Local structure of NiTi nanocrystals studied by EXAFS and XRD

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A series of NiTi nanocrystals with different annealing temperatures, prepared by sputtering method, were investigated by extended x-ray absorption fine structure (EXAFS) and x-ray diffraction. It was found that the structure of nano-phase powder is different from bulk NiTi alloy with bcc structure as target materials. When increasing the annealing temperature, a small fraction of the (Ni,Ti) type nanocrystal with the hexagonal structure was presented except target materials and Ni, and it is atomic occupation in random. Finally there were four Ti and two Ni atoms around central Ni atoms, and the bond length of Ni-Ti and Ni-Ni were 0.2462nm and 0.2585nm at 800°C annealed.

Keywords: NiTi nanocrystals, Phase transition

1. Introduction

The NiTi shape memory alloy (SMA) with an approximately equal atomic ratio is a kind of novel functional materials which has the ability to return to a previously defined shape and size when subjected to the appropriate thermal procedure. These materials can be plastically deformed at a relatively low temperature , and will return to their shapes prior to the deformation during exposure to a higher temperature. Actually the NiTi SMA is unique memory alloy materials with extensive applications (Hwang, C.M., et al., 1983; Ling, H.C. et al., 1980, 1981; Nishida, M., et al., 1986; Miyazaki, S., et al., 1988).

Until now, people have not known what the behavior of NiTi alloy will be when decreasing the grain size to nanometer. No reports have been published on the local structure of nonoscale NiTi alloy. On the other hand, determination of the atomic structure of nanoscale solids is very important for understanding the properties of nano-materials. In the past decades, a huge number of investigations on the characteristic and the microstructure of nano-materials have been presented using various methods of structural analysis. Among them, extended x-ray absorption fine structure (EXAFS) is a powerful tool for identifying the local structure around the absorbing atoms. In this paper, the NiTi SMA was chosen as a target material to prepare the NiTi nanocrystal, then the local structure around Ni atoms was studied using the combination of EXAFS and XRD.

2. Experiments

The raw nano-NiTi powder, with a particle size of 7 nm, was synthesized using DC sputtering on a dedicated apparatus, which was named as “glow discharge-condensation-in situ pressure”, and set up by Institute of Solid State Physics, Chinese Academy of Sciences (Zhu, Y., 1994), then condensed, and finally shaped with a pressure of 1.5 GPa. The target materials is a bulk NiTi SMA with bcc structure. A series of samples with different particle size were prepared by annealing the raw powder in vacuum at 400, 600 and 800°C respectively. EXAFS measurements at the Ni K-edge were performed in the transmission mode at the EXAFS station on beamline 4W1B of the Beijing Synchrotron Radiation Facility (BSRF). The storage ring operated at 2.2 GeV and 40-50 mA. Data analysis was performed using the EXCURV92 program. X-ray diffraction measurements were performed at beamline 4B9A of BSRF. A x-ray diffractomator with the precision of 0.001 degree is the main equipment. The incident beam intensity was monitored with an ion chamber and the diffracted intensity was detected by NaI(Tl) scintillation detector. There were two slits of 0.5 mm on the light path, one was set at the entrance of the beam and the other was at the front of the detector. The incident focused and monochromatic x-ray beam was calibrated by the Cu K-edge (1.54 Å). The energy resolution $\Delta E/E$ was 4×10^{-4}.

3 Results and discussion

3.1 XRD

From transmission electron microscopy (TEM) experiments, it was found that the NiTi grains grow in size when the annealing temperature increases, and finally their particle size increases to about 20 nm by raising the temperature to 800°C (X. Ju et al., 1995).

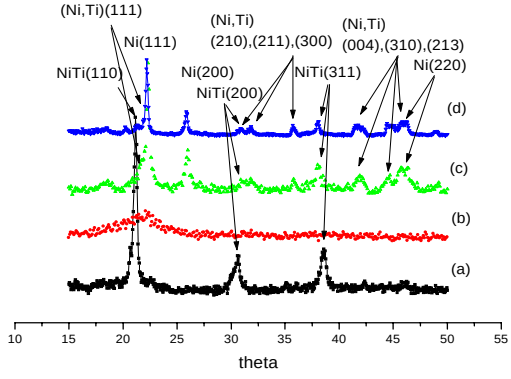

Fig. 1 X-ray diffraction patterns of nano-NiTi samples. (a) NiTi alloy; (b) as-grown NiTi powder; (c) annealing at 400°C; (d) annealing at 600°C

The as-grown NiTi powder was prepared by the DC sputtering method using NiTi SMA target with the bcc structure. Figure 1 shows the XRD pattern of the target material. Three strong peaks are attributed to (110), (200) and (211) as indicated in Fig. 1(a). Fig. 1(b) shows the diffraction pattern of the as-grown NiTi powder. There is a broad peak corresponding to non-crystalline materials. Figures 1(c) and (d) correspond to the samples obtained by annealing at 400 an 600°C respectively. The structure of these samples identified from the diffraction patterns is not the same as the bcc structure of the target material, At first, it can be exhibited a group of strong diffraction peaks of Ni with a cubic structure. As indicated in Fig. 1(c) and (d), the strongest peaks is at θ=22.2 for (111), the peaks at θ=25.6, 38.0 and 46.4
are identified as the (200), (220) and (311) of Ni crystalline with a cubic structure. Meanwhile, it should be pointed out that two groups of weak peaks exist and are corresponding to target material and the (Ni,Ti) type alloy with hexagonal structure, which is atomic occupation in random. As indicated, the peak at θ=30.6

