AN INVESTIGATION ON REACTIVE SINTERING OF NANO-CRYSTALLINE TiO_2 -Al POWDER PROCESSED BY MECHANICAL ALLOYING

S. Alamolhoda*, S. Heshmati-Manesh and A. Ataie

* *alamhoda@ut.ac.ir*

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School of Metallurgy and Materials Engineering, University of Tehran, Tehran, Iran.

Abstract: *In this research an ultra-fine grained composite structure consisting of an intermetallic matrix together with dispersed nano size Al_2O_3 obtained via mechanical activation of TiO_2 and Al in a high energy ball mill and sintering of consolidated samples. Phase composition and morphology of milled and sintered samples were evaluated by XRD and SEM techniques Thermal behavior of 8 hour milled powder was evaluated by DTA technique.*

DTA results showed that, the reaction happens in two steps. The first step is the aluminothermic reduction of TiO_2 with Al. XRD observations reveals that some Ti_3Al phase formed during reduction reaction together with TiAl and Al_2O_3 major phases. This intermetallic phase disappeared when sintering temperature was increased to 850 and 1000 ºC. The second step in DTA is related to a reaction between residual Al in the system (dissolved in TiAl lattice) and the Ti_3Al phase produced earlier at lower temperatures. SEM micrographs reveal that by completion of the reduction reaction more homogeneous and finer microstructure is observable in sintered samples.

Keywords: *γ -TiAl, nano-composite, mechanical alloying, aluminothermic reduction.*

1. INTRODUCTION

Intermetallic alloys based on γ-TiAl have relatively low density, high strength to weight ratio, good oxidation and corrosion resistance and adequate creep resistance at high temperatures. However, they suffer from brittleness and rapid crack growth rate at low to intermediate temperatures [1-4]. Development of in-situ TiAl / Al_2O_3 composite may help to overcome the problems associated with the monolithic γ-TiAl alloys. Such a composite material can be produced by mechanical activation and subsequent heat treatment of TiO_2 and Al powders. Presence of fine and homogenously distributed ceramic particles in the intermetallic matrix may improve the ductility, at least if this property is controlled by planar slip. In addition the final phases in such a composite are thermodynamically compatible [5-6].

In this research an ultra-fine grained composite structure consisting of an intermetallic matrix together with dispersed nano size Al_2O_3 obtained when mechanically activated TiO_2 and Al mixture sintered at a proper temperature. The effect of milling parameters and phase evolutions after sintering at different temperatures was observed on this system.

2. EXPERIMENTAL PROCEDURE

Staring materials in this work were mixed according to reaction (1) and then milled by a planetary ball mill with a ball to powder ratio of 20:1 and running speed of 300 rpm, under argon atmosphere up to 10 hours.

$$3TiO_2 + 7Al \longrightarrow 3TiAl + 2Al_2O_3 \quad (1)$$

10 mole% excess of Al powder was used to ensure the existence of sufficient Al for the reaction. The mean crystallite sizes of the milled powders were calculated by Cauchy Gaussian method using XRD patterns [7]. Thermal behavior of the powder milled for 8 hours was analyzed by DTA with a heating rate of 20 K/min up to 1200 ºC under flowing argon on the Netzsch STA 409 PC/PG instrument.

Based on DTA results, 4 samples were cold pressed and sintered at different temperatures from 550 to 1200ºC. The samples were placed in quartz tubes which were evacuated and backfilled with high purity argon and sealed. They were heated in the furnace to the desired temperature with a heating rate of 20 K/min and kept for 1 hour. The characteristics of the milled as well as sintered samples were evaluated by SEM (CamScan MV2300) and XRD (PhilipsPW-

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1730) using Co K α radiation, respectively. The mean crystallite sizes of sintered samples were calculated by Scherrer equation [8].

3. RESULTS AND DISCUSSION

Fig. 1 shows XRD patterns of samples milled up to 10 hours. The figure shows peak broadening and decreased peak intensities with continued milling, but no reaction was detected during the milling operation. These results are in good agreement with those reported earlier [4, 9].

Results of calculations of mean crystallite sizes in Al and TiO_2 particles, summarized in Table 1, indicate that the milled powders have nano-crystalline structure.

