Effects of Mechanical Alloying on Microstructure and Microhardness of Nanocrystalline NiTi Shape Memory Alloy

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Received: 11 January 2012, Revised: 26 February 2012, Accepted: 9 June 2012

Abstract: In this work, nanostructured NiTi shape memory alloy with equal atomic percentage was produced through mechanical alloying. The result exhibited that after 60 h of mechanical alloying of high purity elemental powder mixtures of nickel and titanium by a planetary high-energy ball mill, the Ti dissolved into Ni lattice and NiTi (B2) phase was obtained. The XRD investigations, SEM observations, TEM examinations and microhardness results concluded that this method is a powerful and high productive process for preparing NiTi shape memory alloy with nanocrystalline structure and appropriate morphology.

Keywords: Annealing, Mechanical alloying, Nanostructure, NiTi Shape Memory Alloy

Reference: Ghadimi, M., and Shokuhfar, A., "Effects of mechanical alloying on microstructure and microhardness of nanocrystalline NiTi shape memory alloy", Int J of Advanced Design and Manufacturing Technology, Vol. 5/ No. 5, 2012, pp. 25-29.

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1 INTRODUCTION

Nickel–Titanium alloy near the equi-atomic concentration is well known for its shape memory effect (SME), and also its unique mechanical and physical properties, such as good ductility at ambient temperature, good vibration damping properties, long fatigue life and corrosion properties in sea water. Shape memory behavior of this alloy is due to thermo-elastic martensitic transformation from austenitic (B2 body centered cubic) to martensitic (B19′ body monoclinic) structure [1-4].

NiTi is readily available in the form of powder, wire, rod, and bar stock with transformation temperature in the range of 173 to 373 K. More recently applications in Micro-Electro-Mechanical-Systems (MEMS) have led to the development of NiTi in the form of sputter deposited thin film [5-7].

Shape memory materials are made by well-known methods related to melting and casting. These methods are high energy consuming and imply difficulties in control of the processed alloy composition [1-7].

In order to obtain inexpensive products, researchers have been focused on nearly synthesis method in efforts to establish to optimum production route and to obtain materials with improved properties.

Mechanical alloying (MA) has attracted wide practical interest as it offers a useful method to fabrication alloys and compounds with nanometric structure and suitable morphology. Nanocrystalline materials exhibit increased mechanical strength, enhanced diffusivity and other valuable properties in comparison to conventional coarse-grained polycrystalline materials.

In this technique, powders are entrapped between balls and also, balls and wall and the impact force of the collision transfers to them. Therefore, powders undergo a severe plastic deformation, which causes a strain rate of $10s^{-1}$ and, therefore, repeated cold welding and fracturing of powders lead to formation of alloyed powders [8-11].

The purpose of this research is to evaluate the formation of nanocrystalline NiTi alloy during milling process. Meanwhile, the effects of milling time and annealing on crystallite size, phase composition and morphological changes will be studied.

2 PROCEDURE FOR PAPER SUBMISSION

Ni and Ti elemental powders with purity of 99.5% were used as starting materials. Fig. 1(a and b) shows scanning electron microscopy micrographs of the elemental Ti and Ni powder particles, respectively. The Ti particles had an irregular shape with a size distribution of 45 μm. Ni particles were nearly uniform in size (~10 μm) with a spherical morphology. Mechanical alloying was carried out in a planetary ball mill. The ball and bowl materials were hardened steel. In all MA runs the ball to powder weight ratio was 10:1 and the bowl rotation speed was approximately 300 rpm. Ni and Ti powder mixtures with composition of Ni50Al50 (in terms of atomic percentages) were milled under Ar atmosphere nominally at room temperature. Structural changes of powder particles were studied by X-ray diffraction (XRD) in a Philips X'PERT diffractometer using 'Cu', 'K', 'α' radiation (λ= 0.1504 nm).

The powder particles morphology was observed by scanning electron microscopy (SEM) in a Philips at an acceleration voltage of 30kV with an energy-dispersive X-ray spectrometer (EDX) attachment and transmission electron microscopy (TEM) operating at 80kV in a Zeiss. The powder-cell and image 'J' software packages were used for indexing of formed phases and measurement of particles size, respectively.

The hardness of powder particles was also determined by microhardness test using a Vickers indenter at a load of 100g and dwell time of 10s. For measurement of microhardness, a small amount of powder particles was mounted.

