Production of Fe-TiN and Fe-Ti(N,C) Composite Powders by Mechanical Alloying

S. Nazari[1♣], A. Saidi[2], A. Shafyei[2]
1- Department of Materials Engineering, Najafabad Branch, Islamic Azad University, Isfahan, P.O.Box 517, Iran
2- Department of Materials Engineering, Isfahan University of Technology, Isfahan, Iran, 84156-83111

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ABSTRACT

In this research, the production of Fe-TiN and Fe-Ti(N,C) composite powders by mechanical alloying was investigated and evaluated. Ferrotitanium (containing 70%Ti), titanium and graphite were used as the raw materials. Initial mixtures were milled in different time durations under the pure nitrogen atmosphere with the pressure of 5atm. The results showed that when N_2 pressure is 5 atm and milling time lasts 5 h, reaction starts and after 10 h, $FeTi_2$ is completely converted to TiN. Also, the role of graphite as the active material of the reaction was investigated and it was found that it leads to the production of titanium carbonitride in the iron matrix.

Introduction

Metal matrix composites are considered as the most important engineering materials because of their hardness and toughness. The most important elements as metallic matrixes are Iron, Nickel, Aluminum and their alloys, while the most reinforcing phases are Nitrides, Carbides, and Oxides. Many researchers have considered Titanium nitride as an important reinforcing phase due to its high hardness and high thermal stability [1-4]. Different methods such as mechanical alloying, combustion synthesis, powder metallurgy, and casting [4-7] have been used for producing metal matrix composites.

Recently, the production of X-TiC type composite powders has been seriously followed. In these powders, X is the metal matrix which can be any kind of metal.
The reinforcing phase, which is shown by TiC, can be any kind of Carbides or Nitrides. Containing more than 70 % reinforcing phase, these composite powders are used as raw materials for producing composite parts by casting or powder metallurgy method. The citedcomposite powders (X-Tic) are generally produced using combustion synthesis or mechanical alloying method [8,9].
In this research, the production of Fe-TiN composite powder with more than 70%TiN, using inexpensive raw material Ferrotitanium, combining Titanium, Graphite and Sodium

♣Corresponding author:S. Nazari, siamaknazarimetal@yahoo.com, 09163612217

azide as the Nitriding agent was investigated through combustion synthesis and mechanical alloying.

Experimental procedure

Ferrotitanium powder, the product of England LSM company, contains 28% Fe and >71% Ti with <600 μm size, Titanium powders, and Carbon with >99 % purity (Merck) were used as the raw materials. Considering Stoichiometry ratios, 5 samples for producing titaniumnitride and titanium carbonitride were prepared and milled according to **Table1**.

A Ball mill (Model, FP2) with the speed of 600 rpm was used for alloying. For complete discharging of air from reaction atmosphere, mill chamber was filled and emptied several times with nitrogen and finally, it was filled with pure nitrogen under the pressure of 5 atm. X-ray diffractometer (model, Philips XPERT-MPD) was used for Phase detection of produced samples. Williamson-Hall technique was used for determining lattice strain and grains size. To minimize error in determining the size of grains, Williamson and Hall simultaneously considered reducing effect of the grain size and increasing effect of strain on the width of the peak; therefore, they attained this equation

$$\beta \cos\theta = \frac{0.9\lambda}{d} + 2\epsilon \sin\theta$$

In this relation, β is the measured width of the diffracted peak at its half height (in radians), d is the average size of the grains, λ is the X-ray wavelength, θ is the diffraction angle, and ϵ is the lattice strain. If ßcosθ data be drawn versus sinθ at different angles for several XRD peaks, these points must be placed on a straight line, from the slope and the intercept of which, one can determine the strain of lattice (ϵ)and the average size of the grain respectively. Such a drawing is known as the Williamson-Hall diagram.

Scanning Electron Microscope (model Seron ALS-2100) was also used for morphology observation of the samples.

