Thermal Stability of $Ni_{50}Ti_{50}$ Amorphous Alloy Prepared by Mechanical Alloying

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Abstract

$Ni_{50}Ti_{50}$ amorphous alloy was prepared by mechanical alloying from a mixture of Ni and Ti powders using conventional ball milling machine. The thermal stability of the NiTi amorphous alloy was studied by means of differential thermal analysis. The thermal stability of the NiTi amorphous alloy increased as milling time proceeded.

1. Introduction

Recently, extensive studies have been carried out on solid state amorphization of the alloy(1,2). Especially, mechanical alloying (MA) and mechanical grinding are considered to be suitable methods of mass production for industrial use. The kinetics of solid state amorphization of the alloy have been proposed by Johnson(3). The atomic structural changes of the alloys through solid state amorphization process by MA were discussed by the authors using EXAFS measurement(4,5). Ni-Ti amorphous alloy have been produced by electron-irradiation(6)and MA(7). The thermal atability of the amorphous alloy is important from the viewpoint of the industrial use. But the thermal stability of the NiTi amorphous alloy produced by MA has not been studied up to now. The main purpose of this work is to investigate the thernal stability of the NiTi amorphous alloy prepared by MA.

2. Methods

A Ni-Ti amorphous alloy powder was prepared in a laboratory ball mill using stainless steel vials filled with high purity argon, with size of 105mm×108mmΦ (inside), and hardened balls with diameter of 15mm and 20mm. The milling was carried out at ambient temperature at the rate of $1.8s^{-1}$. Starting material was a mixture of Ni powder (2~3μm,99.8%) and Ti powder(40~50μ m,99.0%). Its composition was $Ni_{50}Ti_{50}$. This corresponds to the compostion of NiTi metallic compound (8). The total weight of starting material was 30g in mass. The sample preparation was made by stopping the ball milling at 0, 1.8×10^5, 3.6×10^5, 7.2×10^5, 10.8×10^5 and 14.4×10^5s after its commencement, respectively, in a glove bag filled with argon atmosphere.

The X-ray diffraction patterns were measured using Mo Kα-radiation of the laboratory X-ray source (40kV,20mA).

Portions (~20mg) of the powders in the MA process were heated in a differential thermal analyzer (SHIMADZU;DTA-40) at 0.1, 0.2, 0.4, 0.6 $Ks^{-1}$with flowing argon of $1.7mls^{-1}$. The crystallization temperature and the activation energy for crystallization of the alloy as a function of milling time were measured by using Kissinger's plot[9]. The equation derived by Kissinger is as follows.

$$E = -R \frac{d[\ln(q/T_m^2)]}{d(1/T_m)} \qquad (1)$$

Where T_m is the peak temperature, q the heating rate, R the gas constant and E the activation energy for the crystallization.

3. Results and discussion

Figure 1 shows the X-ray diffraction patterns of a $Ni_{50}Ti_{50}$ alloy prepared by MA as a function of milling time.

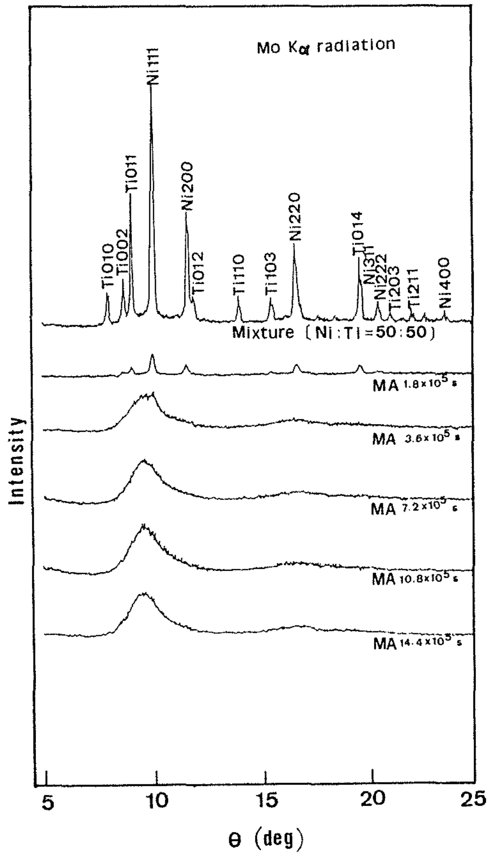

Fig. 1 X-ray diffraction patterns of $Ni_{50}Ti_{50}$ alloy produced by mechanical alloying as a function of milling time.

The intensities of the Bragg peaks decreased rapidly at 1.8×10^5s of milling time. Around 3.6×10^5s of milling time the Bragg peaks due to the Ni and Ti almost disappeared and were replaced by a halo pattern, this showed that the amorphization reaction was carried to completion. A new chemical compound was not produced through the MA process.

Figure 2 shows the DTA curves of the alloy in the MA process.

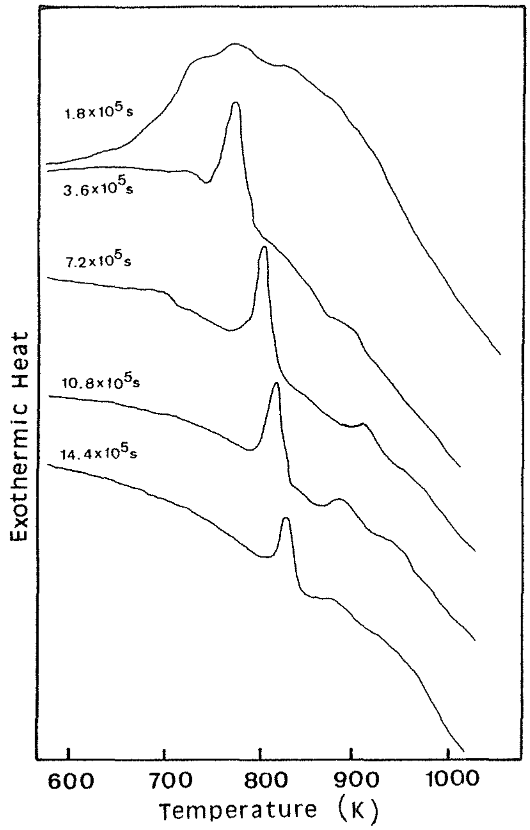

Fig. 2 DTA curves (rate 0.6 K/s) of $Ni_{50}Ti_{50}$ alloy produced by mechanical alloying.

