

Characteristics of the mechanically-alloyed Ni₆₀Ti₄₀ amorphous powders during mechanical milling in different atmospheres

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Mechanically alloyed Ni₆₀Ti₄₀ amorphous powders were further milled in argon, nitrogen and oxygen atmospheres. X-ray diffraction, differential scanning calorimetry and transmission electron microscopy analyses were made to investigate the structural changes during each process. No distinguishable structural changes during further milling of the amorphous powders in argon or nitrogen atmospheres were observed. However, in an oxygen atmosphere, the amorphous phase was crystallized into intermetallic compounds and was accompanied by the occurrence of titanium oxides in the initial stage. On further milling in an oxygen atmosphere, the intermetallic compounds decomposed and only the nickel saturation solution and titanium oxides remained. A thermodynamic explanation of the crystallization and decomposition has been proposed.

1. Introduction

Within the last few years interest has focused on the preparation of amorphous alloys by mechanical alloying. Starting from elemental crystalline powders, a large number of alloy systems, for example Ni–Nb [1], Ni–Ti [2] and several transition metal–Zr systems [3], have been investigated. In general, the milling is performed in an inert gas atmosphere in order to avoid the oxidation of powders. Koch *et al.* [1] prepared amorphous Ni₆₀Nb₄₀ by mechanical alloying of the elemental powders in air and helium atmospheres. The crystallization features and the positions of the maximum of the principal peak in the X-ray diffraction pattern differed, due to the different oxygen concentrations in the alloys. Mizutani and Lee [4] have studied the effect of excessive mechanical alloying on glass formation by continuing ball-milling beyond the completion of the glass formation for the Ni–Zr powders. A partial crystallization took place which was attributed to the oxygen contamination and other impurities. However, no detailed reason was given.

In a previous work [5], we reported the influence of milling atmosphere on the mechanical alloying of elemental Ni₆₀Ti₄₀ powders. The results showed that the intermetallic compound Ni₃Ti and titanium oxides appeared when the powders were milled in an argon atmosphere and subsequently milled in an oxygen atmosphere. More recently, we reported [6] the effect of the atmosphere on further milling of the mechanically alloyed Ni₆₀Ti₄₀ amorphous powders. Here we report in detail the characteristics of mechan-

ically alloyed amorphous Ni₆₀Ti₄₀ powders after further milling in different atmospheres.

2. Experimental procedure

The mechanically alloyed amorphous Ni₆₀Ti₄₀ powders were prepared by mechanically alloying elemental nickel (99.8%, average size 20 μm) and titanium (99.8%, average size 10 μm) powders in an argon atmosphere for 20 h (for details see [5]). Furthermore, the amorphous Ni₆₀Ti₄₀ powders were further milled in argon, nitrogen and oxygen atmospheres. The samples were characterized by X-ray diffraction (XRD) using a Rigaku X-ray powder diffractometer in reflection geometry with CuK_α radiation (λ = 0.154 nm) and transmission electron microscopy (TEM) with a Philips EM420. Specimens for TEM were collected on a copper grid. Differential scanning calorimetric (DSC) measurements were carried out using a Perkin–Elmer DSC 2 system. The heating was done in a sealed gold pan with a heating rate of 20 °C min⁻¹ under a flow of purified argon. The amounts of the gas elements adsorbed by the powder particles during milling were determined by chemical analysis.

3. Results

3.1. Further milling in argon or nitrogen atmospheres

Fig. 1a shows the XRD pattern of Ni₆₀Ti₄₀ elemental powder mixtures milled for 20 h in argon gas. A typical broad maximum of the amorphous phase shows up in the diffraction pattern. This indicates that

