In-Situ TEM Study of the Thickness Impact on the Crystallization Features of a Near Equal-Atomic TiNi Thin Film Prepared by Planar Magnetron Sputtering

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\textit{In-situ} TEM studies were conducted to reveal the crystallization features of equi-atomic TiNi amorphous thin films. The TiNi amorphous thin film crystallization procedure can be divided into two types: the in-homogenous nucleation and growth mode in the ultra thin regions and the homogenous polymorphous mode in the thick areas. In the thin regions, the thickness controls the in-homogenous nucleation mode. The formed nano-crystallites in the thin areas are with a size of 5–20 nm while in the homogenous nucleation and growth mode, the grain size drops to the range of sub-micron level. In general, the stabilized grain size is a function of thin film thickness and can be described as $G = kx\, \text{nm}$, where $x$ is the thickness in nano-meter and $k$ is a constant related to lattice parameter. An intermediate phase forms through the crystallization procedure in the thick region. The intermediate phase possesses a cubic structure with lattice parameter of $a = 9.03\, \text{Å}$. The intermediate phase transforms to the stable B2 phase when the specimen being kept above the crystallization temperature for some time. The crystallization sequence in the thick region is determined to be: TiNi amorphous $\rightarrow$ intermediate phase $\rightarrow$ B2 + Ti$_x$Ni$_{4-x}$.

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1. Introduction

Crystallization sequence and features are important to control the final quality of the materials. Thin films were normally obtained at a status of amorphous and a subsequent crystallization procedure is normally required. However, it is a regular complicate process to control the crystallization adequately regarding the crystallized features such as the phase constituent, the grain size and grain orientations etc. For Ti–Ni thin film crystallization from the amorphous matrix, it has been relatively investigated less intensively comparing to the heavily attention in mechanical properties, phase transformation features of fully crystallized thin films and also the applications of the thin films in MEMS. Some investigations were carried out; however some questions remain unclear even controversial.\textsuperscript{1–4)} Some studies showed one-step crystallization feature which characterized by one exothermal peak\textsuperscript{1,2)} while others reported multiple-step transformations in several Ti–Ni compositions.\textsuperscript{3,4)} The purpose of this study is to utilize \textit{in-situ} TEM observation to clarify the crystallization sequence and features in a near-equatomic Ti–Ni thin film from the structural and microscopic view points.

2. Experimental Procedure

TiNi thin films were prepared by sputtering method using a near-equatomic TiNi target, and the composition of the film is determined to be Ti–50.8 at%Ni. The TiNi thin films with thickness of 0.5–4 microns were deposited onto silicon plates by a dc magnetron sputtering source fitted with a 70 cm\textsuperscript{2} source area. During deposition, the silicon substrate was heated to temperature between 350 and 430 \textdegree C. Film growth rates were 0.65–0.92 nm/s. The obtained TiNi thin film thickness is about 2 microns. Free standing TiNi thin films were peeled from the Si substrate. The \textit{in-situ} TEM observations were conducted with a Gatan heating stage on a CM-12 microscope. The HREM observations were carried out with a JEOL 2010 high resolution TEM.

3. Results and Discussion

3.1 In-homogenous nucleation in the thin areas

The amorphous TiNi thin film behaves different crystallization features through the gradient thickness. Figure 1(a) illustrates the ion-milled thin regions with a gradient angle of 10 degrees. This design is for studying the thickness impact of the crystallization features. We reveal two types of crystallization features of the TiNi thin films through the \textit{in-situ} heating experiment: 1) in-homogenous nucleation mode in the thin region and 2) homogenous grain nucleation and growth mode—polymorphous in the thick area. Figure 1(b) shows the thin film thickness impact on the crystallized grain size. The in-homogenous crystallization nucleation modes and rates dominate the situation in ultra-thin areas. Regarding the accurate amorphous structure of near-equatomic NiTi alloy; we simplify the calculation of the surface atomic volume fraction by using an equal-diameter ball model in a 10-degree wedge shaped container. As shown in Fig. 1(a) the atoms are closed packed in the container and there are three atomic layers in the thinnest region. Forcing the nearest neighboring environment of the NiTi amorphous to be close to a BCC structure, the surface atoms occupy a high volume fraction by up to 88% in the thinnest area. Figure 1(c) shows an illustration of the surface atomic volume fraction and the grain size versus thin film thickness. The high volume fraction surface atoms are highly activated and trigger the in-homogenous nucleation mode. The crystallized grain size is a function of thin film thickness. The grain size and the surface atomic volume fraction can be described as by the following equations. Following Fig. 1(c), the surface atomic volume fraction can be regressed as:

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Where $V$ is the surface atomic volume fraction, $K$ is a regression coefficient, in this study $K = 16.6$, and $T$ is the thickness of film.

And empirically, the grain size is a function of thin film thickness and can be described as a function of thickness:

$$G = kx$$

Where in this study $k = 1.2$.

Figure 2 shows the in-situ observation of the crystallization procedure evolved in the reciprocal space in the thin areas. These areas are next to the milling hole and have a semi-transparent contrast. The images corresponding to these reciprocal space features were also recorded and are shown in Fig. 3. The temperatures and the isothermal holding time are indicated at the bottom of each figure. The selected area diffraction patterns in Fig. 2 were taken at the region indicated by letter “A” in Fig. 3. The diffraction halos/rings through Figs. 2(a) to (f) show the transformation features from amorphous to crystallites. The diffraction rings shown in Fig. 2(f) can be indexed to be Ti$_2$NiO and TiNi (B2). The crystallization started at the temperature of 410°C which is characterized by the appearances of sharp diffraction rings. This crystallization starting temperature is lower than that reported in study.5) The lowered crystallization starting temperature comes from the impact of large volume fraction surface in which the excess free energy $\Delta G_{in-homogeneous}$ is
sharply decreased. The morphologies of the nano-grains are revealed in a high resolution electron microscopy image as shown in Fig. 4 which was taken when the specimen was cooled down to room temperature.