Results and Discussion

X-ray diffraction patterns of the Ferrotitanium and Titanium raw material are shown in **Fig. 1** and **2**, respectively. This analysis was conducted to compare them with milled samples. **Fig. 1** contains only the peaks of Fe-Ti solid solution, which have been moved a little due to the dissolving iron in it. Titanium peaks are clearly visible in **Fig. 2**. Because of the powder production method, which is water atomization, Hydrogen absorption is possible, and the two observed peaks of TiH_2 in **Fig. 2** may be attributed to this phenomenon

Table 1. Milling conditions and productionphases.

sample	Raw material	Mill time, h	Ball/powder ratio	N_2 pressure, atm	production phases
1	100%Ti	6	20	5	**Fe - TiN**
2	$FeTi_2$+50%Ti	5	20	5	**Ti -$Fe_{2.932}O_4$ - TiN**
3	$FeTi_2$+50%Ti	10	20	5	**TiN**
4	$FeTi_2$+50%C	5	20	5	**Ti- Fe- $TiN_{0.7}C_{0.3}$**
5	$FeTi_2$+50%C	10	20	5	**Fe- $TiN_{0.7}C_{0.3}$**

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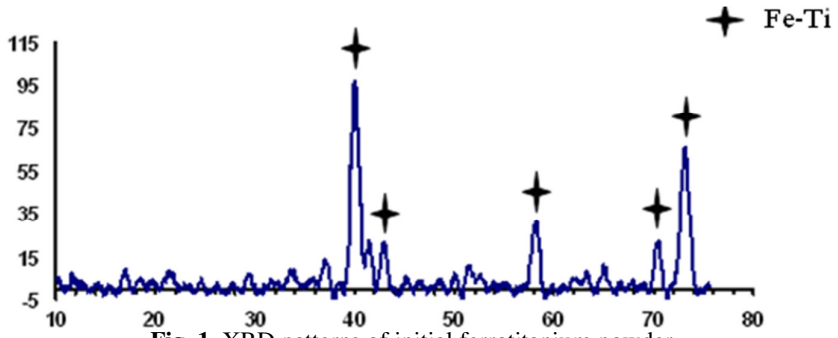

Fig. 1. XRD patterns of initial ferrotitanium powder.

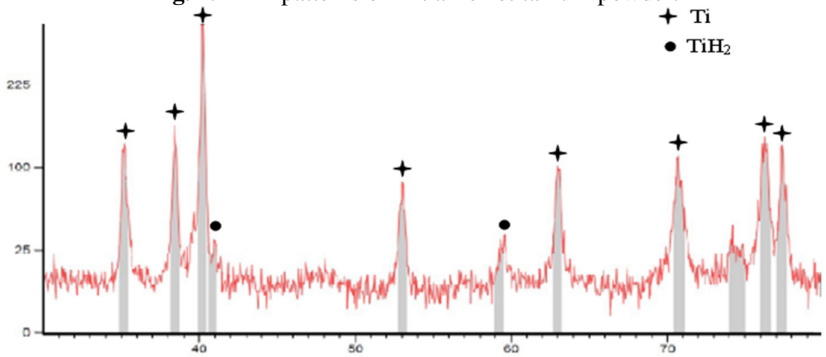

Fig. 2. XRD patterns of initial titanium powder.

After 6 h of milling, under nitrogen atmosphere with the pressure of 5atm, a sample containing 100% pure Ti powder was completely converted to TiN. X-ray diffraction pattern of the sample 1 is shown in **Fig. 3**. As can be seen, TiN peaks are clearly visible. There is also an Iron peak in this pattern. The emergence of this peak is probably due to the wear of milling balls.

SEM micrograph of sample 1 is shown in **Fig. 4**. As can be seen, the TiN produced powder contains particles <200nm in diameter that have been agglomerated. Milling of samples 2 and 3 has been done for 5 and 10 h in nitrogen atmosphere with the pressure of 5 atm. Titanium and Ferrotitanium have been used in these 2 samples. The X-ray diffraction pattern of sample 2 is shown in **Fig. 5**. As can be observed, after 5 h of milling, TiN related peaks are clearly detectable, but the two peaks of Iron oxide and Titanium are also visible in this pattern.The TiN Peaks are broad because of the reduction in the grains size and lattice strain. According to the studies of milling experiments, the amount of Nitrogen in the cup is not sufficient for a complete reaction; therefore, sample No. 3 was prepared for further examination and the milling chamber was filled 2 times with Nitrogen.X-ray diffraction pattern of this sample is shown in **Fig. 6**. As can be seen, the complete conversion of Titanium to TiN occurs after 10 h of milling. This figure only includes peaks of titanium nitride. It is worth noting that the produced Nitride has more prominent and higher peaks. This can be because of the recharging of the cup with nitrogen under the pressure of 5 atm or increasing the milling time. According to this figure, iron peak has been removed as compared with X-ray diffraction diagram of the raw material. Removing the iron peak can be due to the formation of solid solution with nitrogen, or its amorphous state.