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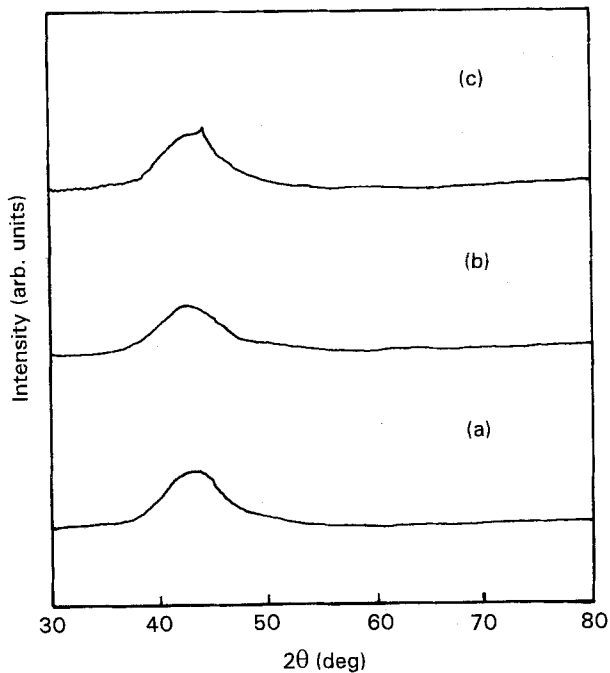


Figure 1 X-ray diffraction patterns of (a) $\text{Ni}_{60}\text{Ti}_{40}$ milled for 20 h in argon gas (Sample A); (b) Sample A further milled for 12 h in argon gas and (c) Sample A further milled for 12 h in nitrogen gas.

the amorphous phase was obtained after mechanical alloying for 20 h in argon gas. The amorphous powders (Sample A) were further milled in argon or nitrogen atmospheres. No further structural changes in the XRD pattern occurred when the amorphous powders were further milled for 12 h in argon gas (see Fig. 1b). There were also no distinguishable structural changes in the XRD patterns when the amorphous powders were further milled for 12 h in nitrogen gas (see Fig. 1c). The nitrogen content increased from 0.23 wt % in the amorphous powders to about 0.80 wt % in the powders further milled for 12 h in nitrogen.

Fig. 2a shows the DSC curve of $\text{Ni}_{60}\text{Ti}_{40}$ powder mixtures after milling for 20 h in argon. Two exothermic peaks can be seen corresponding to the crystallization which occurred. The broader exothermic signal around 470 °C can be attributed to the formation of the amorphous phase in incompletely reacted parts of the sample. The exothermic peak at high temperature can be attributed to the crystallization of amorphous $\text{Ni}_{60}\text{Ti}_{40}$ phase. The DSC result is in good agreement with Buschow's report [7] on the crystallization of melt-spun amorphous $\text{Ni}_{58}\text{Ti}_{42}$ ribbons. For the powders further milled for 12 h in argon, the DSC curve exhibits almost no distinguishable change compared to the curve shown in Fig. 2a (see Fig. 2b). However, the exothermic signal around 470 °C almost disappeared. This indicates that further mechanical milling results in complete formation of the amorphous phase. For the powders further milled for 12 h in nitrogen, the positions of the DSC peaks remain almost unchanged, but the exothermic peak at high temperature exhibits some broadening (see Fig. 2c). The nitrogen atoms adsorbed on newly created surfaces on the powder particles will be adsorbed into the particles by diffusion down many defects. As the ni-

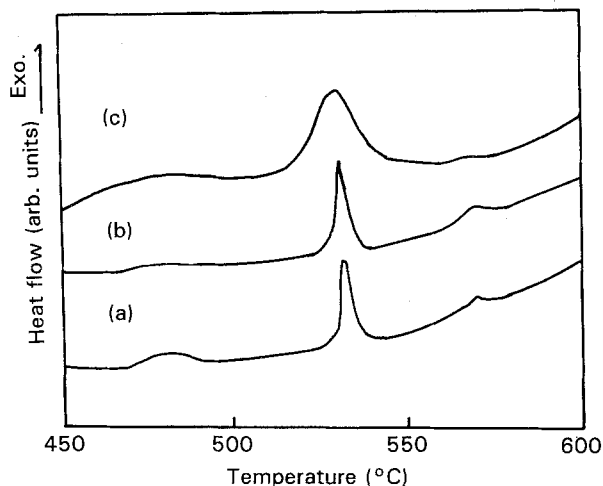


Figure 2 DSC curves of the as-milled powders: (a) $\text{Ni}_{60}\text{Ti}_{40}$ milled for 20 h in argon gas (Sample A); (b) Sample A further milled for 12 h in argon gas, and (c) Sample A further milled for 12 h in nitrogen gas.

trogen atoms are absorbed into the amorphous powders, and the materials may become brittle, the tendency for cold weld decreases, while the rate of fracture increases. Thus, the broadening of the DSC curve (see Fig. 2c) may be due to the surface effect of powder particles and the changes of composition of the amorphous phase.

