FORMATION OF AMORPHOUS Ni-Ti ALLOY BY MECHANICAL ALLOYING①

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ABSTRACT

$Ni_xTi_{(100-x)}$ ($x=10\sim70$) alloys have been prepared by mechanical alloying of elemental titanium and nickel powders. X-ray diffraction, SEM and TEM were used to characterize structural changes of Ni50Ti50 milled powders. The crystallite size, microstrain and lattice parameter of nickel crystals were measured as a function of milling time, and DSC was used to examine the thermal properties of Ni50Ti50 milled powders. It is found that Ni_xTi_{100-x} can be amorphized with $40\leqslant x\leqslant60$.

Key words: mechanical alloying Ni-Ti alloys amorphization

1 INTRODUCTION

In recent years, mechanical alloying technique has been used to prepare amorphous alloys[1], quasicrystalline alloys[2], nano-meter size crystals[3] and intermetallic compounds[4]. This solid state reaction technique for synthesizing new materials attracts much attention at home and abroad. Ni-Ti alloys can be used as hydrogen storage and shape memory alloys, so synthesis of Ni-Ti alloy from elemental titanium and nickel powders by mechanical alloying was widely studied[5-7], but the relationship between structural changes of milled powders and amorphization process was still unclear for this alloy system. Here we chose ball mill elemental Ni and Ti mixtures to investigate structural changes of powders and the amorphization process.

2 EXPERIMENTAL PROCEDURES

Pure elemental nickel powders (99.9%, ~4 μm)and titanium powders (99.5%, ~60μm)were mixed in the composition of Ni_xTi_{100-x} ($x=10$, 20, 30, 50, 60, 70) and milled in a high energy attritor ball milling machine. The milling medium was hardened steel balls of 6mm diameter, rotation velocity was 400 r/min and the ball to powder weight ratio was 40:1.

To protect from contamination of oxygen, the milling container was filled with high purity argon gas, and a few amount of milled powders were removed from container and examined after different milling times.

X-ray diffraction (XRD) analysis of milled powders was carried out using the RIGAKUD/max-rB diffractometer with CuKα radiation. The microstructure of milled powders was observed by scanning electron microscope (SEM) with electron probe microanalyzer, samples were prepared using standard metallographic techniques. Milled powders for TEM examination were suspended in anhydrous alcohol, a few drops of the mixture were pipetted onto a carbon support film.

The thermal properties of milled powders were examinedby a Perkin-Elmer DSC-7 differential scanning calometer under argon atmosphere with a heating rate of 20 ℃/min.

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3 EXPERIMENTAL RESULTS AND DISCUSSION

Fig. 1 shows the backscattered micrographs of Ni50Ti50 powders milled for various time. At the starting milling stage, composite powders of nickel and titanium with layered struture were formed, which can be observed in the sample milled for 15 min in Fig. 1 (a). When subjected to further milling, the layered structure refined as shown in Fig. 1 (b). After 1 h milling, a uniform single-phase microstructure was formed, the contrast of elementary image disappeared completely in the backscattered micrographs.

Fig. 2 shows TEM bright field images and selected area diffraction patterns (SAD) of milled powders, after 15 min milling, the powders were found to be completely crystalline, the SAD pattern indicates significent preferred orientation, which implies the powders suffered large plastic deformation; after half an hour miling the regions of amorphous phase start appearing as in Fig. 2(b). EDX analysis and SAD patterns indicate region A is polycrystalline with more titanium content (56.35 at.-% Ti, 43.65 at.-%Ni), while its neighbouring region B shows amorphous structure with the composition of 51.29 at.-% Ti and 49.7 at.-% Ni, close to the starting nominal composition. After 1 h milling, the fraction of amorphous phase is much high, but the microstructure is still un-uniform, after 2 h milling, the powders were basically amorphous.

The XRD patterns of milled powders of Ni50Ti50 samples milled for various time are presented in Fig. 3, as milling time increased, both the nickel and titanium peaks brodened and the peak intensity decreased. After half an hour milling, a halo pattern appeared, indicating amorphous phase formed. On further milling, the nickel and titanium peaks disappeared and were replaced by halo pattern, showing that amorphization reaction was carried to completion.

Fig. 4 shows the DSC curves of Ni50Ti50 powders milled for various time. With short milling time, the crystallization temperature of amorphous phase is high, it is because the amorphous phase formed at this milling stage possesses high nickel content[5,1]. On further milling, the crystallization enthalpy increases with increasing milling time as shown in Fig. 5 during 0.5 h to 4 h milling period, the crystallization enthalpy rapidly increased, which implies the fraction of amorphous phase increased fast and most of the amorphous phase formed during this period. After 4 h milling, amorphization rate decreases, since the un-alloyed dispersoid embeded in the amorphous matrix needs a long time to diffuse into the matrix. While at the initial milling stage, the deformation-fracturing-welding process greatly raises the reaction interface of nickel and titanium, so the amorphization rate