An obscure, small exothermic peak appeared in the DTA curve at 1.8×10^5s of milling time. This shows that the amorphization reaction started at this time partially. After 3.6×10^5s, the DTA curves have a clear exothermic peak corresponding to the crystallization of the amorphous phase, respectively. The reaction corresponding to this sharp exothermic peak seems to be the reaction of the amorphous to equilibrium phase, NiTi[8]. This was consistent with the results of X-ray differaction measurement. The nucleation of amorphous phase in the NiTi mixture powder occured in a ealier stage of milling process than that in Ni-Nb mixture powder[10].

Figure 3 shows the crystallization temperature of the NiTi amorphous alloy as a function of milling time.

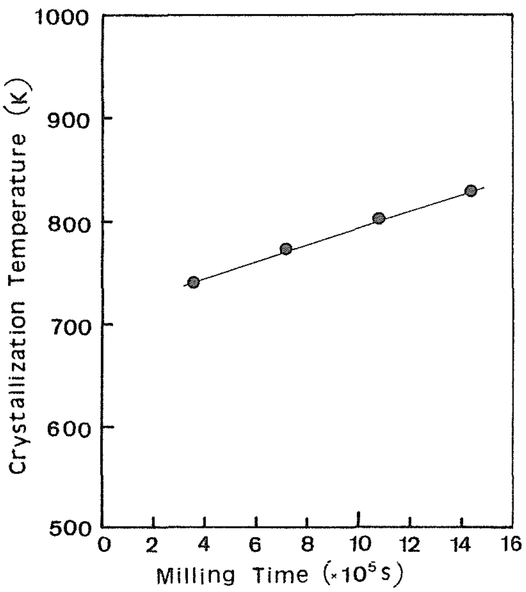

Fig. 3 Crystallization temperature of $Ni_{50}Ti_{50}$ amorphous alloy produced by mechanical alloying.

The crystallization temperature rised as the milling time proceeded. This indicates that the amorphous phase increases the thermal stability as the milling time proceeds. The crystallization temperature of the NiTi amorphous alloy was lower than that of the $Ni_{60}Nb_{40}$amorphous alloy prepared by MA[10].

Figure 4 shows the activation energy for crystallization of the NiTi amorphous alloy as a function of milling time.

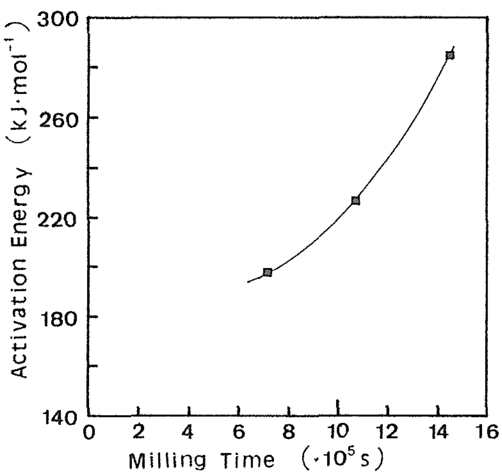

Fig. 4 Activation energy for crystallization of $Ni_{50}Ti_{50}$ amorphous alloy prepared by mechanical alloying.

The activation energy of the alloy at 10.8×10^5s of milling time was 227.7KJ/mol. This value is considerably smaller than the activation energy 334.3KJ/mol for crystallization of the $Ni_{60}Nb_{40}$ amorphous alloy prepared by MA[10]. The activation energy increased as the milling time proceeded. The behaviours of crystallization temperature and activation energy for crystallization of the NiTi amorphous alloy prepared by MA indicate that the amorphous phase increases the thermal stability as the milling time proceeds. The increase of the thermal stability of NiTi amorphous phase is explained well by the diffusion which progress the uniformity of the alloy as the milling time proceeds.

In summary, the thermal stability of the NiTi amorphous alloy produced by MA increases as the milling time proceeds. The NiTi amorphous alloy has the lower crystallization temperature and the smaller activation energy for crystallization compared with those of the $Ni_{60}Nb_{40}$ amorphous alloy by MA.

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概 要

近年，機械的混合法（メカニカル・アロイング）が，アモルファス合金の作成法として注目されている。それは，この方法が他の方法に比べて簡便な方法であり，設備的にも安価であることがあげられる。この方法によって作成されたアルモファス合金の実用的応用を考慮する場合にアルモファス構造の熱的安定性は重要な問題である。これまでにメカニカル・アロイングによって作成したNi-Ti系アモルファス合金の熱的安定性についての研究は行われていない。本研究の目的はこのNi-Ti系アモルファス合金の熱的安定性を検討することである。本研究では示差熱分析の方法によってその熱的安定性を評価した。その結果，メカニカル・アロイングの時間が長期化すると熱的安定性が増大することが分かった。また，メカニカル・アロイングによって作成したNi-Nb系アモルファス合金と比べて結晶化温度は低く，結晶化の活性化エネルギーが小さいことが明らかになった。