3.2. Further milling in an oxygen atmosphere

Fig. 3 shows the X-ray diffraction patterns of amorphous $\text{Ni}_{60}\text{Ti}_{40}$ powders which were further milled in oxygen for different milling times. The oxygen contents of as-milled powders are shown in Fig. 4. After milling for 2 h and 4 h, the X-ray diffraction patterns of the powders showed no distinguishable changes, compared with the pattern shown in Fig. 1a (see Fig. 3a and b). The oxygen content increased to about 2.1 wt % O after milling for 4 h (see Fig. 4). The oxygen atoms may be absorbed in the amorphous powder particles. Compared with the previous work [5], the powders milled for 6 h in argon (partial amorphous phase) were also further milled in oxygen for 2 h. The oxygen content increased from 0.3 wt % to about 4.9 wt %. This means that the resistance to oxidation of the amorphous powders is higher than that of the partially amorphous powders. After further milling of the amorphous powders in oxygen for up to 8 h (accumulative), it was surprising to find that the amorphous phase had almost crystallized (see Fig. 3c). The intermetallic compounds Ni_3Ti and Ti_2Ni appeared. The nickel saturation solution, as well as titanium oxides (TiO_2 and Ti_2O_3) also appeared. Further milling in oxygen for up to 12 h (accumulative) produced only nickel saturation solution and titanium oxide (TiO_2) (see Fig. 3d). From this result, we can infer that the crystallization and decomposition occurred during further milling of the amorphous $\text{Ni}_{60}\text{Ti}_{40}$ powders in oxygen.

Fig. 5 shows the TEM image of amorphous powder milled in oxygen gas for 4 h. The existence of amorph-

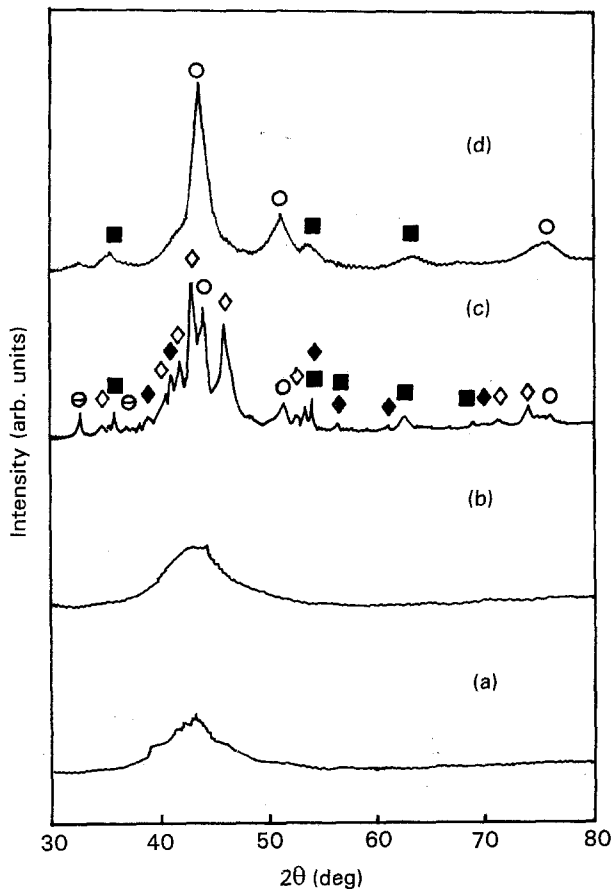


Figure 3 X-ray diffraction patterns of Sample A further milled in oxygen gas for (a) 2 h, (b) 4 h, (c) 8 h and (d) 12 h. (○) Ni, (◇) Ni_3Ti , (◆) Ti_2Ni , (■) TiO_2 and (⊖) Ti_2O_3 .