Comparing **Fig. 5** and **6** shows that as the milling time is increased, the TiN peak intensity is increased and the peaks get sharper.

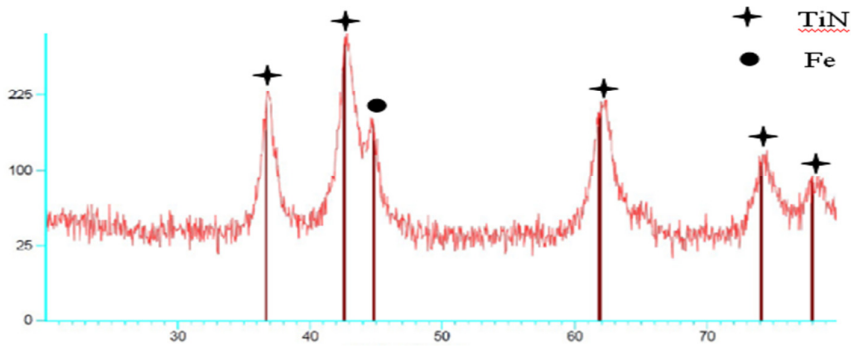

Fig. 3. XRD patterns of sample No.1 (6 h of milling).

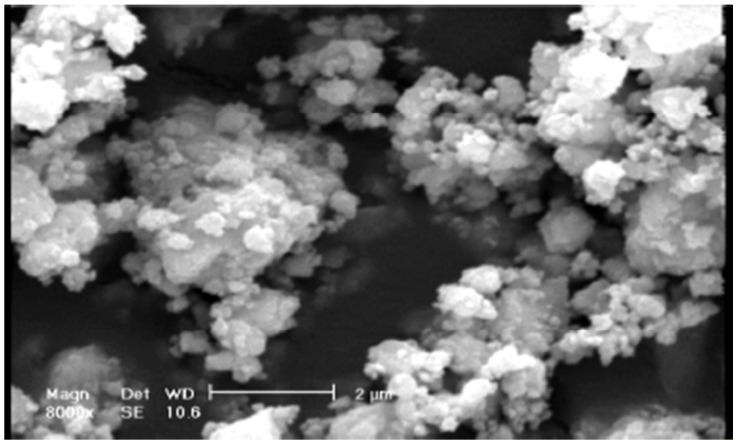

Fig. 4. Morphology of sample1 (Milled for 6 h).

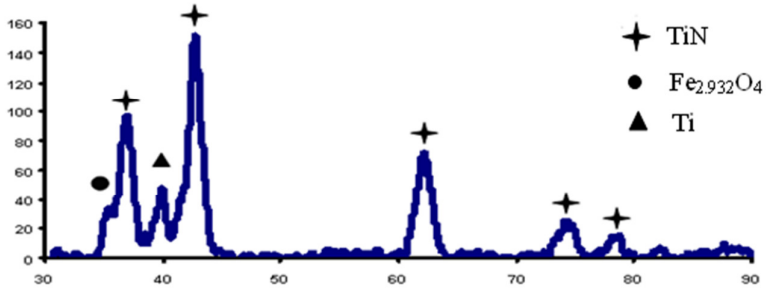

Fig. 5. XRD patterns of sample 2 (Milled for 5 h).

