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Effect of hydrogenation on the martensite transformation in nano-crystalline $Ti_{50}Ni_{25}Cu_{25}$

N.E. Skryabina[a,b,*], D. Fruchart[b], A.V. Shelyakov[c]

[a] *Perm State University, 15 Bukireva Street, 614990 Perm, Russia*
[b] *Laboratoire de Cristallographie, CNRS, BP 166, 38042 Grenoble Cedex 9, France*
[c] *Moscow Physical-Technical Engineering Institute, Kashyrskoe sh. 31, Moscow 115409, Russia*

Abstract

Hydrogen saturation in amorphous state of $Ti_{50}Ni_{25}Cu_{25}$ alloy leads to the suppression of the well known martensite phase transformation that occurs after heating, nano-crystallization and cooling down to room temperature.

Keywords: Metal and alloy; Amorphization; Phase transitions; X-ray diffraction and calorimetry

1. Introduction

TiNi type materials can be prepared in nano-crystalline state via two synthesis routes. After a primary crystallization at 400–450 °C, a melt-quenched amorphous ribbon can exhibit the B2 phase in nano-crystalline state. Then, after a subsequent cooling down to room temperature, the austenite–martensite transformation B2 $\rightarrow$ B19 occurs. A second route we have considered is based on a fine control of the quenching rate. Usually, the optimized rate of quenching should be approximately 5×10^5 K/s. In both cases, the resulting ribbons exhibit at room temperature the B19 structure type of martensite. A few years ago, Rösner et al. [1] and Gleser et al. [2] found that the austenite to martensite transformation can be suppressed via a controlled decrease of the grain size. In particular, it was shown that there is a critical grain size for the nano-particles (~15 nm) for which in $Ni_{50}Ti_{25}Cu_{25}$, the thermo-elastic martensite transformation does not occurs. In a previous work [3], the impact of hydrogenation on the martensite transformation in nano-crystalline $Ti_{50}Ni_{25}Cu_{25}$ was considered first. We observed that hydrogenation of alloy leads to a partial suppression of the martensite transformation. In the present paper, we report on a new investigation of this phenomenon, starting from primary crystallized nano-crystalline samples formed from amorphous state.

2. Experimental

The amorphous $Ti_{50}Ni_{25}Cu_{25}$ samples were prepared by the melt spinning technique. The nano-crystalline state was obtained by a primary crystallization performed at 440 °C. Introduction of hydrogen in the samples was made at room temperature using a H_2SO_4 based electrolyte, the cathode current density being varied in the range 50–800 A/m^2. For such experiments, the sample was the cathode and a platinum wire was the anode. The structure was checked by X-ray, using a Philips PW 1720 (Cu Kα radiation). A differential scanning calorimetry (DSC) analysis was made using a DSC-7 device Perkin-Elmer apparatus, applying a heating rate of 20 K/min.

3. Results and discussion

As is well known [4], heat treatment applied to the amorphous state alloy up to 500 °C leads to its crystallization. We obtained the B2 type of structure just after crystallization. Cooling down the as-received crystallized material for rates ranging from 5 to 40 K/min promotes the martensite type transformation leading to the B19 orthorhombic structure. After applying this procedure, no other phase was observed to form as shown in Fig. 1 (curve 2), in fair agreement with the phase diagram [5]. However, the DSC thermogram shows two peaks in Fig. 2 (curve 1). It is supposed that a double peak sequence should result from a martensite type phase transformation occurring in a two grain size distribution system [6].

After hydrogenation in amorphous state, the sequence of phase transformations was seen to drastically change. In this case it is possible to retain a structure resulting from the crystallization process (nano-crystalline state) that does not undergo

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* Corresponding author. Fax: +7 3422 37 16 36.
E-mail addresses: magicflight@permonline.ru, nataliya.skryabina@grenoble.cnrs.fr (N.E. Skryabina).

