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Hydrogen induced structural phenomena in amorphous and crystalline shape memory alloys

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ABSTRACT

Hydrogen interacting with shape memory alloys can be accompanied by several types phenomena related to the structure, those are: atomic rearrangements, hydrogen induced amorphisation, change of structural parameters of crystallised materials, suppression of the martensite type of phase transformation B2 → B19, and hydrogen induced reversible and irreversible embrittlement.

1. Introduction

In a previous work [1], the impact of hydrogenation on the martensite transformation in nano-crystalline $Ti_{50}Ni_{25}Cu_{25}$ was first considered. We observed that hydrogenation of such alloys leads to a partial suppression of the martensite transformation. In the present paper, we report on new investigation of this phenomenon.

Hydrogen interaction with intermetallic compounds, binary A_xB_y or ternary $A_xB_yC_z$, can be accompanied by:

- hydrogen induced amorphisation (HIA) (reported for the first time on Zr_3Rh by Yeh et al. [2] and as common features for A_3B-, A_2B-, AB_2- type by Aoki et al. [3]),
- hydrogen induced atomic rearrangements (HIAR) [4–6],
- martensite type phase transformation [7],
- change of structure parameters.

We have shown that in $Ti_{50}Ni_{25}Cu_{25}$ alloy it is possible to find all the here above indicated phenomena.

2. Experimental methods

We have investigated $Ti_{50}Ni_{25}Cu_{25}$ alloys in amorphous, crystalline and nano-crystalline states. Samples were prepared by using the melt spinning technique. 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. The cathode current density was monitored reference made to a specific measurement of the polarization curves in 0.5 M H_2SO_4. Such data used to determine the Tafel slopes. Accordingly, the cathode current density has been fixed to 250 A/m^2. For such experiments, the sample was the cathode and a platinum wire was the anode. Please refer for details to Ref. [1].

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 (aluminum lid and crucibles), applying a heating rate of 5–20 K/min and SEM investigations were performed using JSM-5600LV and S-3400N HITACHI microscopes.

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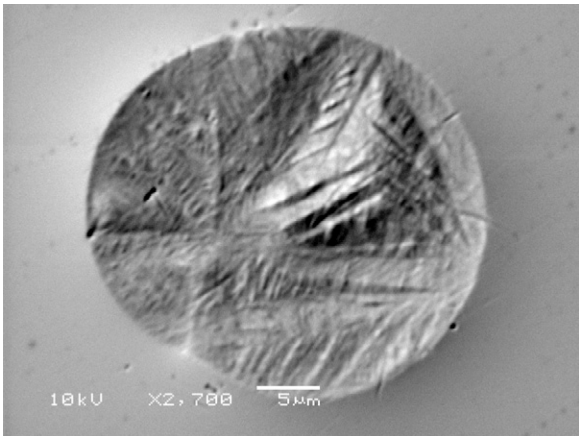

Fig. 1. Microstructure of a $Ti_{50}Ni_{25}Cu_{25}$ alloy in amorphous initial state: before hydrogenation, ×2700, secondary electron mode.

3. Results and discussion

The sample in crystalline state without hydrogen underwent the thermoelastic martensite transformation B2 → B19 on subsequent cooling to room temperature. However, hydrogen (deuterium) charged samples did not show the thermoelastic martensite transition. The DSC investigation confirms this result. Hydrogenation of the amorphous ribbon leads to other type of structural transformations. The initial state (before hydrogen treatment) is characterized by small spots of approximately 30 µm diameter, with crystalline structure surrounded by an amorphous matrix (Fig. 1).

After hydrogenation in amorphous state, the microstructure of the alloy changes drastically and we have pointed out two phenomena for that.

The first one is appearance inside of the amorphous matrix of spots with gradient of grey on electron microphotography (Fig. 2) related to composition (backscattering mode). It reveals a different but less typical structural organization, however, martensite corrugations are found absent into such areas. The appearance of composition gradients in the amorphous matrix is an example of the hydrogen induced atomic rearrangements (local atom redistribution) in this type of alloy.

The other one reveals appearance of cracks inside the crystalline areas and a limited suppression of martensite corrugations (Fig. 3a). No crack penetrates in the surrounding amorphous structure. In this case, there is no redistribution of element inside of the crystalline regions (Fig. 3b).

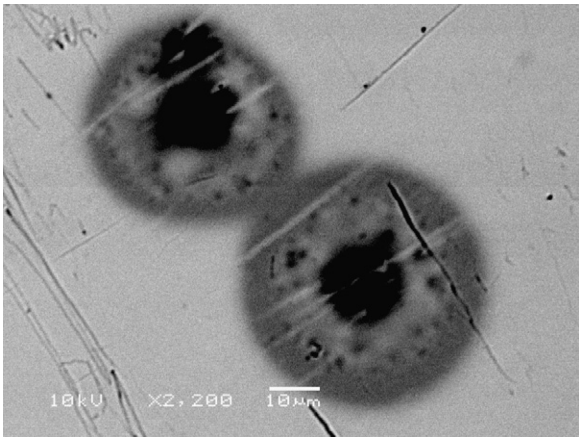

Fig. 2. Microstructure of a $Ti_{50}Ni_{25}Cu_{25}$ alloy in amorphous initial state just after hydrogenation: ×2200, backscattering electron, composition mode.

