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Coherent Subnanometric Plate Precipitates Formed during Crystallization of As-Sputtered Ti-Ni films

K. Ogawa, T. Kikuchi, S. Kajiwara, T. Matsunaga* and S. Miyazaki*

National Research Institute for Metals, 1-2-1 Sengen, Tsukuba 305, Japan
** Institute of Material Sciences, Tsukuba University, Tennoudai, Tsukuba 305, Japan*

Abstract. It is shown by high resolution electron microscopy that coherent plate precipitates with 0.5-1 nm thickness are formed in Ti-rich Ti-Ni thin films when heat treated directly from the sputter-deposited amorphous state near the crystallization temperature. The precipitates are Ti-rich and formed on {100} planes of the B2 matrix phase with perfect coherency. The crystal structure of the precipitate is a body centered tetragonal with the c-axis normal to the habit plane. Owing to the existence of these coherent subnanometric precipitates, the parent phase is greatly strengthened, resulting in very excellent shape memory properties such as 6 % recoverable shape memory strain at the stress level of 300 MPa without any appreciable plastic deformation.

1. INTRODUCTION

Machines in micron size, so-called micromachines, have a vast area of application ranging from medical equipment to semiconductor industry. To achieve such sophisticated machines, development of proper materials for the use of micro-actuators is one of the key steps. Ti-Ni shape memory alloy films are considered to be one of the most promising materials for this application and intensive work has been done in this area for the past several years [1-6]. For use of Ti-Ni shape memory films as an actuator of the micromachines, the thickness of the films must be less than 10 μ m. To make such thin films of Ti-Ni alloys, the method of sputtering is being widely used and, as a result, the initial state of specimens is inevitably amorphous. In most of the previous investigations, the heat treatment of sputter-deposited Ti-Ni films was done twice; that is, as-sputtered specimens were first heated at high temperatures to induce the crystallization, and then subjected to ageing heat treatments in order to produce appropriate amounts of precipitates which are necessary to exhibit good shape memory effects.

Very recently we found that, instead of employing these two step heat treatments, if as-sputtered Ti-Ni amorphous specimens with a Ti-rich composition are directly heated at relatively low temperatures, thin coherent plate precipitates and unique nanocrystals are formed [7, 8]. Uniformly distributed thin precipitates with only 0.5-1 nm thickness are produced by the heat treatment near the crystallization temperature, while nanocrystals of 20-40 nm in diameter, which have the exactly same orientation within one grain, are generated by the heat treatment at a temperature about 50° below the crystallization temperature. Owing to these substructures, the parent phase is greatly strengthened and, consequently, excellent shape memory properties are obtained. In this paper we describe some more details of the subnanometric coherent plate precipitates. The more detailed description of the nanocrystals and related shape memory properties will be reported somewhere else [9].

2. EXPERIMENTAL METHOD

The same specimens as those used in the previous studies[7, 8] were employed also in the present work; that is, the sputter-deposited Ti-48.2at.%Ni thin films of about 7 μ m thickness were heat treated at 745 K for 1-4 h. The crystallization temperature of this alloy films was found to be 737 K by DSC measurement. Thin foil specimens for

electron microscopy were prepared by electrolytic polishing at room temperature, using a twin-jet polishing apparatus. A 200 kV electron microscope (JEM 2000EX) was employed to obtain high-resolution electron micrographs.

3. RESULTS AND DISCUSSION

It was confirmed by electron diffraction that the as-sputtered specimens were in amorphous state. Figure 1 shows a high resolution electron micrograph of a specimen which was heated at 745 K for 1h. There are seen many extremely thin plates of about 1 nm thickness, which accompany dark contrasts. The corresponding electron diffraction pattern is shown in the inset of Fig. 1. The zone axis of this diffraction pattern is <100> of the b.c.c. structure of the parent phase. Although the pattern shows diffraction spots due to R-phase and should be then indexed after the trigonal system [10], the Miller indices based on the cubic system (b.c.c., B2) of the parent phase are used in the present paper for simplicity. Streaks along [100] and [010] directions are seen in this diffraction pattern. It is considered that these streaks have been caused by very thin platelets observed in Fig. 1 , which lie on {100} plane. Each of the platelets is about 0.5-1 nm thick and has a disk shape with the radius of 5-10 nm. These platelets are distributed about 10 nm apart. A part of this micrograph is enlarged in Fig. 2 to see the detail of the platelets. In this enlarged high resolution micrograph, we can see lattice images of {100} planes with 0.30 nm spacing or ,in some areas, {200} planes with 0.15 nm spacing. and find that each plate consists of only two to three {100} lattice planes. It is generally observed that {110} lattice planes are bent at these precipitates, especially, such bend can be clearly seen at the precipitates indicated by arrows. From the fact that the bent angle of the {110} planes is always in the direction away from the {100} habit plane, we can assume that the precipitate structure is body centered tetragonal (b.c.t.) as schematically shown in the inset of Fig. 2. The tetragonality, c/a, can be easily measured by the deviation angle of {110} lattice planes and it turned out to be very large; for example, it was found to be 1.23 (the corresponding deviation angle of 6°) in the case of the precipitate nearby the schematic picture of the inset in Fig. 2. In some cases, the c/a values as large as 1.4 were observed. It is considered that sucn tetragonal structure is generated as a result of segregation of excess Ti atoms, for the atomic radius of Ti is much larger than that of Ni. Furthermore, we could confirm the Ti enrichment at the precipitates by ultra microanalysis of energy-dispersive spectroscopy (EDS) in a field emission electron microscope.

