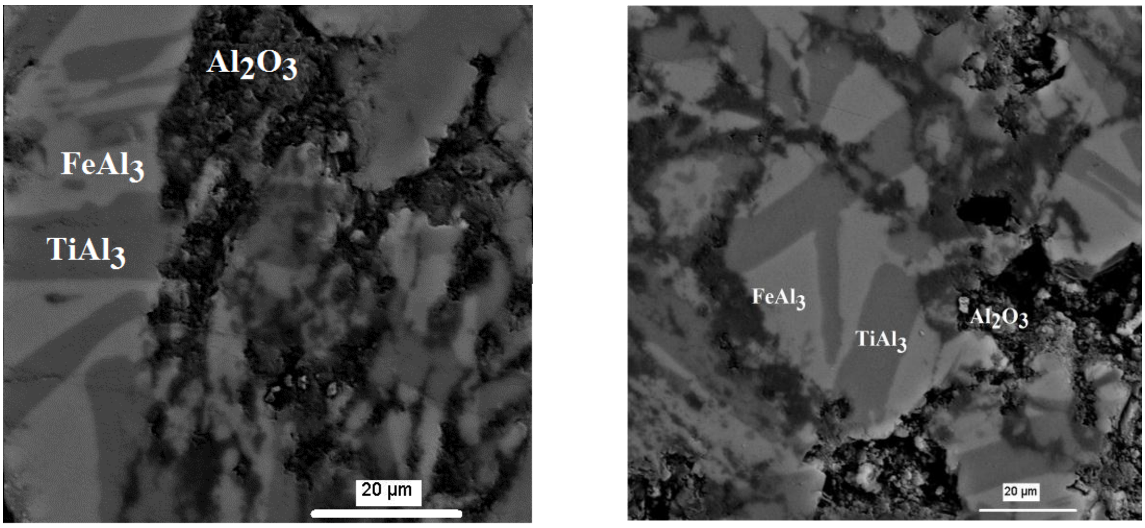


Figure 9. XRD result from the sample containing the molar ratio of 1:8 of ilmenite to aluminum, heat-treated at 740°C for 15 hours

The composition and morphology of produced alumina phases does not change even at the higher temperature. At 870°C, after 2h and 15h, the titanium and iron aluminides are produced with the same structure, similar to what happened at 740°C. (Fig. 10)

It seems that the reaction 3 is carried out between the raw materials.

$$FeTiO_3 + 8Al = FeAl_3 + TiAl_3 + Al_2O_3 \quad (3)$$



(a) (b)

Figure 10.: Electron microscopic image for the sample with the molar ratio of 1:8 of ilmenite and aluminum heat treated for a) 2h and b) 15h at 870°C

Considering the equilibrium composition (HSC software) of a system containing ilmenite in which Al is systematically added (see Fig. 11), it is clear that the first produced products are as follows Fe, TiO_2 and Al_2O_3. Through increasing the aluminum content of the raw material, Fe_2Ti and $TiAl_3$ can form. Unfortunately, due to the lacking ermodynamic information about iron aluminides, this prediction is just a guide line that can be justified the previous processes.

To thermodynamically compare the aforementioned reactions, the information listed in Table1 is required. In this Table, the formation Gibbs free energy of each reaction has been mentioned at 740°C and 870°C. As can be seen the formation Gibbs free energy of reaction 1 is more negative than reaction 2, thus, reaction 1 has a greater tendency to be carried out in comparison with reaction 2. On the other hand, the formation of Fe (reaction1) needs the least amount of aluminum, therefore, Fe can be formed easier than Fe_2Ti (reaction 2). After the formation of Fe and TiO_2, by reducing the amount of available aluminum, the conditions for reaction 2 are satisfied.

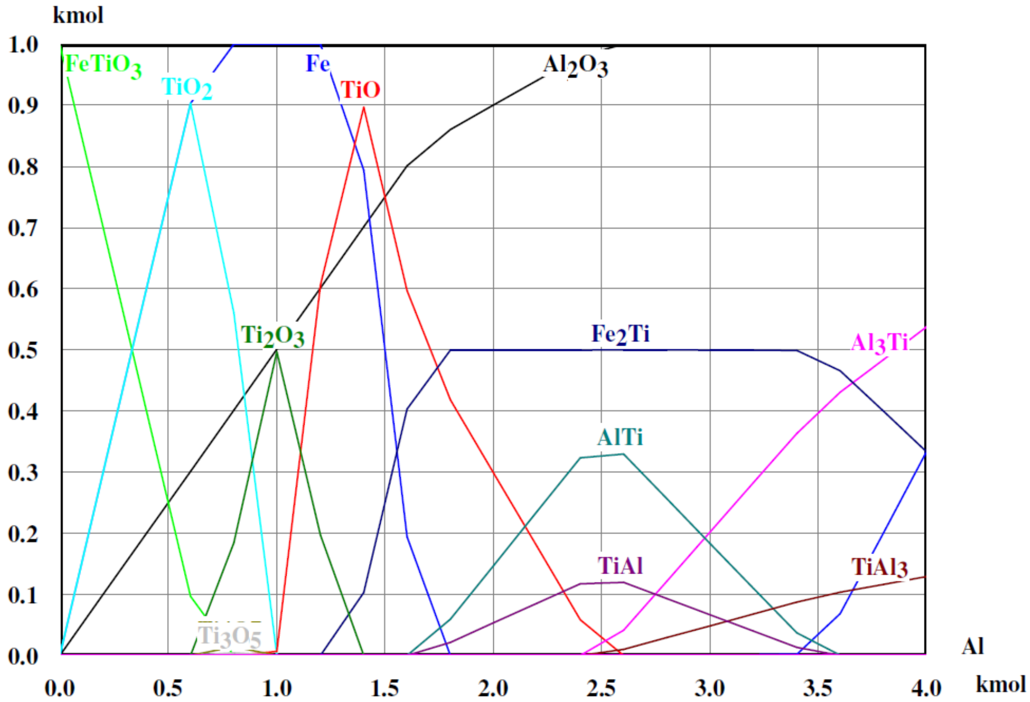


Figure11. The predicted equilibrium composition (HSC software) of a system containing ilmenite in which Al is systematically added

TABLE 1. The formation Gibbs free energy of the aforementioned reactions

	Reaction	**740 (°C)**	**870 (°C)**	
1	$3FeTiO_3 + 2Al = 3Fe + 3TiO_2 + Al_2O_3$	-850.733	-214.051	ΔG°(kJ)
2	$2FeTiO_3 + 2.667Al = Fe_2Ti + TiO_2 + 1.333Al_2O_3$	-187.387	-192.295	
3	$FeTiO_3 + 5Al = Fe + TiAl_3 + Al_2O_3$	-130.34	-130.66	

4. CONCLUSION

Two composites with a different structure and composition were produced using the reaction of ilmenite and aluminum. Spherical Fe_2Ti in the matrix of TiO_2 and Al_2O_3 was formed using the molar ratio of 1:2 of ilmenite to aluminum. The composite of $FeAl_3$ / $TiAl_3$ - Al_2O_3 appeared applying the molar ratio of 1:8 of ilmenite to aluminum. In other words, by increasing the amount of aluminum, we observed the formation of iron, alumina and titania. Via increasing the aluminum amount as a raw material, the production conditions of the Fe_2Ti are satisfied. It also leads to the production of titanium and aluminum aluminides. It was also found that the activation of the primary powder could allow the reaction to take place in a shorter time.

5. ACKNOWLEDGMENTS

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