ous phase can be clearly seen. From the TEM image, particles with very small size can be seen in the amorphous matrix. These may be the oxides of titanium or nickel. However, from the XRD and TEM diffraction patterns, the existence of these oxides cannot be determined. Polk *et al.* [8] reported the effect of oxygen upon the glass-forming ability, the glass transition behaviour, the ductility of the glasses and their crystallization products. For the $\text{Zr}_{0.50-x/2}\text{Cu}_{50-x/2}\text{O}_x$ alloys, glasses were obtained with up to 8 at% oxygen using the arc-melting quench unit. However, for the $\text{Ti}_{0.667}\text{Ni}_{0.333}$ alloys, repeated attempts to produce fully amorphous Ti-Ni-O samples containing even only 1 or 2 at% oxygen by using the arc-melting quench unit were unsuccessful. In the present case, we can obtain the amorphous Ti-Ni phase which contains some amounts of oxygen (less than 2.1 wt % O).

DSC measurements were also taken in order to characterize the thermal properties of the amorphous $\text{Ni}_{60}\text{Ti}_{40}$ powders which contain different oxygen contents. For the powders further milled for 2 h in oxygen, the DSC peaks were similar to that of the as-milled amorphous $\text{Ni}_{60}\text{Ti}_{40}$ powders (see Fig. 6a), indicating that there is no influence on the thermal behaviour of amorphous powders by an increase of the oxygen content up to 1.4 wt %. For powders further milled for 4 h in oxygen, the DSC curve exhibits an obvious change (see Fig. 6b). The first exothermic peak at low temperature in Fig. 6b can be attributed to the crystallization of amorphous phase, which is similar to the

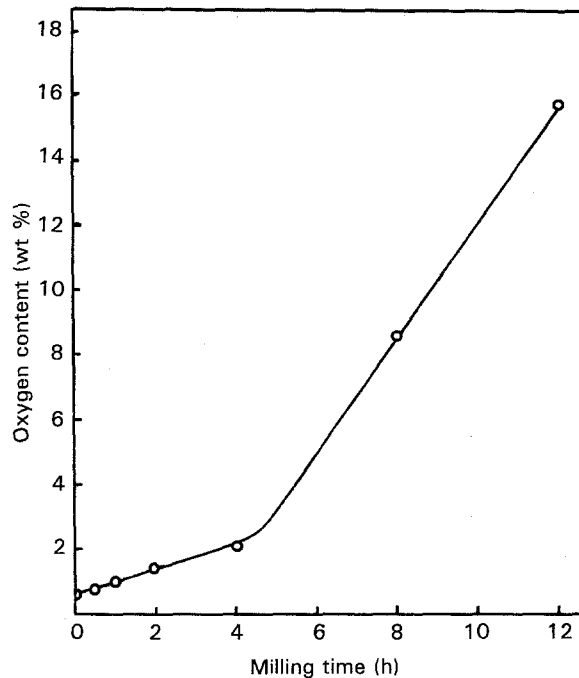


Figure 4 The oxygen content in $\text{Ni}_{60}\text{Ti}_{40}$ powders (Sample A) milled in oxygen gas, plotted as a function of milling times.

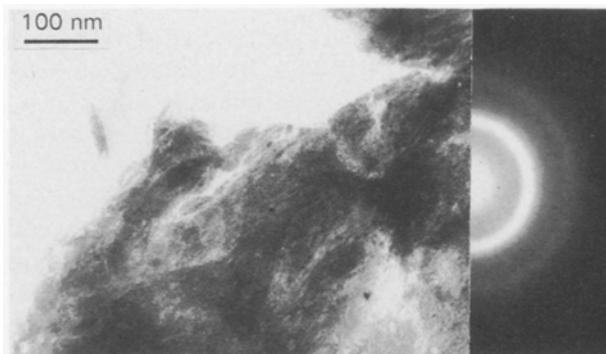


Figure 5 JEM images of Sample A further milled in oxygen for 4 h.