In order to see the atomic arrangement of the precipitate in more distinctly, the inverse fast Fourier transform images of the observed high resolution structure images of the precipitates have been obtained and shown in Figs. 3 (a) and (b). These figures show the arrangement of atom rows parallel to <100> when the habit plane of the precipitate is parallel to the incident beam. The two layers indicated by arrow are those of the precipitate corresponding to (001) plane of the b.c.t. structure. In this figure, it is clearly seen that the atom rows on the habit plane are perfectly coherent. Although we can not say from this figure whether or not the separation of the two layers of the precipitate is different from the spacing of {100} planes of the parent phase, it may be presumed to be larger than that of the parent phase. This is because the bend of {110} planes at the precipitate were clearly observed in the case of somewhat thicker precipitate plates as shown in Fig. 2, indicating the existence of b.c.t. structure there.

Figure 4 shows transformation temperatures, Ms, Mf, As and Af, which were obtained by thermal cycling tests under various applied stresses. Comparing those of the sample heat treated at 873 K, which contained small spherical Ti_2Ni precipitate such as shown in Fig. 5, these transformation temperatures are shifted towards the lower values, especially, Ms and Mf become much lower in the present case. It was observed by in the situ cooling experiment in electron microscope that thin foils containing coherent precipitates such as shown in Figs. 1-3could not be transformed by cooling down to about 100 K. DSC measurement also revealed that no transformation occurred in the sample heat treated at 745 K for 1h even cooled to about 150 K. These facts indicate that the Ms temperature of the present sample (heated at 745 K for 1 h) is below 100 K. It is considered that such decrease in Ms may have been caused by strengthening of the parent phase by the aforementioned coherent plate precipitates. However, it is puzzling that the application of a small stress of only 30 MPa raises Ms by more than 200 K as seen in Fig. 4.

Owing to those coherent subnanometric precipitates, the yield strength of the parent phase is greatly