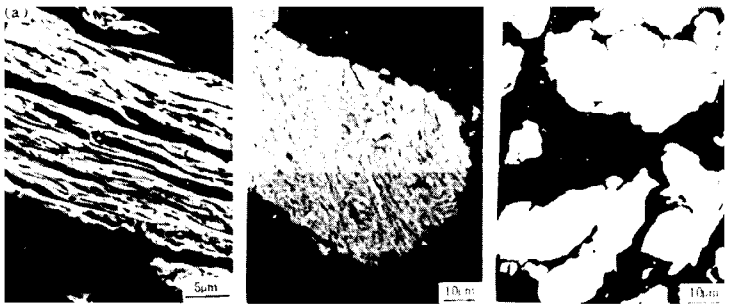

Fig. 1 Microstructure of Ni50Ti50 powders milled for various time
(a) 15 min; (b) 0.5 h; (c) 2 h

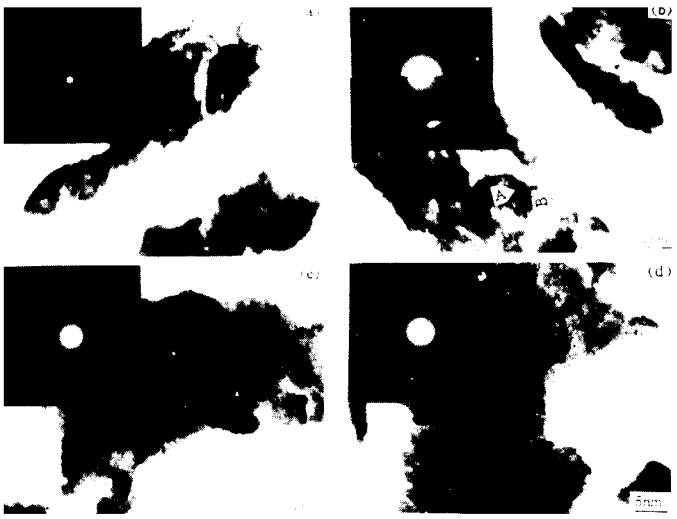

Fig. 2 TEM picture and SAD patterns of $Ni_{50}Ti_{50}$ powders milled for various time
(a)—15 min; (b)—0.5 h; (c)—1 h; ; (d)—2 h

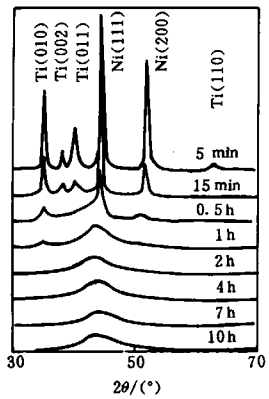

Fig. 3 XRD profiles of $Ni_{50}Ti_{50}$ powders ball milled for different time

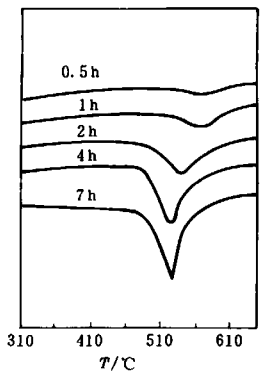

Fig. 4 DSC curves of $Ni_{50}Ti_{50}$ powders milled for different time

is high in this period. After 7 h milling, the sample becomes fully amorphous, the crystallization enthalpy is 3.92 kJ/mol.

Fig. 6 shows the structural parameters of Ni50Ti70 samples as a function of milling time. At the starting milling stage, the layer thickness of layered structure decreases, making the reaction interface between nickel and titanium increases; in addition, the grain size deminishes and the microstrain increases owing to severe plastic deformation, indicating the dislocation density and grain boundaries increase, which enhancing the diffusion rate, so the lattice parameter changes rapidly. Fig. 6 also shows that the hardness of powder reaches saturation value after 1 h milling, and powder size also reaches saturation value, but microstructure is still un-uniform at this time, and the alloying process is not completed. So we can not decide whether the alloying process has finished according to the hardness and powder size reaching a stable stage.

Fig. 7 shows the XRD patterns of Ni_xTi_{100-x} ($x=10$, 20, 30, 50, 60, 70)powders milled for 7 h. It can be seen that the Ni70Ti30 samples turned to nickel solid solution, while samples with the composition of $40 \leqslant x \leqslant 60$ became amorphous, for Ni20Ti80 and Ni10Ti90 samples, the mixture of titanium solid solution and amorphous phase were obtained.