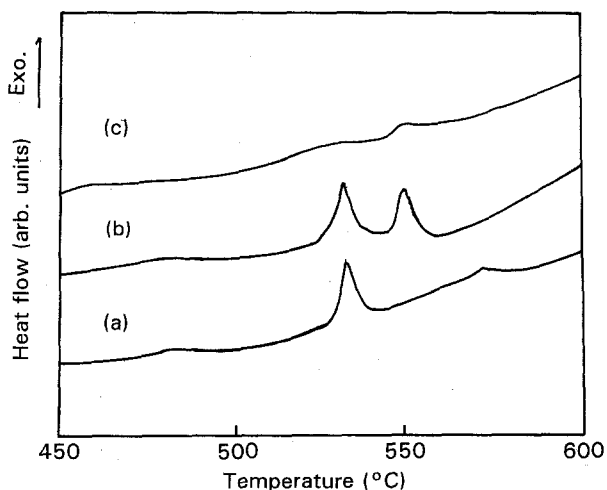


Figure 6 DSC curves of Sample A further milled in oxygen gas for (a) 2 h, (b) 4 h and (c) 8 h.

amorphous phase free of oxygen. The second exothermic peak at high temperature in Fig. 6b may be attributable to the oxidation reaction due to the existence of some amount of oxygen atoms. For powders

further milled for 8 h in oxygen, there is almost no exothermal peak in the DSC curve (see Fig. 6c). This indicates that the amorphous phase almost crystallized. The result is in good agreement with the XRD results.

4. Discussion

From the above DSC results, it can be seen that the exothermic peak corresponding to the crystallization of the amorphous phase does not shift to a lower temperature with increasing oxygen content. Thus the thermal stability of the milled amorphous $\text{Ni}_{60}\text{Ti}_{40}$ powders cannot be affected by the oxygen content (less than 1.4 wt % O).

Bakker *et al.* [9] reported results for ball milling of crystalline alloys containing zirconium or lanthanum as one of the components. Some of these alloys amorphize (Ni-Zr, Co-Zr, V-Zr, Pd-Zr and La-Au), and some seem to decompose into the constituent elements (Cr-Zr, La-Ag, La-Co and La-Ni). They concluded that these phenomena contributed to the high energy (50 kJ mol^{-1}) introduced by the ball milling.

In our experiments, the structure shows no change during further milling for 12 h in argon (see Fig. 1b). The enthalpy of formation of the amorphous phase is 31 kJ mol^{-1} [2]. Thus the increase of enthalpy is about 30 kJ mol^{-1} in our apparatus under the present experimental milling conditions. Therefore, the amorphous phase cannot be crystallized or decomposed by the energy introduced by the apparatus under these milling conditions. In the case of nitrogen, no traces of nitrides of nickel or titanium were found in the XRD pattern, indicating that the nitrogen was adsorbed by the surfaces of the amorphous powder particles and that no nitrogenation of nickel and titanium occurred during milling.

In the case of oxygen, the condition is different from that above in argon or nitrogen gas. It is common knowledge that the crystallinity value obtained by X-ray analysis is $4\% \pm 3\%$ at the limit of detection. For amorphous $\text{Ni}_{60}\text{Ti}_{40}$ powders milled for 20 h in argon gas, some amount of unreacted crystalline nickel and titanium in the as-milled powder is found. Owing to the inhomogeneity of composition during mechanical milling, the surfaces of one part of the amorphous powders may be enriched in titanium. The oxygen atoms were adsorbed in the surface of amorphous powder particles or the surface of unreacted titanium powder particles during the first few hours of milling (up to 4 h). With increasing milling time (up to 8 h), oxygen atoms adsorbed on newly created surfaces on the powder particles will be absorbed into the particles by diffusion down many defects. Owing to the high local reaction temperature and newly created surfaces during collision, the oxygen will react with the titanium. Oxidation reaction will release a large amount of heat which will introduce some amount of energy. The oxygen content of powders further milled for 8 h in oxygen is about 8.6 wt % O (see Fig. 4). The following assumption can be made: one part of oxygen is adsorbed in the intermetallic compounds and nickel saturation solu-

tion; another part of the oxygen reacts with titanium, which is determined to be 6.0 wt % O, and exists as oxides. A crude estimation can be given as follows: the mole fraction of oxides (TiO_m , $1.5 \leq m \leq 2$, $m = 1.75$) is taken to be x , that of the powder matrix ($\text{Ni}_{60}\text{Ti}_{40}$) to be $(1 - x)$. Thus, the mole fraction of the oxides is calculated to be 0.089 in the final powders.

