Amorphization in Ni-Ti-Ta system through mechanical alloying

SRIKANTH KANCHIBHOTLA, NORMAN MUNROE*, TRICHI KARTIKEYAN
Department of Mechanical and Materials Engineering, Florida International University, 10555 W Flagler St., Miami, FL 33174, USA
E-mail: munroen@fiu.edu

In recent years, advances have been made in synthesizing amorphous alloys with superior properties via solid-state reactions as opposed to traditional rapid solidification techniques [1, 2] because of improved properties of the alloys produced by the former techniques. Of the many solid-state reaction techniques, mechanical alloying (MA) has proven to be a simple yet very effective technique for producing amorphous alloys. Ever since the amorphization in mechanically alloyed $Ni_{60}Nb_{40}$ powder mixture was achieved by Koch [3], the technique has been widely applied for various binary systems. However, amorphization in ternary alloys have hardly been studied [4–7]. The reason being, a lack of proper understanding of the process and variation of the products with subtle changes in the process parameters.

Mechanical alloying of both Ni-Ti and Ni-Ta systems has been studied extensively [2, 8–11], but no attempt has been made on mechanical alloying of the ternary Ni-Ti-Ta system. Ta, added as a ternary element in the NiTi-alloys has been proven to impart radiopassity, thermal stability, etc. [12, 13]. Hence in this research, an attempt has been made to study the amorphous phase formation in the $(Ni_{51}Ti_{49})_{1-x}Ta_x$ system in the range of 0–20 at.% Ta through mechanical alloying.

Pure powders (99.9%) of Ni, Ti and Ta with particle sizes less than 45 μm (-320 mesh) were mixed under inert argon atmosphere according to the formula $(Ni_{51}Ti_{49})_{1-x}Ta_x$ ($x = 0, 2, 4, 10, 15, 20$). All powder mixtures were subjected to high-energy ball milling (HEBM) in a SPEX 8000 mill. A ball to powder ratio (BPR) of 10:1 was maintained with stainless steel balls of two diameters (0.5 in. and 0.25 in.) as grinding medium. All powder mixtures were initially milled for 0.5 hr and then powders with Ta at 4 and 20 at.% were subjected to 24 hrs of milling to study the process of amorphization in the system.

Microstructural analysis to assess the overall physical particle size variation and interlayer thickness of the alloyed particles with milling time was performed using a scanning electron microscope (SEM). Phase transformation during the process of amorphization was performed using a Bruker Axis transmission powder diffractometer with Mo-Kα radiation (0.71073Å). In order to conduct both microstructure and phase analyses, a small amount of powdered mixture was withdrawn from the vial at intermittent milling time intervals.

The average physical particle size variation with milling time is illustrated in Fig. 1. It was observed that the average particle size increased to about 1200 μm (about 25 times the starting size of the individual elemental particles) with milling up to about one hr. This drastic increase in size during the initial stages of milling is attributed to agglomeration or welding of particles, which is prevalent in the initial stages due to high surface energy of the fine particles. Subsequent to 1 h of milling, the particle size gradually decreased to about 20 μm (about half the initial starting size of the individual elemental particle) due to fracture and strain hardening until about 16 hrs, after which the particle size is expected to remain the same due to the equilibrium between cold welding and fracturing.

Figs 2a and b illustrate the variation of interlayer thickness for 4 at.% Ta powder mixture milled for 0.5 hr and 2 hrs. It can be observed that the layer thickness almost reduced to nanometer range with just 2 hrs of milling. Also, the clarity with which the layers were observed in Fig. 2a was not observed in Fig. 2b. No significant image was obtained for powders milled at times greater than 2 hrs.

The process of amorphization was studied by subjecting the milled powders to XRD at regular milling times. The XRD patterns for the powder mixtures (with Ta at 0, 2, 4, 10, 15, 20 at.%) milled for 0.5 hr (see Fig. 3a) indicated a predictable format in the sense that the peaks corresponding to Ta increased with the increase in the percentage of Ta in the powder mixture while the corresponding peaks for Ni and Ti decreased proportionately. Therefore, only two compositions of 4 and 20 at.% Ta, both in the extremes of the range considered (0–20 at.%) were chosen for studying the process of amorphization in the system.