Fig. 2 shows SEM micrographs of the un-milled sample together with those milled for various periods of time. Decreasing of particles sizes by increased milling time is obviously seen in milled powders. The images roughly confirm nano-structure of the milled powders. After 2

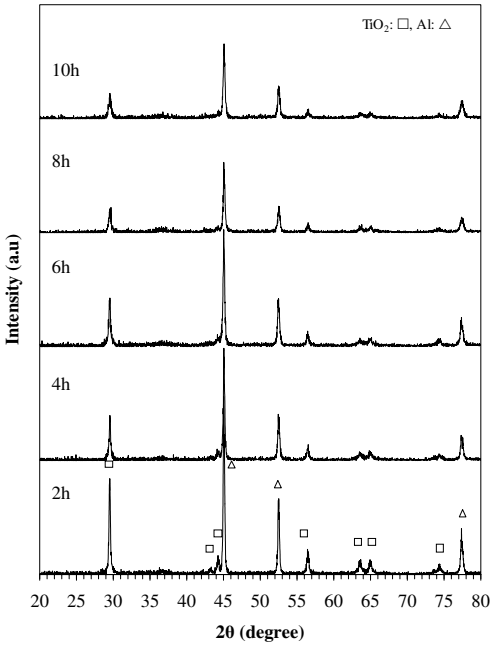

Fig. 1. XRD patterns of samples milled up to 10 hours.