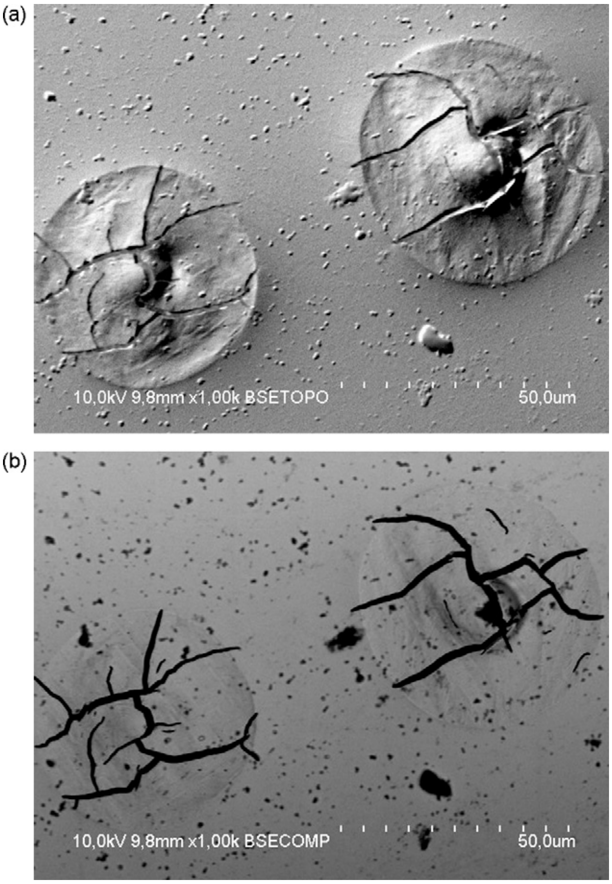

Fig. 3. Microstructure of a $Ti_{50}Ni_{25}Cu_{25}$ alloy in amorphous initial state just after hydrogenation, ×1000, backscattering electron: (a) topological mode; (b) composition mode.

Crystallization of $Ti_{50}Ni_{25}Cu_{25}$ alloys has been monitored before and just after hydrogenation, using different rates ranging between 5 K/min and 20 K/min. If charged with hydrogen, a marked shift of the crystallization peak of the alloy is observed towards higher temperatures. With the prolongation of hydrogenation process, an additional peak appears at low temperature. The result of crystallization differs markedly from those of samples without hydrogen treatment where we can see only one peak corresponding to full crystallization.

A few years ago, Glezer et al. [8] found that the austenite to martensite transformation in pseudo-binary alloys TiNi–TiCu 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 nanoparticles (∼15 nm) for which in $Ni_{50}Ti_{25}Cu_{25}$, the thermoelastic martensite transformation does not occur. Based on this feature, we have supposed that hydrogenation of the alloys induces some fragmentation of the structure. However, as shown in Figs. 2 and 3, there another type of impact of hydrogenation (deuteration) occurs since the surface of the crystalline ribbon looks has partly turned to an amorphous state.

From results of X-ray diffraction patterns, the martensite phase transformations as analyzed before and after hydrogenation using differential scanning calorimetry leads to assume a mechanism of structural transformation induced by the hydrogenation process.

The cell parameters of the orthorhombic B19 phase in initial state are: $a = 0.2909(3)$ nm, $b = 0.4300(4)$ nm, $c = 0.4515(3)$ nm. The monoclinic phase (B19′) of $Ti_{50}Ni_{25}Cu_{25}$ alloy does not exist at room temperature, according to the phase diagram [9]. However, if ones admits the possible existence of a B19′ type phase, the cell parameters should be as follows [9]: $a = 0.2880(2)$ nm, $b = 0.4110(4)$ nm, $c = 0.4650(4)$ nm and $\beta = 97.53(5)^\circ$. After hydrogen insertion for 60 min, the resulting crystal structure of sample is found much complicated as reported in [1], and three phases B19 + B19′ + amorphous are pointed out. The orthorhombic phase has cell parameters as follows: $a = 0.2906(3)$ nm, $b = 0.4272(4)$ nm, $c = 0.4550(5)$ nm. A comparison of the corresponding parameters of the unit cells shows, that a change structure parameters should promote the phase transition B19 → B19′. Pre-condition for such type of transformation can be the internal strains developed in the alloy at hydrogen insertion. Changes of the initial structural parameters are accentuated, and consequently the symmetry of the starting structure decreases.

So, electrolytical hydrogen (deuterium) insertion in quenched alloy $Ti_{50}Ni_{25}Cu_{25}$ either in initial amorphous state or with martensite B19 structure, leads to favors the occurrence of the monoclinic B19′ type of phase. Such phase transformations are made possible either during hydrogenation of the initial crystalline state or after crystallization of the amorphous or nanostructured material. The advancement of the phase transformation (amount of final phase) is found directly related to the hydrogen exposure time. Besides, a redistribution effect of elements forming the alloy monitors the structural transformation, as seen from the cell parameters behaviors.

4. Conclusions

1. Hydrogen is a forming structural factor, as well this occurs versus composition or/and temperature.
2. Hydrogen treatment offers possibilities to change or to fully suppress the thermoelastic martensite transformation B2 → B19.
3. In pseudo-binary alloys such as TiNi–TiCu, hydrogen provokes both reversible and irreversible embrittlement effects. The resulting state depends on the duration of the hydrogenation process and the current density.

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