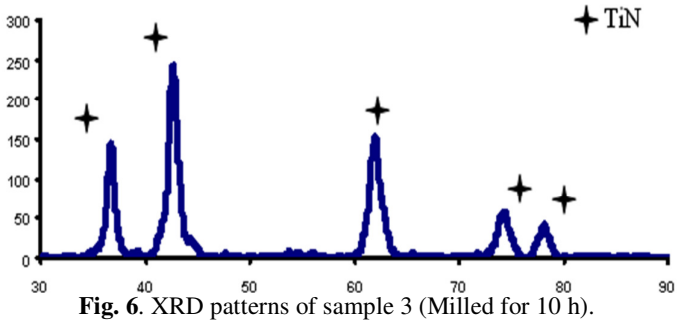

Fig. 6. XRD patterns of sample 3 (Milled for 10 h).

Morphology of sample 3 is shown in **Fig. 7**. X-ray diffraction pattern of samples 4 and 5 is shown in **Fig.8** and **9**. The use of carbon in these two cases was because of the reaction excitation. As a result of the reaction between Ferrotitanium and graphite, a very exothermic reaction occurs, and the amount of heat accelerates the reaction with N_2. Also, the Carbon penetrated in the lattice of titanium nitride, which was formed due to the reaction of Ferrotitanium with the existing nitrogen gas in the cup and at the end, Titanium Carbonitride is formed. As can be seen in the Fig**.** 8, after 5 h of milling, weak peaks of titanium carbonitride are visible. A strong peak of titanium can also be seen in this pattern. This indicates that the milling time for complete conversion of titanium to titanium carbonitride is not enough. **Fig. 9** shows X-ray diffraction pattern of sample 5 after 10 h of milling. Diffraction spectra of titanium carbonitride are detectable in this figure. The titanium peak has been completely removed as compared with **Fig. 8**, and there are sharper peaks of titanium carbonitride. As mentioned earlier, this event was predictable given the increase in the milling time and recharge of the cup of nitrogen. Morphology of sample 5 is shown in **Fig. 10**.

Atomic radius of Carbon and Nitrogen are 0.78 and 0.74 Å, respectively. According to **Fig. 9**, 10 h of milling leads to the production of Titanium Carbonitride with $TiN_{0.7}C_{0.3}$ formula. In comparison with **Fig. 6**, the peaks have shifted to the left. So it can be concluded that with continuing milling, as the balls are forced into the powder particles, carbon atoms could be placed in the titanium lattice with a larger radius than nitrogen atoms. The lattice will be expanded, and the peaks of titanium nitride move to the lower angels and Ti-N-C solid solution is formed. The crystallites size measured by Williamson-Hall method is shown in **Table2**. It indicates a significant reduction in grains size to less than 2 nm. It is shown that in Williamson-Hall method, strain zones adjacent to the grain boundaries in nanostructured materials cannot be identified. Therefore, due to the strains of grain boundary, size of the grains is determined smaller than their actual size [10].

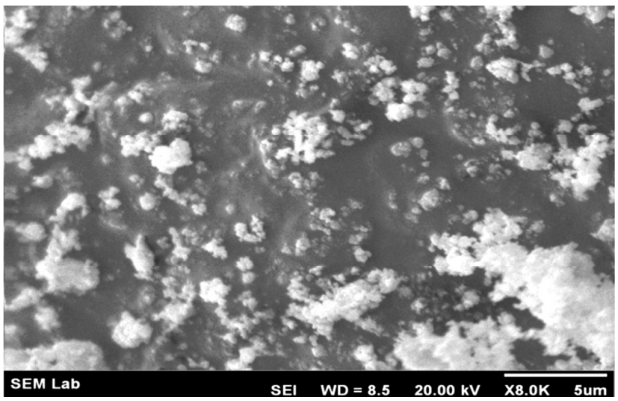

Fig. 7. Morphology of sample3 (Milled for 10 h).

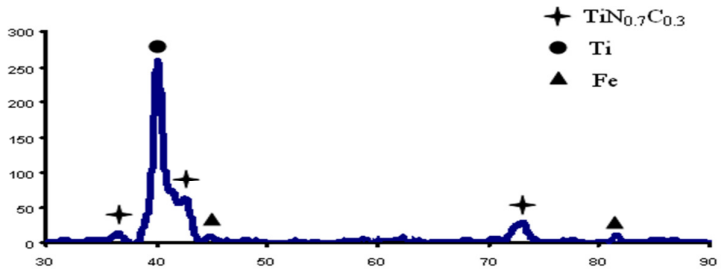

Fig. 8. XRD patterns of sample 4 (Milled for 5 h).