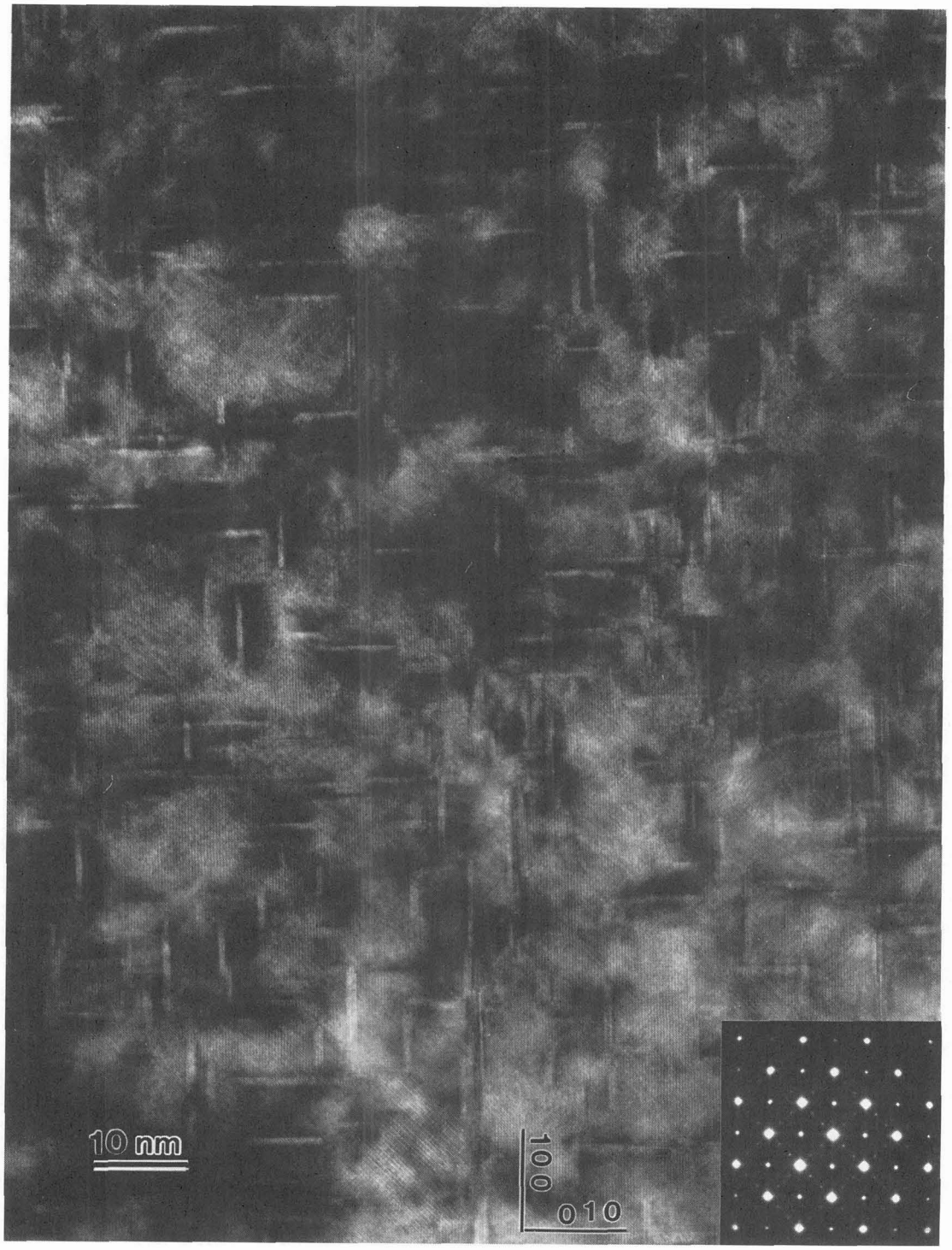

Figure 1. High resolution electron micrograph of a Ti-48.2at.%Ni thin film specimen heat treated at 743 K for 1 h. The corresponding electron diffraction pattern is shown in the inset. The zone axis is <100> of the parent bcc phase (B2).