During MA, destabilization of the crystalline phase is thought to occur by the accumulation of structural defects such as vacancies, dislocations, grain boundaries, and anti-phase boundaries. The continuous decrease in grain size (and consequent increase in grain boundary area) and a lattice expansion contribute to an increase in free energy of the system [14] to a level greater than that of the crystalline phase. This

---

[*] Author to whom all correspondence should be addressed.

0022-2461

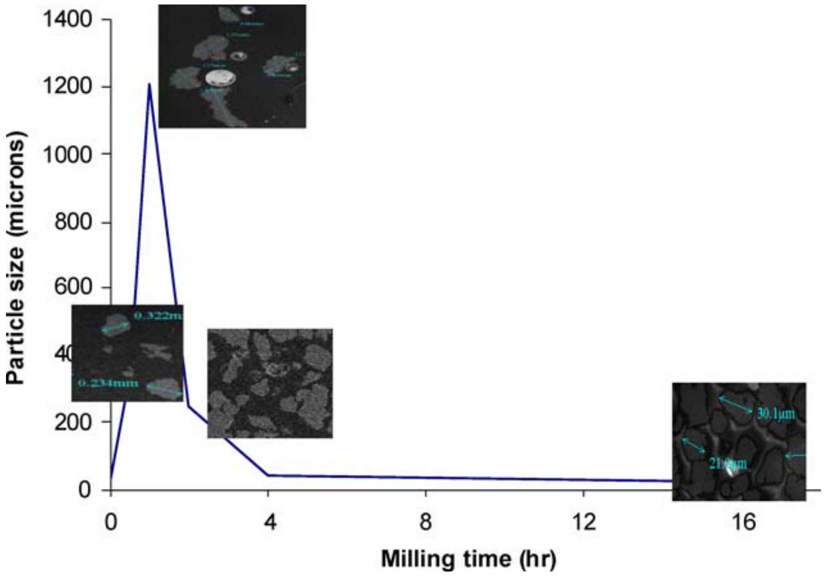

Figure 1 Variation of average particle size with milling time for powder mixture containing 4 at.% Ta.