for (200) of NiTi alloy with a bcc structure can be observed, but the peaks at θ=21.1 for (110) and 38.6 for (211) emerge with those of Ni crystalline with a cubic structure.For the (Ni,Ti) type alloy with hexagonal structure, there is a similar behavior that the strongest peaks at θ=22.0 for (111) is overlapped with the (111) of Ni crystalline. Three weak peaks at θ=41.5, 44.6 and 45.7 can be assigned to (004), (310) and (213) of this alloy. Moreover, there are three small peaks at θ=31.1, 32.9 and 35.8, and can be identified to (210), (211) and (300) of the hexagonal structure of (Ni,Ti) alloy. On the other hand, the diffraction intensity of the bcc phase is much weaker than the one of the crystalline as indicated.

Finally the above phenomena mean that a large fraction of Ni atoms were separated out in the sputtering process. On the other hand, the diffraction intensities of the bcc- and hexagonal phase of NiTi alloy were much weaker than that of the Ni crystalline as shown in Fig. 1.

3.2 EXAFS

The Fourier Transforms of the EXAFS spectra, and the structural parameters determined by fitting with EXCURV88 for various NiTi nanocrystalline samples are shown in Fig. 2 and Table 1. It was found that there are four Ti atoms and two Ni atoms around central Ni atoms, and the bond length of Ni-Ti and Ni-Ni were 0.2462 nm and 0.2585 nm after annealing at 800°C It is consistent with the conclusion attracted from the XRD experiments, in which a large fraction of Ni crystalline was separated out after the sputtering process. Meanwhile the structure was relaxed because the atomic occupation is random in the (Ni,Ti) alloy with a bcc- and hexagonal structure,. The experimental values of Ni-Ti and Ni-Ni interatomic distances were deviated from those of Ni-Ti alloy and the Ni crystalline presented in the PDF cards. From the amplitude of the overlapping Ni-Ni and Ni-Ti peak, it is found that the coordination number (CN) increases with rising the annealing temperature and the Ni-Ti and Ni-Ni distances come to keep stable. On the other hand, the higher shell peaks disappear rapidly and the degree of disorder increases with decreasing the annealing temperature, which can be interpreted that the long range order in the structure has been destroyed with the decreasing of the particle size.

Table 1 The structural parameters fitting with EXCURV88 Program

Condition	Distance (nm)		Coordination Number		Debye-Waller factor (10^{-3})	
	Ni-Ti	Ni-Ni	Ni-Ti	Ni-Ni	Ni-Ti	Ni-Ni
Raw powder	0.2398	0.2586	2.3	0.8	3.7	4.8
Annealed at 400°C	0.2463	0.2583	4.0	1.3	3.9	4.0
Annealed at 600°C	0.2459	0.2580	3.8	1.8	2.0	2.0
Annealed at 800°C	0.2462	0.2585	4.2	1.8	1.7	1.7

These structural changes can be attributed to the preparation of the nano-NiTi with the sputtering method. As known, there is a very high internal energy of the system in plasma heating, and most of chemical bonds of NiTi SMA as target materials are broken. Finally the Ti and Ni atoms are evaporated and deposited randomly on the substrate. A weak bonding between Ni and Ti atoms can be formed when the temperature of the plasma is lower since a strong bonding in plasma is impossible,. Therefore the bcc- and hexagonal phase are observed in the nano-(Ni,Ti) alloy when annealing at different temperatures. Moreover, it is known that eight Ti atoms are around each Ni atom in the NiTi SMA with bcc structure. According to the results of EXAFS and XRD experiments, the phase transition occurs from bcc- to hexagonal-structure in the synthesis process of the as-grown NiTi powder, and the structural relaxation also does. So their structural parameters should be changed. To sum up, the Ni and Ti atoms or a little ultrafine alloy particles produced by sputtering at the beginning are cooled and deposited in disorder on the substrate. Among them, ultrafine alloy particles are of the initial bcc-structure. Following, with the increase of annealing temperature, the (Ni,Ti) type alloy with the atomic occupation in random is produced with the hexagonal structure except the formation of Ni crystalline.

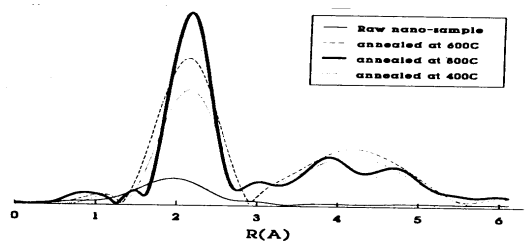

Fig. 2 RDF of Ni-K-edge

It is reported that the Ni_3Ti phase with nano-dimension will result in the serious decay of SMA performance and further fracture of the SMA material (Wen, S.L. et al., 1999). In our experiment, no Ni_3Ti phase was observed.

4. Conclusion

The structures of NiTi nanocrystals with different annealing temperatures, prepared by sputtering method,. were different from bulk NiTi alloy with bcc structure as target materials. When increasing the annealing temperature, a small fraction of the (Ni,Ti) type nanocrystal with the hexagonal structure was presented except target materials and Ni crystalline, and it is atomic occupation in random.

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Received 31 July 2000 • Accepted 4 December 2000