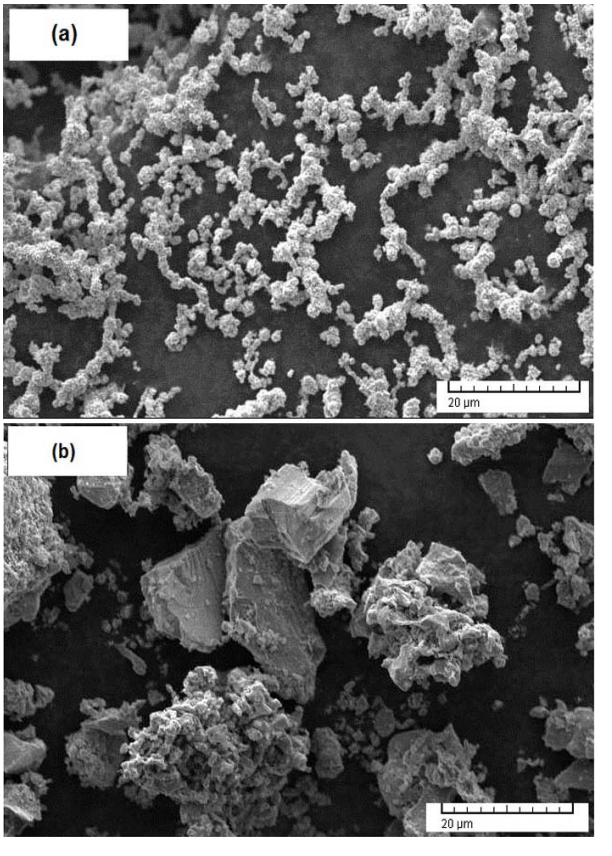

Fig. 1 SEM images of initial powders: (a) Ni and (b) Ti

3 RESULT AND DISCUSSION

Figure 2 shows XRD diffraction patterns of Ni-Ti milled powders at various milling times. As can be seen in the figure, the peaks related to raw materials can be seen in starting materials. The intensity of Ni and Ti diffraction peaks decreased and gradually weakened and broadened during milling. The weakening of Ni and Ti peaks and the move of Ni peaks toward lower angels indicated that Ti atoms diffused in the Ni lattice. After 40 h milling, the Ni peaks varnished completely and only broadened NiTi (B2) peaks with a body centered cubic structure were identified. The broadening of the NiTi peaks is considered to be due to the refinement effect of crystallite size.

The crystallite size of powders was calculated using XRD peak broadening and Williamson–Hall formula as follows [11]:

$$\sqrt{B_i^2 - B_0^2}\cos\theta = 0.89\lambda/d + 2e\sin\theta \quad (1)$$

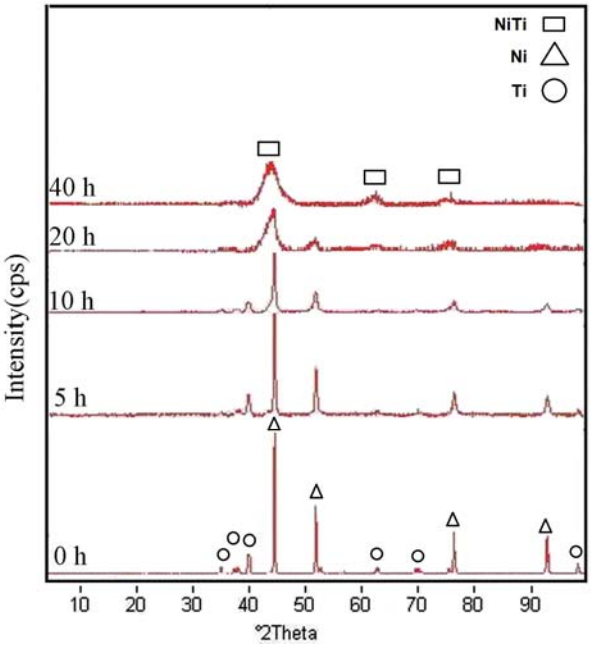

Fig. 2 XRD diffraction patterns of powders at several milling times

where 'B_i' is the peak full-width at the half of the maximum intensity of XRD patterns (FWHM), 'B_0' is the correction factor for instrument broadening, 'θ' is the Bragg angle, 'λ' is the wavelength of the X-ray used, 'd' is the crystallite size and e is the lattice strain. Using Eq. (1), for each peak a point is made on a diagram with $\sqrt{B_i^2 - B_0^2}\cos\theta$ and $\sin\theta$ axis. Then a linear function is fitted to the diagram, in which case, slope of the function would be 'd'.

Variations in the crystallite sizes versus milling time are shown in Fig. 3. Based on this figure, crystallite size initially decreased sharply with prolonged milling time. This effect is attributed to the formation of high density of dislocations during milling and consequently formation of sub-grain structure. The formation of sub-grains is due to the decrease of the atomic level strain. Further ball milling time leads to excess deformation occurring in the shear bands located in the unstrained parts of the powders which leads to sub-grain size reduction.