For predicting the composition range of

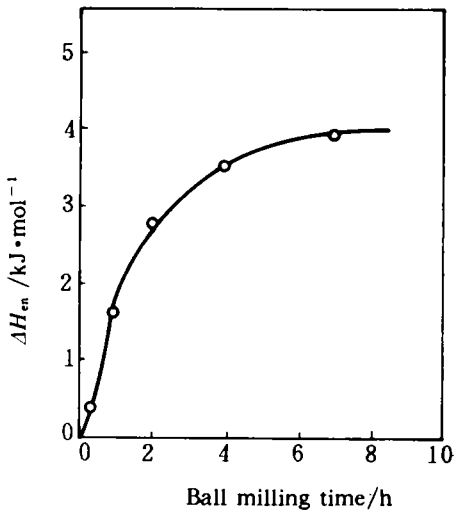

Fig. 5 Crystallization enthalpy of ball milled Ni50Ti50 powders versus milling time

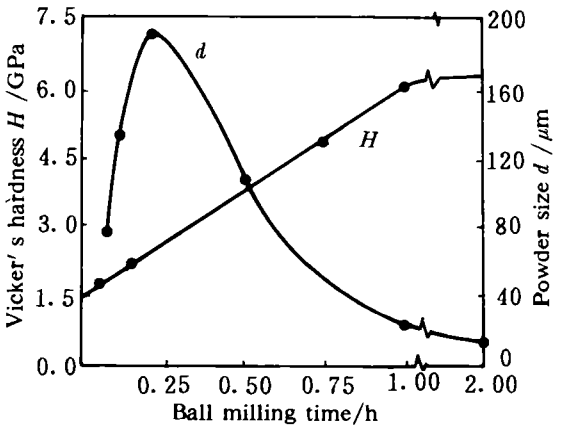

Fig. 6 Variation of structural parameters of Ni50Ti50 powders with milling time

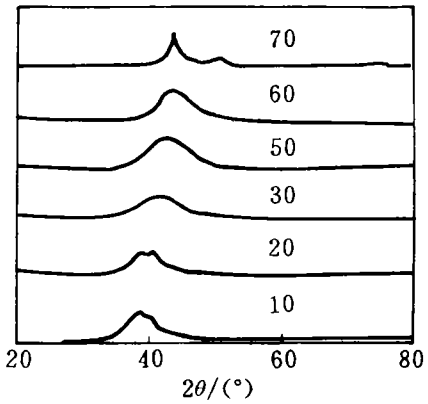

Fig. 7 XRD profiles of Ni_xTi_{100-x} powders ball milled for 7 h

amorphous phase formed by mechanical alloying, the free energy of formation of amorphous phase and solid solution of Ni-Ti system at 227 ℃ (generally, the temperature of powders in ball milling process is 227 ℃) were calculated using the empirical equation given by Miedema A R [6], as shown in Fig. 8. According to double tangent rule, Ni_xTi_{100-x} alloys can be fully amorphized at the composition range of $30 \leqslant x \leqslant 77$, which is basically in agreement with experimental results. Owing to serious plastic deformation of powders the free energy of both amorphous phase and solid solution changes, and can not be accurately calculated, so the formation range of amorphous phase can not be

(*To page 90*)

structure of nonferrous alloys by STM in the air at ambient temperature under appropriate heat treatment and surface protection measures.

(2) The fine structure of bainite in the Cu-Zn-Al alloy-subunit has been found for the first time. The subunits take on a regular shape and range in proper order. The maximum subunit is about 800 nm × 300 nm while the minimum one is 60 nm × 60 nm or so.

(3) The maximum depth between the subunit and the boundary of two subunits is ca. 30 nm and the corrugation on the surface of subunit is ca. 3 nm.

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(*From page 86*)precisely predicted.

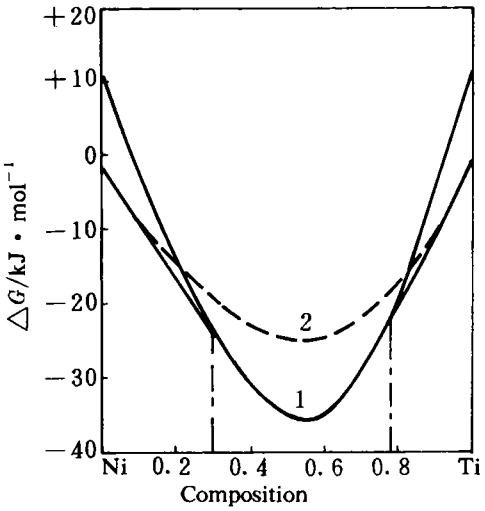

Fig. 8 Free energy of formation for amorphous phase and solid solution in Ni-Ti system at 227 ℃
1—amorphous phase; 2—solid solution

4 CONCLUSIONS

(1) Mixed elemental Ni-Ti powders formed composite powders with layered structure at the starting milling stage; on further milling, the layered structure refined, the crystallite size of nickel crystal diminished, and microstrain increased with the increasing plastic deformation. After 1 h milling, the hardness and size of powders reached saturation values.

(2) For Ni50Ti50 samples, the fraction of amorphous phase increased very rapidly during 0.5 ~2 h milling period, because the deformation-fracturing-welding process made the reaction interface between nickel and tiatnium increase. At the final milling stage, amorphization rate decreased, after 7 h milling, amorphization process completed.

(3) Ni_xTi_{100-x} ($40 \leqslant x \leqslant 60$) amorphous alloys were obtained, which is basically in agreement with the result calculated by thermodynamics method.

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