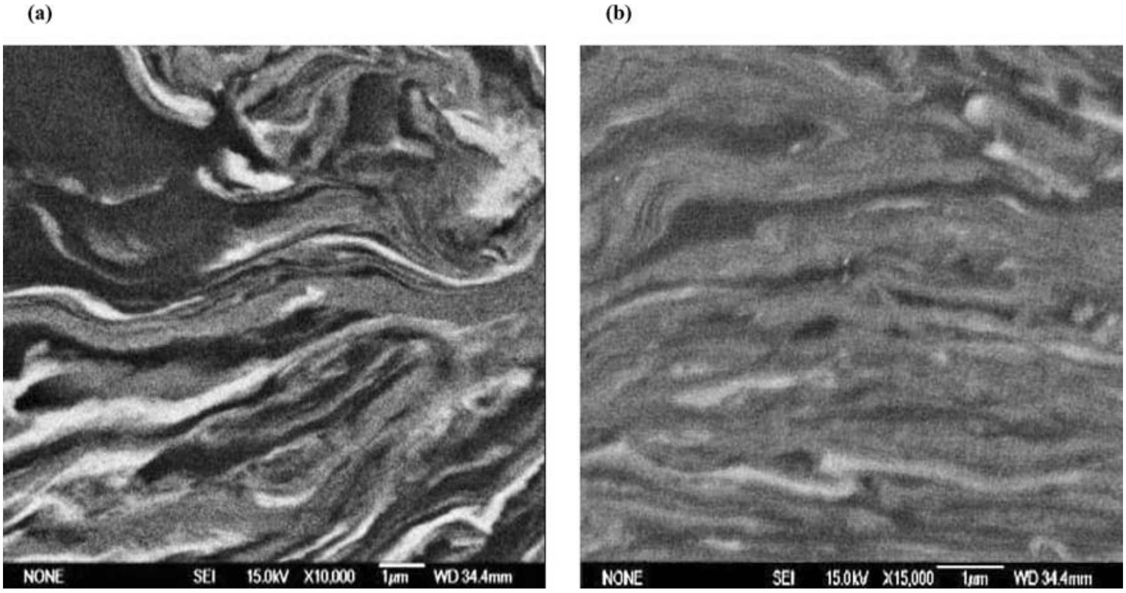

Figure 2 Interlamellar distance with varying milling time for powder mixture containing 4 at.% Ta. (a) 0.5 hr. (b) 2 hrs.

facilitates the formation of an amorphous phase. Figs 3b and c illustrate the process of amorphization in the Ni-Ti-Ta system at the two chosen compositions of 4 and 20 at.% Ta.

A very peculiar phenomenon of recrystallization (after amorphization) was observed in powder mixture containing 20 at.% Ta after 16 hrs of milling (see Fig. 3c). The peaks corresponding to the recrystallization were observed on the left side of both primary and secondary amorphous peaks, which can be clearly seen in the XRD pattern of the powder milled for 24 hrs (see Fig. 3d). The recrystallzied phase was tentatively identified as binary $NiTa_2$. However, more research, which is in progress, is required to further establish this phase.

The crystallite size of the individual elements was determined from the peak broadening of the X-ray diffraction peaks using the Scherrer formula [15]. In order to precisely measure the full width at half maximum (FWHM), the curve fitting software, DatLab was used to fit a pseudovoigts function to the major peak of each individual element.

Fig. 4 depicts the crystallite size variation of the individual elements as a function of tantalum content for the powder mixtures milled for 0.5 hr. The crystallite size variation format was identical for all three elements. It was observed that the crystallite sizes of both Ni and Ti were almost similar at any given