3.2 Polymorphous homogenous nucleation in the thick regions

The crystallization procedure at the thick areas obeys the homogenous nucleation mode of polymorphous. As shown in Fig. 5, the grain nucleation, growth, coarsening can be revealed which is similar to the results obtained by study.\textsuperscript{5)} Figures 5(a) and (b) were taken with a time period of 5 min at 490°C. The grain growth rate is similar to the results reported in Ref. 5). The nucleation temperature of the intermediate phase is below 490°C but is higher than the temperature of nano-nucleate formation temperature and is also higher than the crystallization temperature reported in Ref. 5).

However in the present investigation we reveal the embryo phase at the early crystallization stage is an intermediate one. The crystallized grains possess spherical feature with dendrite-like contrast. The dendrite-like contrast is believed to derive from the transformation strain. The crystalline structure of the intermediate phase was studied by series tilting the specimen along several low miller index axes. The intermediate phase would transform to stable B2 phase quickly if the specimen were kept above the crystallization temperature for several minutes. The series tilting of the specimen was conducted at room temperature in which the specimen containing the intermediate phase was cooled to room temperature quickly after its appearance. Figure 6 shows a set of composite electron diffraction patterns to reveal the lattice structure of the metastable phase. It possesses cubic lattice and is perfectly 3-time lattice constant comparing to the stable B2 phase. The grain nucleation is homogenous and the old grains consume the new nucleates. The final grain size reaches a level of sub-microns. This process was re-done multiple times and the formation of the metastable phase is repeatable. Isothermal keeping the specimen for several minutes, the metastable TiNi phase
transforms to the stable B2 structure with Ti$_3$Ni$_4$ precipitates in the matrix as shown in Fig. 7(c). Cooling the specimen to room temperature, the specimen conducted reversible B2 $\leftrightarrow$ R phase transformation. The features of R phase are revealed in Fig. 7 in the reciprocal space as indicted by the 1/3 super reflections among [110] main reflections.

The morphological features of the crystallized phase in study$^5$ are similar to the present study while there was no intermediate phase reported in that study. The reason of absence of the intermediate phase in study$^5$ may come from two reasons: firstly the specimen was kept at the temperature of 470 °C for too long and the intermediate phase transformed to the stable B2 phase quickly and secondly, the intermediate phase only appears in a range of composition and it excludes the composition of study.$^5$

As studied by the composite EDPs analysis on the intermediate phase, the crystal structure can be determined to be cubic with lattice parameter of $a = 0.903$ nm which is 3 times of the stable B2 phase. 1/3 (110) type super-reflections are easily appearing features in Ti (Zr) based beta phase alloys when the phase transition occurred. Omega phase is one of the phases easily formed in the Ti, Zr alloys when the high temperature phase quenched to low temperatures.$^5$ The omega phase was widely investigated as an intermediate phase in 1960s. Although the omega phase was suggested to be a cubic structure with a large unit cell by several researchers, it has been clarified to possess hexagonal symmetry with $c/a = 0.662$. The crystal structure features of the metastable phase are clearly distinguishable with the R phase. The similar phase found in the TiNi alloys was the intermediate phase formed by explosion from a mixture of Ti and Ni powder with 1:1 ratio.$^7$ However, the lattice parameters of the phase found in study$^7$ is smaller and large lattice mis-match strain can be imagined in that study due to the lattice parameter variance. The present study believes that the formation of the metastable phase in this study and in$^7$ have similar pre-requisite: a) mixture of Ni/Ti atoms but disordered for at least long range and b) both cases produced large strains. To accommodate the large strain exist in the matrix, the metastable phases were easily formed at high temperatures such as 490 °C. In this study, the strain exist in the matrix derives from the Ni-rich amorphous matrix which deviating from the 1:1 Ti/Ni ratio. The oversaturated solute matrix of Ni in Ti generates large strains which must be accommodated by a metastable phase formation. To adjust the strain more effectively, the Ti$_3$Ni$_4$ phase was formed with longer aging time. Therefore, the adequate sequence of the crystallization of TiNi amorphous thin film at the thick areas is:

Amorphous $\rightarrow$ cubic intermediate phase $\rightarrow$ B2 + Ti$_3$Ni$_4$

4. Conclusions

Based on the above research results, the following conclusion can be summarized:

1) Through the in-situ TEM studies on the gradient TiNi thin film, the TiNi amorphous thin film crystallization procedure has been revealed to belong to two types: the in-homogenous nucleation and growth mode in the ultra thin regions and the homogenous polymorphous mode in the thick areas.

2) In the thick regions, the thickness controls the in-homogenous nucleation mode. The formed nano-crystallites in the thin areas are with a size of 5–20 nm.

3) In the homogenous nucleation and growth mode, the grain size drops to the range of sub-micron level.

4) In general, the stabilized grain size is a function of thin film thickness and can be described as $G = kx$, where $x$ is the thickness in nano-meter and $k$ is a constant related to lattice parameter.

5) An intermediate phase forms through the crystallization procedure in the thick region. The intermediate phase possess a cubic structure with lattice parameter of $a = 0.903$ nm.

6) The intermediate phase transforms to the stable B2 phase when the specimen being kept above the crystallization temperature. The crystallization sequence in the thick region is determined to be: TiNi amorphous $\rightarrow$ intermediate phase $\rightarrow$ B2 + Ti$_3$Ni$_4$.

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