SYNTHESIS AND CHARACTERIZATION OF TiB_2 NANOCRYSTALLINE POWDER BY MECHANICAL ALLOYING

MAHBOOBEH MOALLEM

*Department of Materials Engineering, Isfahan University of Technology,
Isfahan, 84156-83111, Iran
m.moallem@ma.iut.ac.ir*

MOHAMMAD HASAN ABBASI

*Department of Materials Engineering, Isfahan University of Technology,
Isfahan, 84156-83111, Iran
Abbasi32@cc.iut.ac.ir*

FATHOLLAH KARIM ZADEH

*Department of Materials Engineering, Isfahan University of Technology,
Isfahan, 84156-83111, Iran
Karimzadeh-f@cc.iut.ac.ir*

In this investigation, TiB_2 nanocrystalline powder was synthesized by mechanical alloying of the elemental mixture of Ti and B powders in argon atmosphere. In order to study the structural evolution of the powder during ball milling, X-Ray diffraction (XRD) and scanning electron microscopy (SEM) were used. Adiabatic temperature calculations were performed for characterization of TiB_2 powder. Also, the effects of heat treatment on the structural evolution and thermal stability of mechanically alloyed powders were investigated. It was found from the XRD patterns that TiB_2 was formed via combustion mechanism. By increasing milling time, the grain size decreased while the lattice strain increased. SEM micrographs showed that TiB_2 particles were spherical. The grain size and lattice strain reached 24 nm and 1.8% respectively, after 60 hours ball milling.

Keywords: TiB_2 , nanocrystalline, Mechanical alloying.

1. Introduction

Nowadays, nanostructured materials have attracted scientist's attention because of their exceptional mechanical properties such as high hardness, strength, diffusivity, specific heat, ductility and toughness, and low elastic modulus. One of these materials is TiB_2 ¹⁻⁴. TiB_2 has been widely used in various industrial fields due to properties such as high melting point (2970 °C), thermal diffusivity, hardness, electro-conductibility, excellent refractory properties and chemical inertness. It has been generally fabricated by reduction of TiO_2 and B_2O_3 with active metals and carbon via self-propagating high temperature

synthesis. Because of high reaction temperature, the grain growth rate of TiB₂ is rapid. So this temperature has unavoidable effect on its' properties. It is mostly used as reinforcement in composites and cladding ². There are different methods for producing nanocrystalline materials. MA is an easy way for producing high melting point compounds. Compared to the energy consuming reduction processes, one of the advantages of this method is that it's a simple method for producing nanocrystalline materials at room temperature ⁵. In this process, nanometer sized grain structures can be obtained in metals, intermetallic compounds, composites, and ceramics. In the MA of metal compounds, the produced powder with a final composition corresponding to the initial composition is developed through the repeated cold welding and fracturing of the starting powder ⁶.

Several methods have been used for producing TiB₂, until now. Generally, transition metal borides are usually synthesized by the reduction of Boron oxide with metal oxides and Carbon at high temperature. TiB₂ as a transition metal boride has been synthesized by the reduction of TiO₂ and B₂O₃ with Carbon and active metals, and self-propagating high-temperature synthesis ⁶.

Several research works have been performed to show the formation mechanism of TiB₂ in recent years, but they are not in a good agreement. For example, Wming et al. produced TiB₂ nanostructured powder by mechanical alloying and introduced a gradual diffusion reaction mechanism ⁶, while Hwang et al. prognosticated it as a combustion reaction ⁷.

In the present study, MA process is used to produce TiB₂ nanocrystalline powder via elemental powders of Ti and B, and the formation mechanism of TiB₂ is extracted. The influence of heat treatment on the thermal stability and structure of mechanically alloyed powder is studied too.

2. Experimental

The elemental powders of Ti (purity > 99 %) and B (purity > 99 %) were combined with stoichiometric composition. Raw materials were mechanically alloyed in a planetary ball mill (Fritsch p7 type) under argon atmosphere (99.999% purity). The applied Argon, was high purity to stop the formation of TiN during milling. The steel vial was hardened steel with 150 ml volume that was filled with five steel balls of 20 mm diameter. The experiments were carried out at room temperature. Ball milling was done with ball-to-powder mass ratio of 15:1 and rotation speed of 500 rpm. About 50 mg of sample were taken for X-ray diffraction (XRD) investigation, after 0, 10, 12, 15, 20, 40, 60 hours of ball milling. Structural changes and phase transformation of powders during ball milling and following heat treatment were studied by X-ray diffraction (XRD) in a Philips Diffractometer (40kV) with Cu α radiation ($\lambda=0.15406$ nm). Crystallite size and lattice strain in the ball milled samples were calculated from the broadening of XRD peaks using Williamson-Hall equation ⁸. The morphology of 20 and 60 hours ball milled powders was considered by scanning electron microscopy (SEM) in a philips XL30 at an

accelerating voltage of 30kV. Heat treatment of 20 hours ball milled powder was performed in a conventional tube furnace under Argon atmosphere for 1 hour in 1000°C.

3. Results and discussion

Fig. 1 shows the XRD patterns of TiB_2 powder mixture as-received and after different milling times. XRD pattern of powder mixture up to 12 hours of milling was identified as a mixture of boron (B) and titanium (Ti) indicating that ball milling up to 12 hours did not have any influence on as-received powder mixture except broadening of Bragg peaks caused by reduction of the crystallite size as well as microstrain induced in the powder particles.