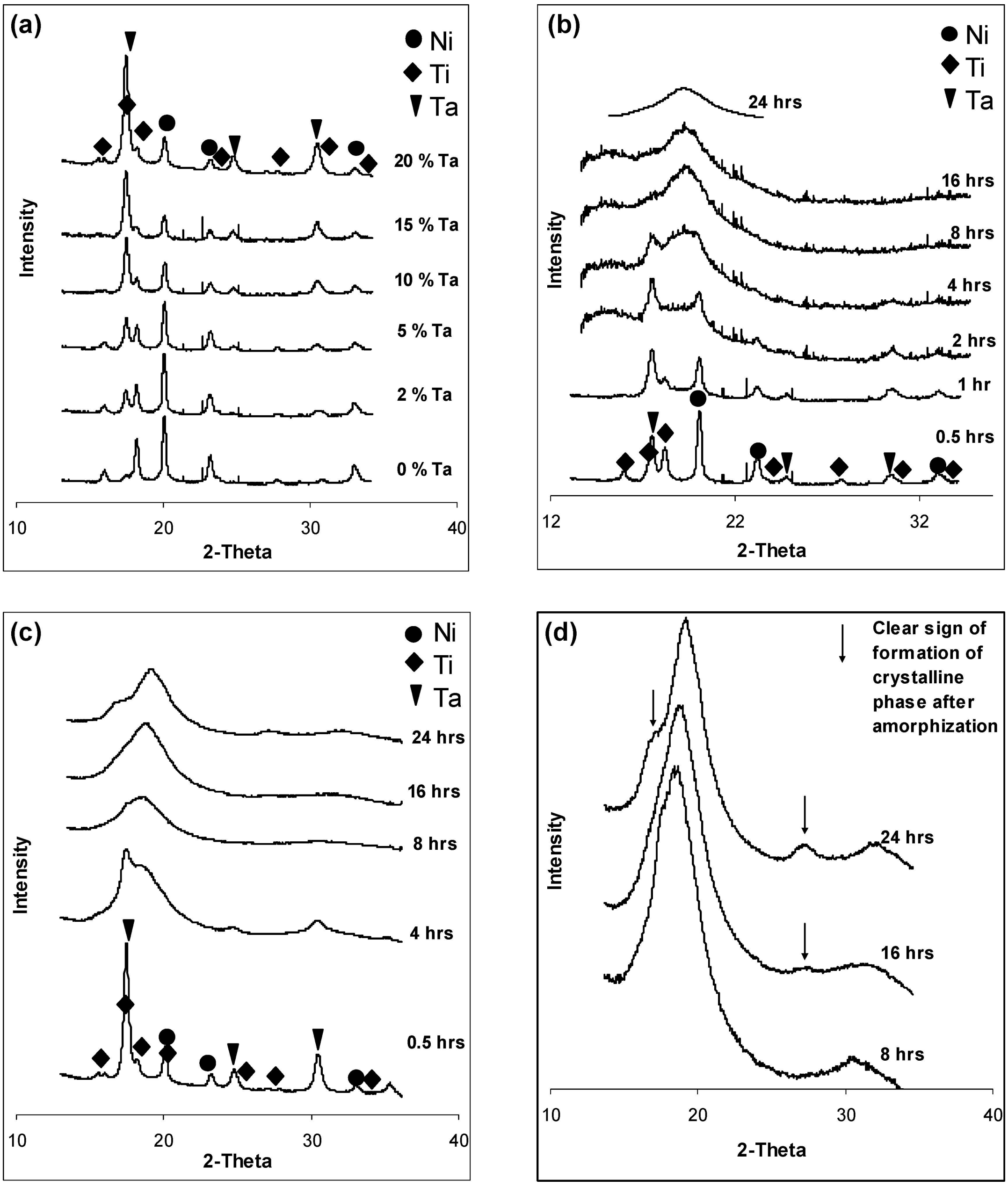

Figure 3 X-Ray diffraction spectra of powdered mixtures. (a) 0.5 hr milled powder mixtures with Ta varying from 0-20 at.%. (b) 4 at.% Ta powder mixture as a function of milling time. (c) 20 at.% Ta powder mixture as a function of milling time. (d) 20 at.% Ta powder mixture indicating a new crystalline phase formation.

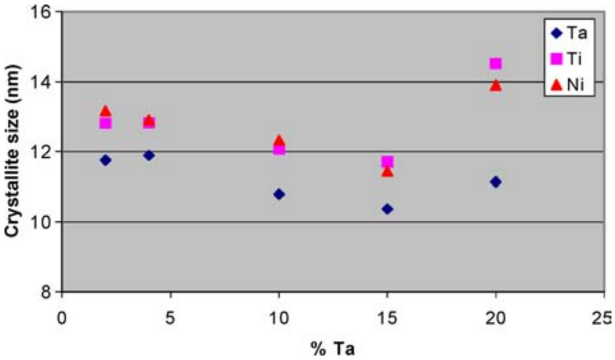

Figure 4 Elemental crystallite size variations with Ta content in powders milled for half hour.

percentage of Ta (Ta being the element with the lowest concentration).

Fig. 5a and b illustrate the variation of crystallite size of Ta with milling time for powder mixtures containing 4 and 20 at.% Ta, respectively. The crystallite size varied logarithmically with milling time. For both compositions, the crystallite size reduced from 12 nm to about 6 nm with just 4 hr of milling.

In conclusion, amorphization in $(\mathrm{Ni}_{51}\mathrm{Ti}_{49})_{1-x}\mathrm{Ta}_x$ system for compositions of 4 and 20 at.% Ta was achieved through mechanical alloying after 16 hrs of milling. However, since $\mathrm{Ni}_{51}\mathrm{Ti}_{49}$ has been proven in the literature to exhibit amorphization [2], and the results of this investigation indicated that various compositions milled for a shorter time (see Fig. 3a) showed a predictable format, it is anticipated that amorphization would occur through out the range from 0–20 at.% Ta. Also, a unique phenomenon of recrystallization after amorphization started to appear in alloy mixture with 20 at.% Ta after 16 hrs of milling.