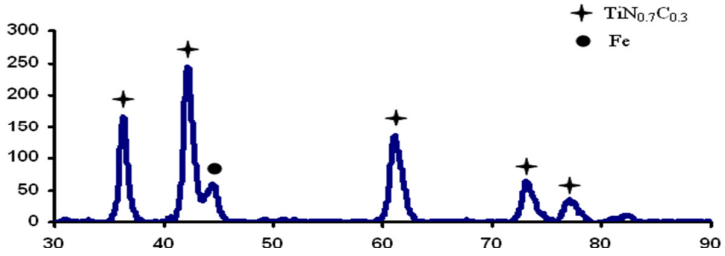

Fig. 9. XRD patterns of sample 5 (Milled for 10 h)

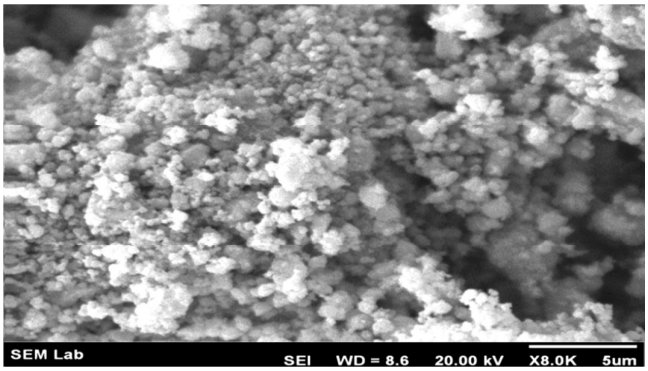

Fig. 10. Morphology of sample5 (Milled for 10 h).

According to **Table 2**, a slight increase in grains size is seen with increasing alloying time to 10 h. Both Stoichiometric titanium nitride and titanium carbonitride crystal lattice are FCC. In cubic structures, lattice parameter can be calculated from the following equation:

$$a = \frac{\lambda \sqrt{h^2 + k^2 + l^2}}{2 \sin \theta}$$

In this equation, α is the lattice parameter, λ is the X-ray wavelength, (*hkl*) are Miller indices of crystal plates, and θ is the diffraction angel. Lattice parameter of titanium nitride and titanium carbonitride was determined using the above equation. As shown in **Table 2**, the lattice parameter of TiN is less than its stoichiometric value (0.4242 nm), indicating that the produced titanium nitride is not stoichiometric. Comparison between lattice parameter of sample 2 and 3 shows that with increasing the milling time and recharging the cup with 5atm nitrogen, the lattice parameter is significantly increased. The lattice parameter of sample 5 is higher than the stoichiometric value. This may be related to the existence of carbon with a larger atomic size in the titanium nitride lattice, which has increased titanium nitride lattice parameter.

Table 2. lattice profile.

sample	grain size (nm)	lattice strain (%)	Lattice parametr (nm)
2	1.37	0.48	0.3410
3	1.75	0.40	0.4233
4	1.33	0.21	0.4234
5	1.81	0.48	0.4291

Conclusions

1- Production of Fe-TiN composite powder, using titanium raw material with mechanical alloying method is possible, and the minimum timeofmillingfortheproductionofTiNis6h

2- Both Titanium and Ferrotitanium have been used to determine the titanium effect. The minimum time for producing titanium nitride is 5 h, but continuing milling to 10 h will complete the reaction between N_2 and Ti.

3- It is possible to produce Fe-Ti(N,C) composite with mechanical alloying method, under nitrogen pressure of 5 atm, and with the minimum time of 10 h. With increasing the time of milling and recharging the cup with nitrogen, the peaks will be more pronounced and sharper. Also, the lattice parameter will be higher than the stoichiometric value. This is because of the existence of carbon atoms in the titanium nitride lattice.

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