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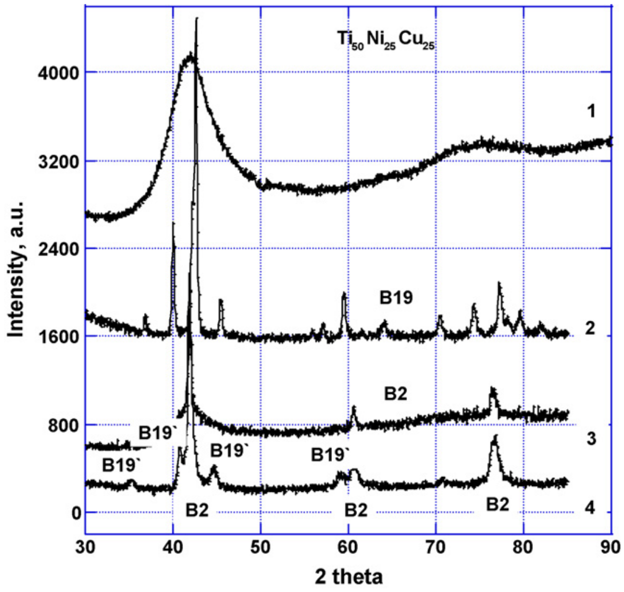

Fig. 1. X-ray diffraction patterns of $Ti_{50}Ni_{25}Cu_{25}$ alloys: (1) initial amorphous state, (2) after annealing at 440 °C, (3) after hydrogenation and annealing at 440 °C, and (4) after hydrogenation and two cycles of annealing at 440 and 520 °C, respectively.

any martensite type transformation upon cooling down to room temperature. In Fig. 1, we show report an X-ray pattern corresponding to this type of structural state. It is clear that after the hydrogenation treatment the B2 (bcc) type structure was retained at room temperature. A DSC analysis we have performed subsequently confirms this result as shown in Fig. 2 (curve 2). The double peak due to the martensite type phase transformation is completely absent for the hydrogenated sample. In fact we consider that the formation of a bcc-type structure is a direct consequence of a redistribution of the elements in the structure. A new near neighbor ordering (e.g. coordination) leads to two steps crystallization. The onset of two step crystallization is typical for the nano-crystalline materials. In the first step, nano-sized grains are found to precipitate in an amorphous matrix. This agrees well with what was already shown by Gleser et al. [2] for the $Ni_{50}Ti_{25}Cu_{25}$ alloy for which there is a critical size of grains where the martensite transformation was suppressed on cooling down. We anticipate that a similar phenomenon takes place in our hydrogenated compound. The nucleation of the nano-grain at the first step of crystallization suppress the B2 → B19 transformation due to the reduced size of the grains. Moreover, after full crystallization the structure of the material is not similar to that of the fresh sample (before hydrogenation). In this case, X-ray diffraction analysis reveals the existence of two phases as shown in Fig. 1 (trace 4). There is a B2 type component as crystallized at first and a B19' component having a monoclinic type of structure. The result is quite different from the crystallization of a non-hydrogenated nano-structured alloy forming a unique B19 system.

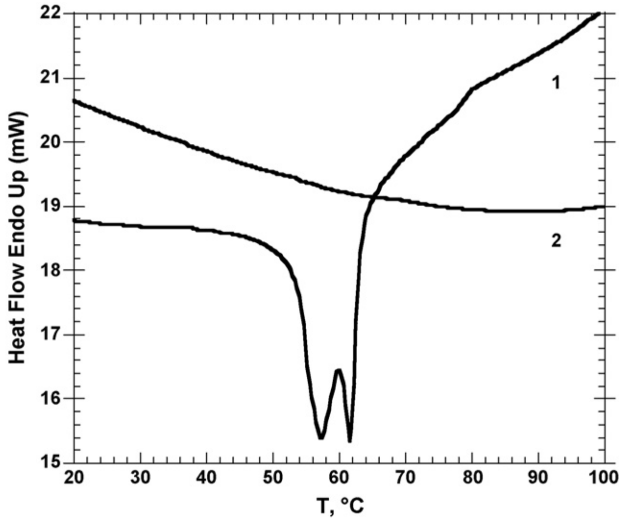

Fig. 2. DSC analysis of $Ti_{50}Ni_{25}Cu_{25}$ alloys after annealing at 440 °C: (1) without hydrogenation (fresh sample) and (2) hydrogenation before annealing.

Acknowledgments

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