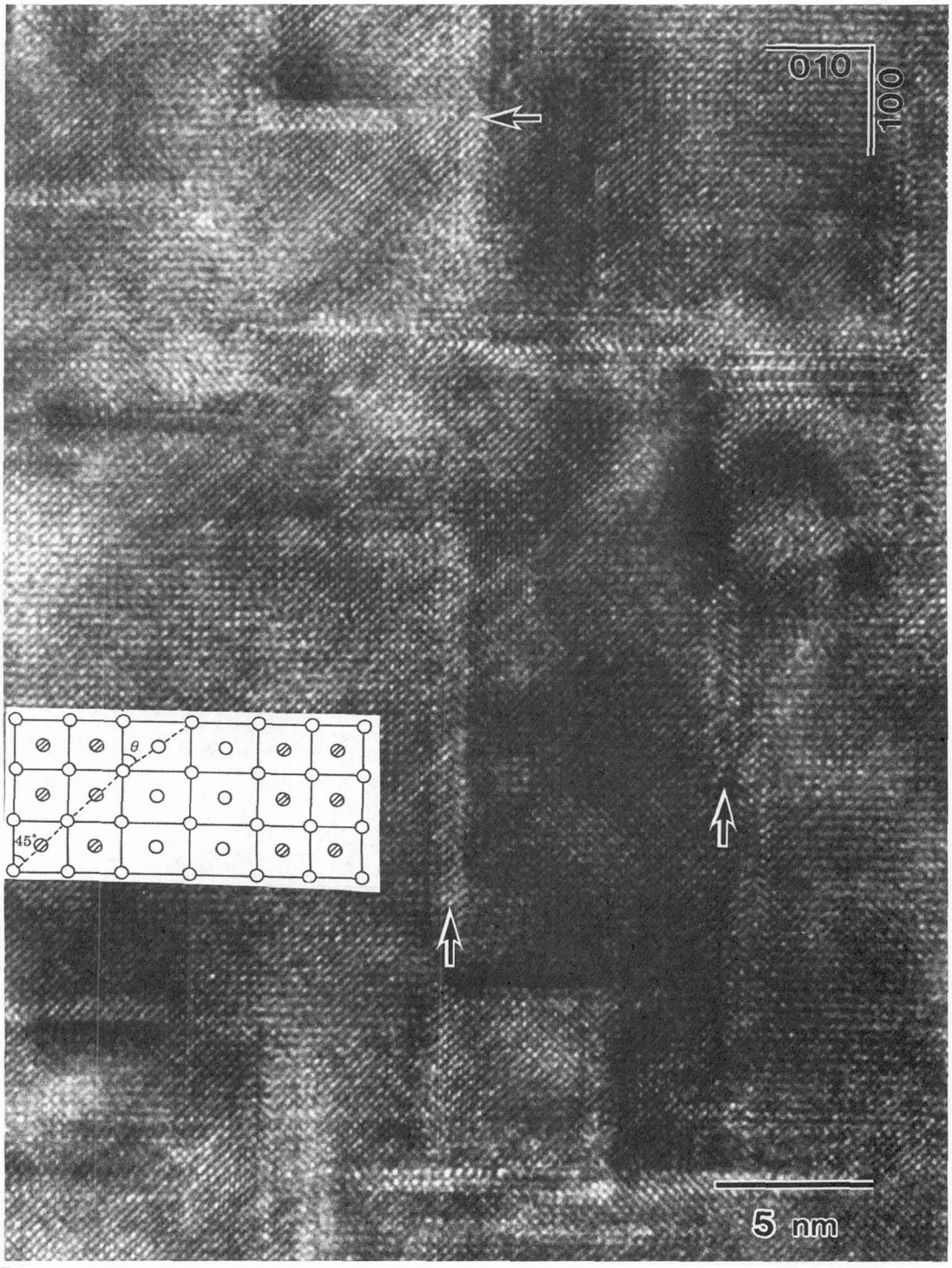

Figure 2: High magnification micrograph of structure images showing the details of plate precipitates. Individual <100> atom rows are resolved. Note that {110} lattice planes are bent at the precipitates. Schematic picture of the precipitate is shown in the inset.

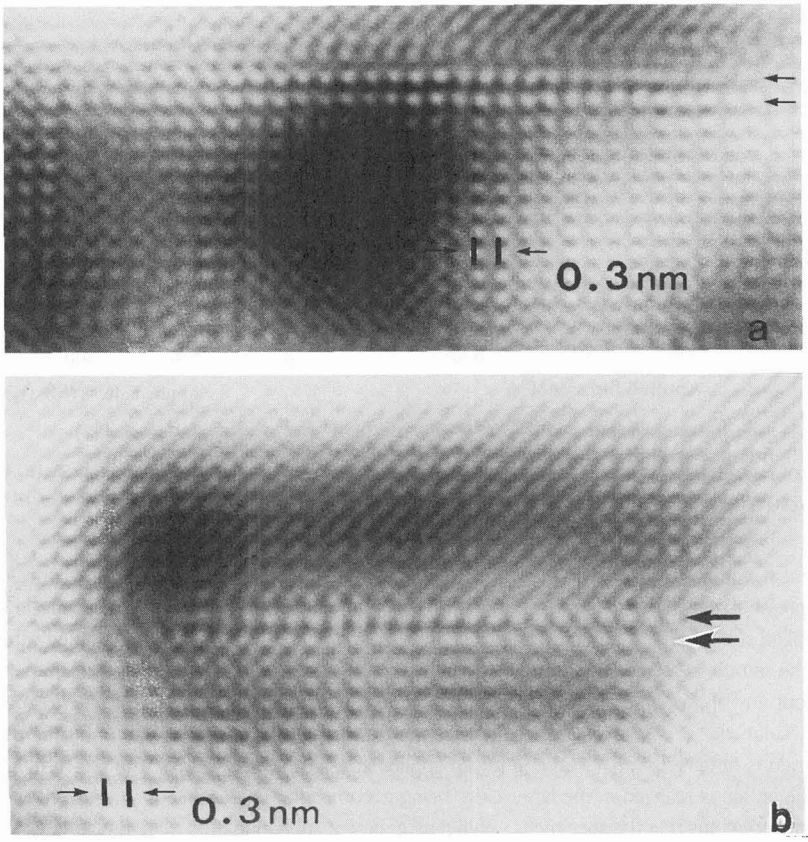

Figure 3: (a) Inverse Fourier transform image showing the arrangement of <100> atom rows. Arrows indicate {001} plane of the b.c.t. precipitate. Note the perfect coherency of the atom rows at the {100} habit plane. (b) Another example of inverse Fourier transform image of the precipitate, being accompanied by large dark contrast of elastically deformed area.