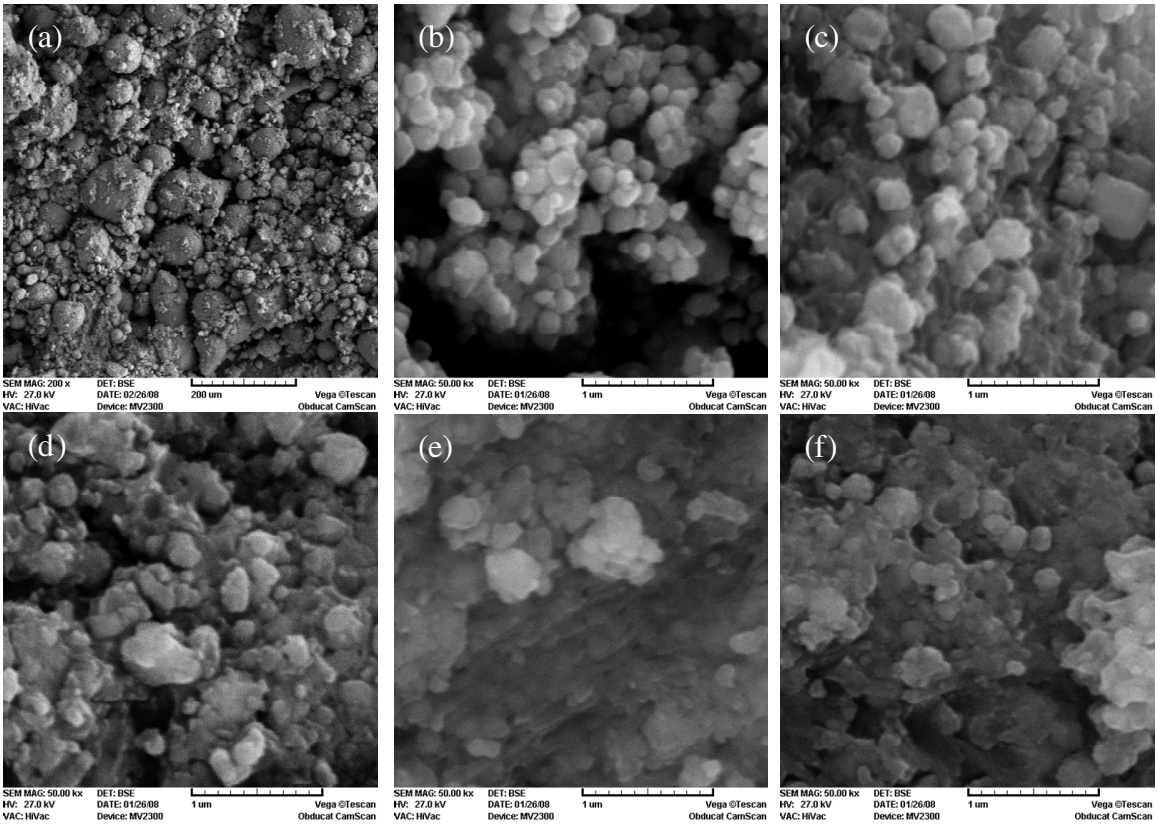

Fig. 2. SEM micrographs of a) un-milled sample and samples milled for b) 2, c) 4, d) 6, e) 8 and d) 10 hours.

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Table 1. Mean crystallite size of particles calculated by Cauchy- Gaussian methods

Milling time (hour)	Mean crystallite size (nm)	
	Al	TiO_2
2	127	62
4	62	74
6	56	41
8	58	28
10	74	27

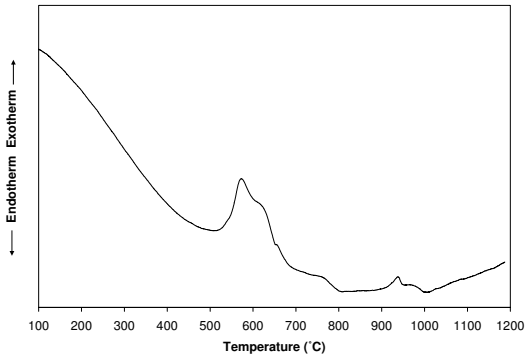

Fig. 3. DTA trace of sample milled for 8 hours.

hours of milling, particles become as flakes by a size of about 200nm with a more homogenous size and shape comparing with the un-milled sample. By increasing of milling time to 4 and 6 hours, agglomerates of small particles are formed due to increased surface energy of particles and increased number of broken atomic bonds. It seems that a steady state in particle size is achieved by increased milling time.

Fig. 3 is DTA trace of the sample milled for 8 hours which shows no reaction between TiO_2 and Al at temperatures below 500 ºC.

An exothermic reaction begins at about 500 ºC which relates to the aluminothermic reduction of TiO_2 by Al. There is a step on this peak below 600 ºC which shows reduced reaction rate in the activated material which shifts the reaction to higher temperatures and goes to be concurrent with the melting of residual Al which is an endothermic transformation. Also there is a tiny dip near melting point of Al which is believed to be related to the melting of residual Al. It should be noted that in contrary with the results reported by other researchers [3-5], the reduction reaction is almost completed before melting of Al. In fact in most cases the reaction occurred between liquid and solid phases.

There is also another exothermic peak at about

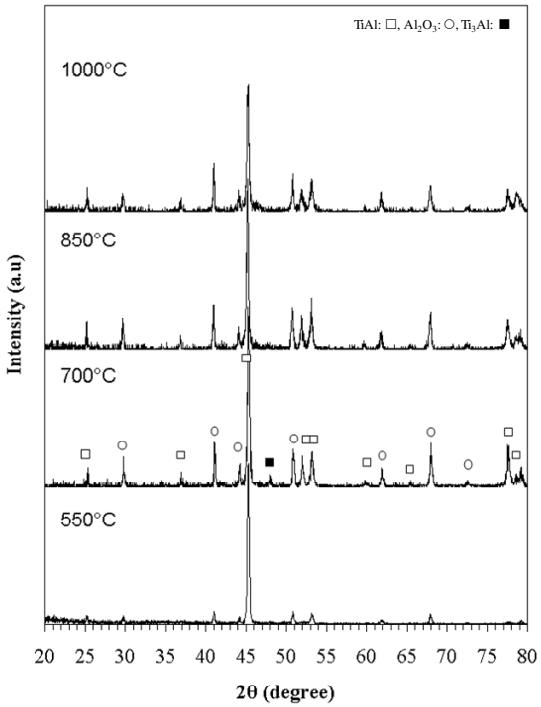

Fig. 4. XRD patterns of samples sintered at 550 to 1000ºC for 1 hour.