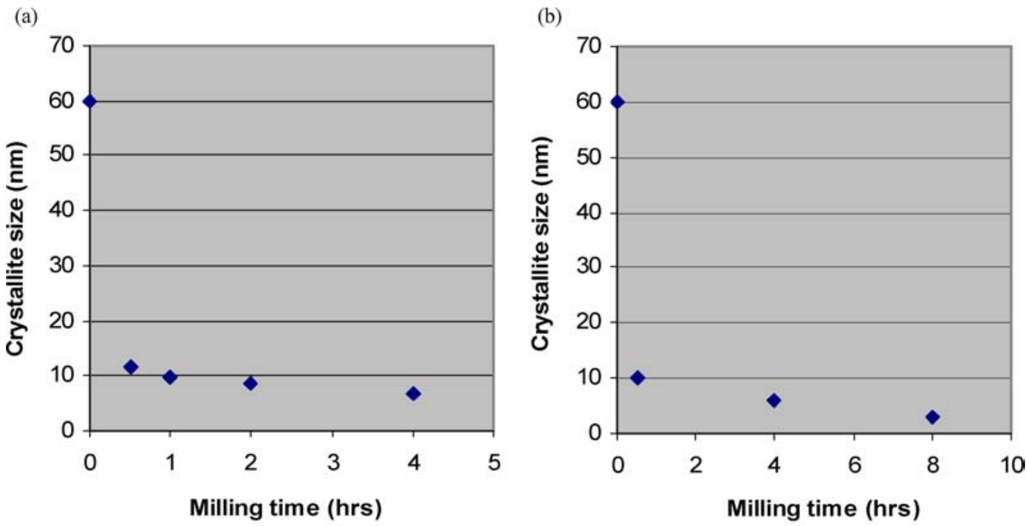

Figure 5 Crystallite size variation of Ta with milling time. (a) 4 at.% Ta powder mixture. (b) 20 at.% Ta powder mixture.

References

1. P. DUWEZ, R. H. WILLENS and W. KLEMENT JR, *J. Appl. Phys.* **31** (1960) 1136.
2. R. B. SCHWARZ, R.R. PETRICH and C. K. SAW, *J. Non-Crystalline Solids* **76** (1985) 281.
3. C. KOCH, O. B. CAVIN, C. G. MCKAMEY and J. O. SCARBROUGH, *Appl. Phys. Lett.* **43** (1983) 1017.
4. B. S. MURTHY, M. MOHAN RAO and S. RANGANATHAN, *Scripta Metallurgica et Materialia.* **24** (1990) 1819.
5. C. POLITIS, *Physica* **135B** (1985) 286.
6. K. MATSUKI, A. INOUE, H.M KIMURA and T. MASUMOTO, *Mater. Sci. Eng.* **97** (1988) 45.
7. R. SUNDERASEN, A. G. JACKSON, S. KRISHNA MURTHY and F. H. FROES, *Mater. Sci. Eng.* **97** (1988) 1115.
8. G. COCCO, S. ENZO, L. SCHIFFINI and L. BATTEZZATI, *ibid.* **97** (1988) 43–46.
9. Y. L. PEE, J. L. YANG and H. M. LIN, *J. Mater. Sci.* **33** (1) (1998) 235.
10. T. SELL and H. MEHRER,*Zeitschrift fur Metallkunde*, **88**, (11) (1997) 842.
11. G. F. PROKOSHINA, O. K. BELOUSOV, *Russian Metallurgy* **6** (1989).
12. J. L. MA, *Masters Thesis*, Florida International University, 1999.
13. S. KANCHIBHOTLA, *Masters Thesis, Florida International University*, 2004.
14. E. GAFFET, F. FAUDOT and M. HARMELIN, *Mater. Sci. Forum*, **88–90** (1992) 375.
15. B. D. CULLITY, in Elements of X-Ray Diffraction, 2nd Ed. (Addison Wesley Publishing Company, Reading, MA, 1978).

Received 28 October 2004
and accepted 14 March 2005