The enthalpies of formation of TiO_2 and Ti_2O_3 are -943.8 and $-759.7 \text{ kJ mol}^{-1}$ [10], respectively. The average enthalpy of formation is $-851.75 \text{ kJ mol}^{-1}$ and the mole fraction of oxides in the final powders is 0.089. Thus, the average heat released due to oxidation can be estimated as $-75.8 \text{ kJ mol}^{-1}$. As mentioned above, the increase in enthalpy is about 30 kJ mol^{-1} in our apparatus under the present experimental conditions. The average enthalpy during the milling process in oxygen gas may reach 100 kJ mol^{-1} . This may lead to crystallization of the amorphous phase due to a rise of the actual temperature during milling to values above the crystallization temperature. The crystallized products of amorphous $\text{Ni}_{60}\text{Ti}_{40}$ alloy obtained by melt spinning are Ni_3Ti and NiTi phases in sequence [11]. However, no existence of NiTi phase can be seen in Fig. 3c. From the Ni-Ti phase diagram [12], we suggest that the NiTi phase may demix into Ni_3Ti and Ti_2Ni phases due to a rise of the actual temperature. The nickel saturation solution may also be obtained by demixing of Ni_3Ti or Ti_2Ni phases due to a rise of local temperature. After further milling in oxygen gas for up to 12 h, nickel saturation solution as well as titanium oxides can be seen. Thus we can infer that the crystalline alloys Ni_3Ti and Ti_2Ni decomposed into the constituent elements due to the high energy introduced by the oxidation of titanium. Because of the reaction of titanium with the oxygen, the existence of elemental titanium cannot be found.

5. Conclusion

We can conclude that the structure exhibits no distinguishable change when the amorphous $\text{Ni}_{60}\text{Ti}_{40}$ powders were further milled in argon or nitrogen atmospheres. When the amorphous powders were further milled in oxygen, however, the amorphous phase crystallized into intermetallic compounds and subsequently decomposed into the constituent elements due to the heat released during the oxidation reaction between titanium and oxygen.

Acknowledgement

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References

1. C. C. KOCH, O. B. CAVIN, C. G. McKAMEY and J. O. SCARBROUGH, *Appl. Phys. Lett.* **43** (1983) 1017.
2. R. B. SCHWARZ, C. K. PETRICH and C. K. SAW, *J. Non-Cryst. Solids* **76** (1985) 281.
3. E. BELLSTERN and L. SCHULTZ, *Appl. Phys. Lett.* **48** (1986) 124.
4. U. MIZUTANI and C. H. LEE, *J. Mater. Sci.* **25** (1990) 399.

5. K. Y. WANG, T. D. SHEN, J. T. WANG and M. X. QUAN, *Scripta Metall. Mater.* **25** (1991) 2227.
6. *Idem*, *J. Mater. Sci. Lett.* **11** (1992) 1170.
7. K. H. J. BUSCHOW, *J. Phys.* **F13** (1984) 563.
8. D. E. POLK, C. E. DUBE AND B. C. GIESSEN, in "Proceedings of the Third International Conference on Rapidly Quenched Metals", edited by B. Cantor (Metals Society, Brighton, UK, 1978) p. 220.
9. H. BAKKER, P. I. LOEFF and A. W. WEEBER, *Defect Diffus. Forum* **66-69** (1989) 395.
10. R. C. WEAST, "CRC Handbook of Chemistry and Physics", 63rd Edn (CRC, Boca Raton, FL) p. D-92.
11. A. J. JANICKI and P. J. GRUNDY, *J. Phys. D Appl. Phys.* **19** (1986) L49.
12. M. HANSEN and K. ANDERKO, "Constitution of Binary Alloys" (McGraw-Hill, New York, 1958) p. 1049.

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