Fig. 1. XRD patterns taken from the Ti-B mixture milled for different hours.

Decreasing the crystallite size to nanometer range and increasing the defect densities can propagate the reaction kinetically by providing short-circuit diffusion paths⁹. Because of the lower intensity of boron peaks compared to titanium, B peaks in the initial raw materials are not shown completely and after 5 hours of ball milling, B peaks are disappeared. After 12 hours ball milling, Ti and B peaks are completely disappeared and TiB_2 peaks are appeared.

During ball milling the temperature of vial was measured by pyrometer and it was illustrated that the temperature increased rapidly after 12 hours of milling. This could be an indication of a combustion reaction between elemental B and Ti. Variation of vial temperature during MA is illustrated in fig. 2.

Fig. 2. Variation of vial temperature during MA.

In a self-propagating combustion reaction in a thermally ignited system, when adiabatic temperature, T_{ad} , is above 1800K, a combustion reaction occurs¹⁰. Meanwhile, the minimum temperature that is required for the happening of self-propagating combustion reaction during ball milling, T_{ad} , can be changed^{11, 12}. The value of T_{ad} is calculated using equation 1:

$$Q = (-\Delta H_{298}) = \int_{298}^{T_{ad}} \sum C_p (\text{Products}) dT \quad (1)$$

Where Q is the heat of reaction, ΔH_{298}° is the Enthalpy changes at 298 K and C_p is the heat capacities of products. Calculation of T_{ad} for the reaction was carried out. For this reaction T_{ad} is 3200K which is an indication of a combustion reaction mechanism.

The crystallite size and lattice strain of powders were calculated using the Williamson-Hall method according to equation 2¹³.

$$B \cos \theta = 0.9 \lambda / D + 2\varepsilon \sin \theta \quad (2)$$

Where B is the peak width at half maximum intensity, λ is the wave length of X-ray used, D the average crystallite size, θ is the Bragg angle and ε is the average lattice strain. Crystallite size and lattice strain of Ti-B powder are shown in fig 3 at several MA times.

Fig. 3. Crystallite size and lattice strain of Ti-B powder at several MA times.

In the early stages of MA, powder grain size decreased sharply due to the predominance of the fracturing of powder particles over the cold welding process.

Figs. 4 and 5 show the SEM images of B and Ti as initial raw materials. Ti particles had a sponge structure and B powder was polyhedral in shape. The size distribution of B and Ti were in a wide range below 500 and 400 μm , respectively.

Fig. 4. SEM micrographs of initial B powder particles.

Fig. 5. SEM micrographs of initial Ti powder particles

Figs. 6 and 7 are the SEM images of the powder after 20 and 60 hours of milling, which shows agglomeration of particles. The shape of the starting powder after 20 hours became semi-spherical. The powder particle size is in a wide range below 600 nm. After 60 hours of milling the particles are spherical too. As a result of fracturing, the powder's size became finer with the size distribution below 500 nm, but the composition and phase did not changed.

The powder particles after 60 hours of milling were agglomerates of ultrafine particles ranging from 600 to about 50 nm.

Fig. 6. SEM micrographs of powder particles after 20 h of milling at different magnifications.

Fig. 7. SEM micrographs of powder particles after 60 h of milling at different magnifications.

Nanocrystalline structures are thermodynamically unstable because of the large excess free energy stored in their grain boundaries. Significant grain growth was observed in several nanocrystalline materials^{14, 15}. Fig 8 shows the XRD patterns of samples milled for 20 hours and then annealed for 1 h at 1000°C. TiB_2 crystallite size remained in nanometer range, and no changes occurred in phase composition after annealing. Only the peak's intensity increased and the peak's broadening reduced. The reason is due to stress releasing as well as grain growth. In the milled powder, as the lattice deformation is high, and lattice ordering degree is low, so, the powder is in non-equilibrium state¹⁶.

During the heat treatment of milled powder, the decreasing of lattice deformation and increasing of lattice ordering degree is occurred. So, the high lattice deformation energy acted as the driving force for the grain growth of TiB_2 in the milled powder. If the annealing temperature (1000°C) is more than $0.3T_m$ (T_m : melting Temperature of TiB_2), recrystallization occurs causing the release of internal strain and grain growth. As in this case it's not more than $0.3T_m$, grains did not grow very much. Because of grain growth, lattice distortion and lattice ordering degree changes, which can affect the XRD peaks.

Fig. 8. The XRD patterns of Ti-B (a) milled for 20 h and (b) after subsequent annealing at 1000°C for 1 h.

4. Conclusions

The following conclusions can be drawn from the present study;

- 1) TiB_2 nanostructure particles can be synthesized from Ti and B elemental powders by mechanical alloying.
- 2) The formation mechanism of TiB_2 by mechanical alloying is a combustion type which is predictable using adiabatic temperature criteria.
- 3) The annealing process for 1h at 1000°C does not have much effect on grain growth which shows a stable structure.
- 4) Scanning electron microscopy used for 20 and 60 hours milled powder shows a wide range of particle size below 500 nm.

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