900 ºC which may be possibly related to a reaction between residual Al in the system (dissolved in TiAl lattice) and the Ti_3Al phase produced earlier at lower temperatures. The reaction could be as follows and its product would be intermetallic TiAl:

$$Ti_3Al + 2Al \longrightarrow 3TiAl \quad (2)$$

Occurrence of this reaction was further confirmed by XRD results.

Fig. 4 shows XRD patterns of the sample milled for 8 hours after sintering at 550, 700, 850 and 1000ºC. XRD pattern of the sample sintered at 550 ºC shows formation of TiAl and Al_2O_3. XRD pattern of the sample sintered at 700 ºC shows presence of TiAl, Ti_3Al and Al_2O_3 phases.

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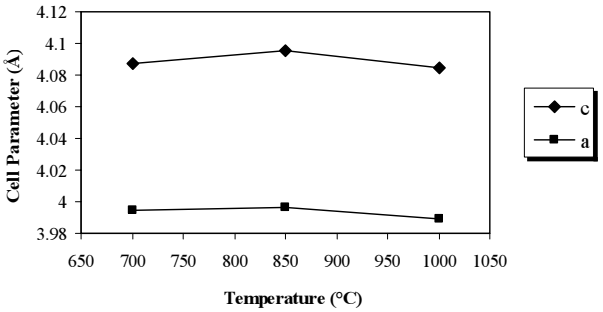

Fig. 5. Variation of TiAl lattice parameters with temperature calculated from XRD results of samples sintered at 700, 850 and 1000ºC.