Thus, the orientation of final grains becomes random in crystallographic orientations of the numerous grains and hence, the direction of slip varies from one grain to another [9-11]. Finally, with enough longer times, milling was observed to have no considerable effect on crystallite size. On further milling, grain size almost did not change and became constant due to the balance between rate of cold welding and fracturing of powders particles. After 60 h milling, crystallite size of milled powders reduced to 23 nm.

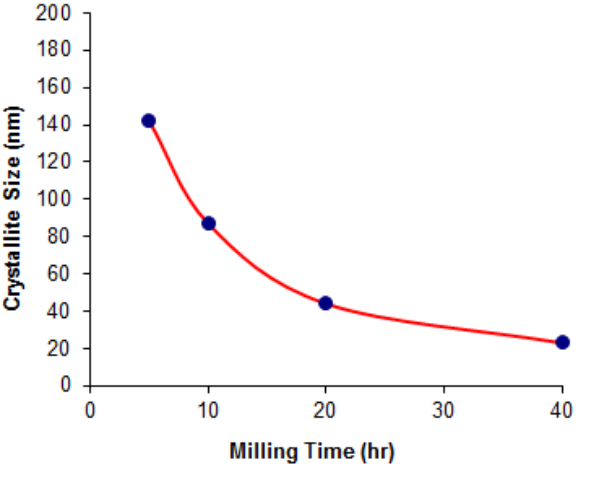

Fig. 3 Crystallite size of mixture powders at diffraction milling times

The SEM micrograph of milled powders after several milling was shown in Fig. 4. As can be seen in the figure, at the beginning of MA process, a lamellar structure was observed, because of continuous cold welding between laminate during ball milling of ductile particle (Fig. 4a). Increasing milling time up to 40h led to refinement of layered microstructure and therefore formation of very fine microstructure comprise alternative 'Ni' and 'Ti' layers due to the repeated cold welding and fracturing of powder particles. Formation

of this microstructure with very faceted interface between layers and also decrease in thickness of layers with increasing milling time promote the interaction between layers, and finally led to the formation of homogenous microstructure at longer milling times (Fig. 4b).

The size of particles decreases with longer MA time because increase in brittleness leads to formation of smaller particles with granular shape. On the other hand, the repeated processes of cold welding and fracturing result in formation of an agglomerations consisting of nanosized Ni and Ti particles. According to EDX analysis, specimen had homogeneous structure after 40h milling, which was in good agreement with the nominal composition of compound. On the other hand, elemental dispersion of Ni and Ti is satisfactory, and Ti distributed into Ni matrix, which confirms homogeneous structure formation (Fig. 4c).

Fig. 5 displays TEM image of as-milled powders after 60h. It is shown that the morphology of the particles is globular, and the morphology and size of particles becomes more uniform. The average microhardness values of powder particles at different MA times are shown in Fig. 6. In the initial stages of MA, a drastic increase in microhardness is observed. Formation of NiTi intermetallic is responsible for considerable increase in microhardness after 1h of MA. With the progress of MA, microhardness gradually increases due to the formation of fine crystalline grains and high density of defects in the powder. The microhardness for produced alloy after 60h of MA was measured to be about 961HV which is significantly higher than ~350 HV reported in the literatures.