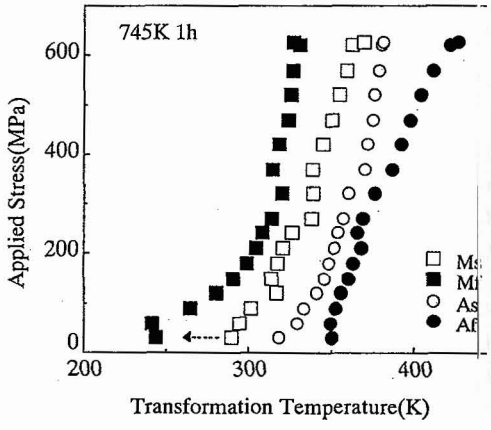

Figure 4: Transformation temperatures. Ms, Mf, As and Af, measured by thermal cycling under various applied stresses.

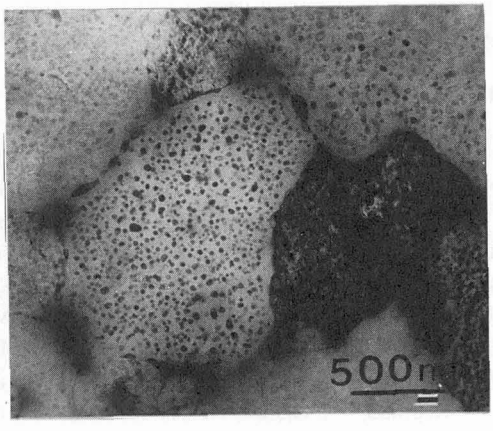

Figure 5: Spherical precipitates formed by heat treatment at 873 K for 1 h. The size of precipitates is in the range of 20-40 nm within the grain and, at the grain boundary, it is much larger.

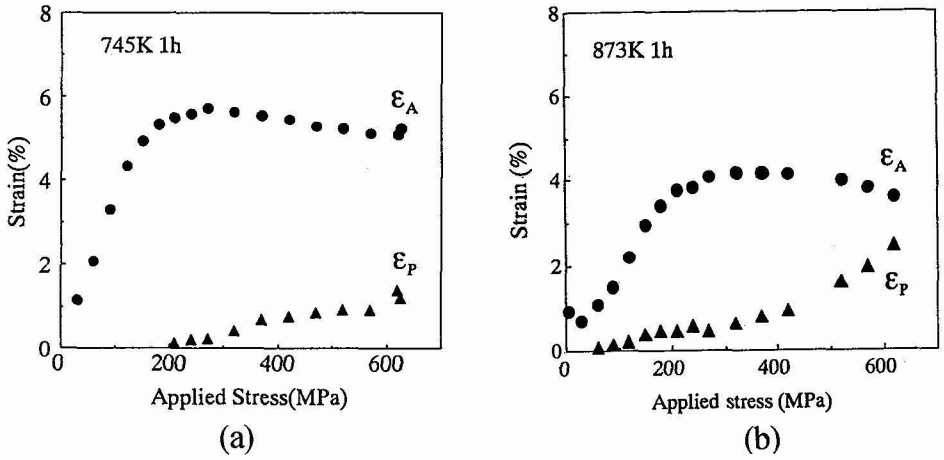

Figure 6: Recoverable shape stain, ε_A, and plastic strain, ε_P, as a function of applied stress; (a) for heated at 745 K for 1 h, (b) for heated 873 K for 1 h.

increased; about two times greater than that for the sample containing non-coherent Ti_2Ni spherical precipitates as shown in the previous paper [7]. Figure 6 (a) and (b) shows recoverable strain, ε_A, and plastic strain, ε_P, as a function of applied stress in the thermal cycling tests of shape memory effect; (a) for the sample heated at 745 K for 1 h and (b) for the sample heated at 873 K for 1 h. It is seen from these figures that nearly 6 % recoverable strain is obtained without any appreciable plastic strain for an applied stress of about 300 MPa in the former case, while the corresponding value of ε_A is only 2 % with an applied stress of about 100 MPa. Furthermore, nearly 5 % recoverable strain is obtained with 1 % ε_P for an applied stress of about 600 MPa in the former case, while only 4 % recoverable strain is realized in the latter case, being accompanied by 2.5 % ε_P at the corresponding applied stress. Thus it is obvious that the specimens containing coherent subnanometric plate precipitates show better shape memory properties compared with those containing ordinary incoherent precipitates.

As a concluding remark, we would like to emphasize that those subnanometric coherent precipitates described in the present paper can be produced only when heat treated directly from the amorphous state. If the crystallization is completed first, then, any kinds of heat treatments can not bring such precipitates with a transient structure. On the other hand, those subnanometric coherent precipitates will be able to be produced also in the bulk specimens of Ti-Ni alloys if the amorphous state can be realized.

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