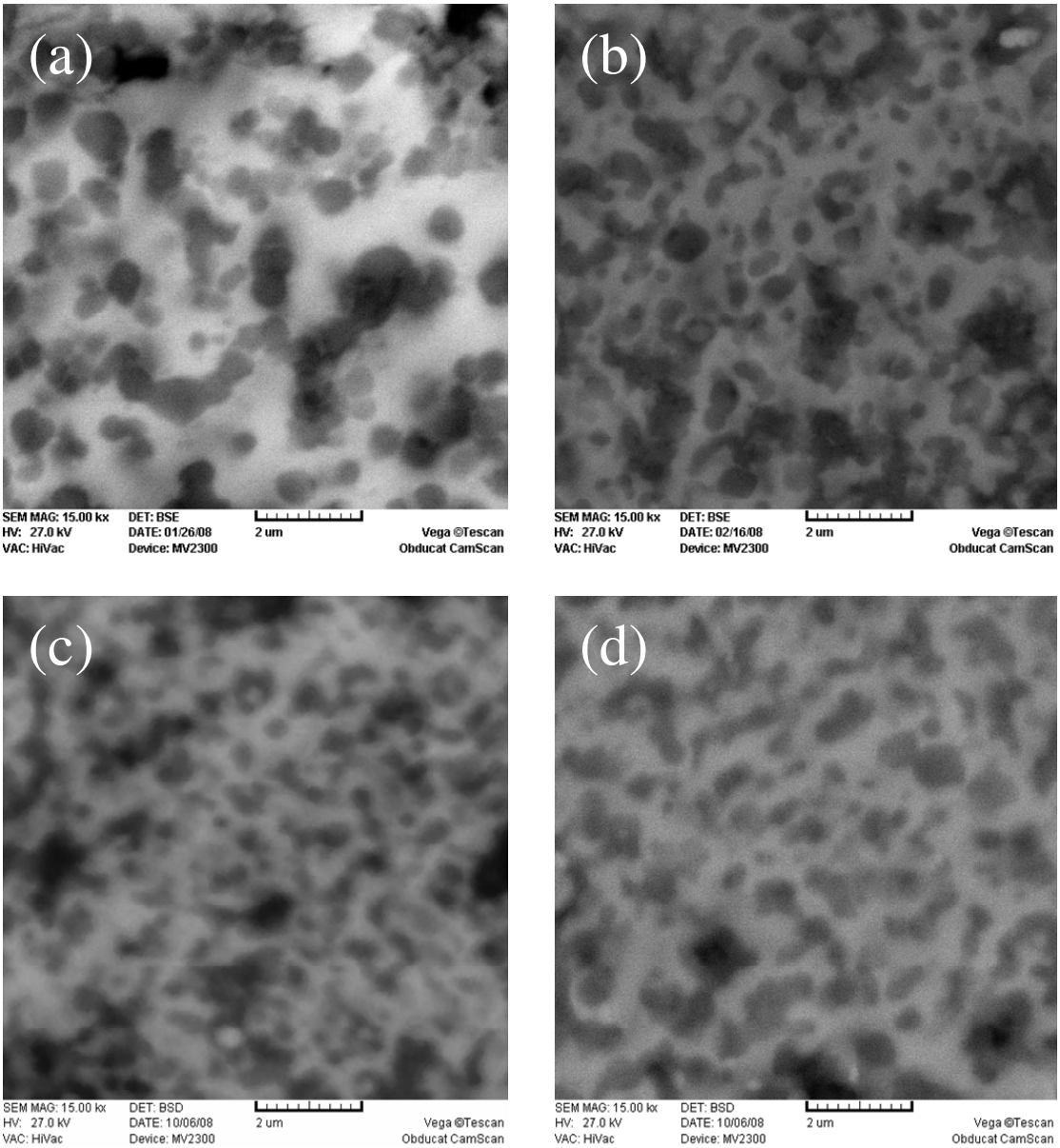

Fig. 6. SEM micrographs of samples sintered at a) 550, b) 700, C) 850, d) 1000ºC for 1 hour.

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Table 2. Mean crystallite size of TiAl phase in samples sintered at 550-1000ºC calculated by Scherrer equation

Sintering Temperature (ºC)	Mean Crystallite size of TiAl (nm)
550	56
700	72
850	83
1000	100

By increasing the sintering temperature to 700ºC, more TiAl peaks were detectable which shows formation of more TiAl phase by increasing of sintering temperature. A weak peak of Ti_3Al phase is also detectable in this temperature. Formation of Ti_3Al phase may be attributed to concentration fluctuations during exothermic reaction. In the sample sintered at 850 ºC, the only Ti_3Al peak weakens and at 1000 ºC completely disappears.

Changes in TiAl lattice parameters with temperature calculated using XRD results are shown in Fig. 5. TiAl tetragonal lattice is saturated with Al. By increasing of temperature from 700ºC to 850ºC, dissolved Al atoms leave this phase and Ti atoms with bigger atomic size occupy their positions. Increase of TiAl lattice parameters by increased sintering temperature in this step seems to be due to this phenomenon. These Al atoms react with Ti_3Al phase according to equation (2) and results in formation of more TiAl phase. Increasing the sintering temperature to 1000 ºC causes immigration of more Al atoms out of TiAl phase. Although it might be expected that TiAl lattice parameters to be increased further, but Fig.5 shows an opposite trend. This could be due to the higher density of vacancies dissolved in TiAl lattice achieved at higher temperatures.

Fig. 6 shows SEM micrographs of sintered samples at various temperatures. The dark phase in these images is Al_2O_3 and the bright phase is TiAl or mixture of TiAl and Ti_3Al phases. In the sample sintered at 550ºC, Al_2O_3 phase has an inhomogeneous distribution within the matrix. By increasing of the sintering temperature to 700ºC distribution of Al_2O_3 in matrix becomes more homogeneous which could be a sign of completion of the reduction reaction. Sever grain growth was not occurred by increasing the sintering temperature from 700 ºC to 1000 ºC.

The mean crystallite sizes of sintered samples which were calculated by Scherrer equation are shown in Table 2. It could be observed that all phases have nano crystallite size and the mean crystallite sizes increase with increasing of sintering temperature.

4. CONCLUSIONS

In this research an ultra-fine grained composite structure consisting of an intermetallic matrix together with dispersed nano size Al_2O_3 obtained via mechanical activation of TiO_2 and Al in a high energy ball mill and sintering of consolidated samples. DTA results showed two steps in formation of final phases. Some Ti_3Al phase formed during the course of the aluminothermic reduction reaction together with TiAl and Al_2O_3 major phases in the first step. This intermetallic phase disappeared when sintering temperature was increased to 850 and 1000ºC.

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