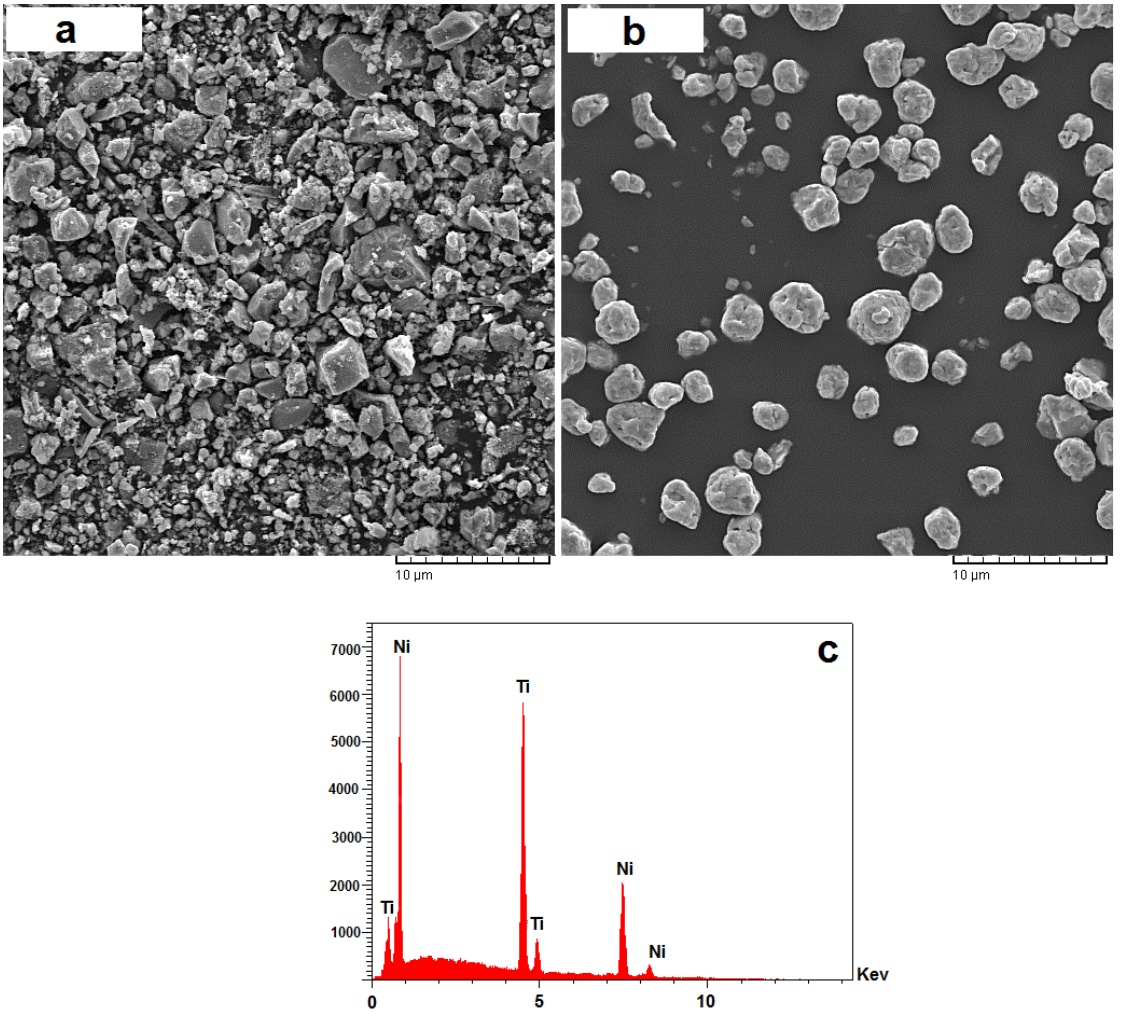

Fig. 4 SEM images of milled powders after: (a) 10h and (b) 40h milling, and (C) EDS spectrum of sample b

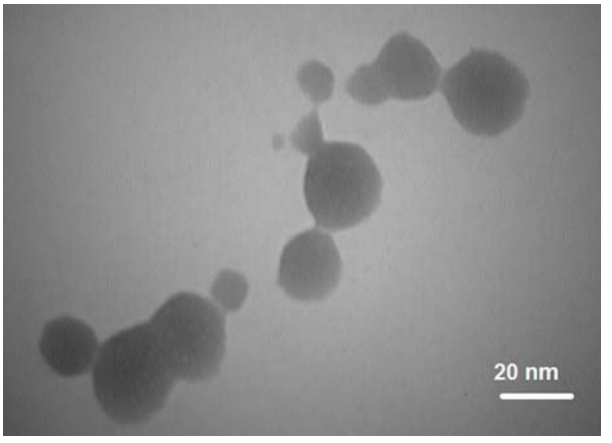

Fig. 5 TEM images from of as-milled powders after 60h in two different magnifications

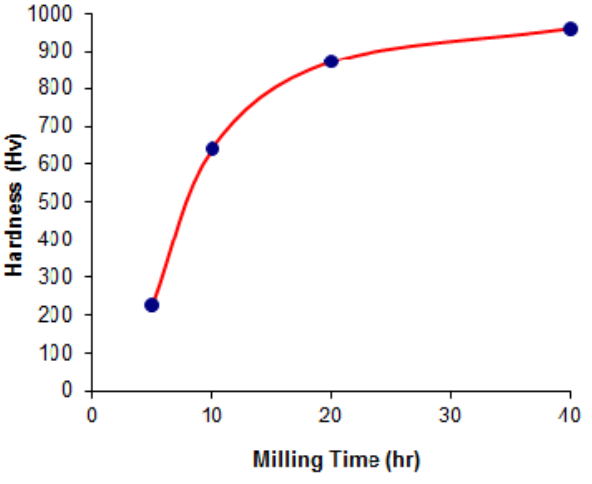

Fig. 6 Micro hardness values of NiTi alloy as a function of milling time

4 CONCLUSION

Based on the results obtained from the research and experiments used in the present work, the following conclusions can be inferred:

1- Nanocrystalline NiTi was successfully synthesized directly from Ni and Ti microsize powders using high energy ball milling process.

2- TEM observation indicated that morphology and particle size distribution are uniform and particles have a globe-like morphology with an average diameter of about 23 nm after 40h milling.

3- The Fabricated alloy exhibited a high microhardness value of about 961Hv.

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