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A study of hydrogen charging of 10M Ni-Mn-Ga single crystal

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Abstract

The effect of hydrogen charging on twinning stress and surface microstructure was investigated in 10M Ni-Mn-Ga ferromagnetic shape memory alloy. During hydrogen charging on the bulk sample, cross-like pits formed which gradually evolve into diamond shaped cracks on the surface. The cell boundaries are well visible and there is about 20 μm wide area next to the cell boundary is less cracked. The evolution of the microstructure before and after hydrogen charging is also studied by transmission electron microscope (TEM). There is no visible change in the average twinning stress during hydrogen charging even if the surface is dramatically covered with pits and microcracks.

Keywords: Ni-Mn-Ga; Hydrogen charging; TEM;

1. Introduction

Ni-Mn-Ga alloys have been under intensive investigations in last two decades for various potential applications due to the multifunctional properties, e.g. magnetic shape memory effect (MSM) up to 12% [1,2]; magnetocaloric effect (MCE)[3]. In general hydrogen embrittlement is a severe environmental type of failure that affects almost all metals and alloys. For example hydrogen embrittlement has been known to cause degradation of mechanical properties and fracture in stainless steels [4,5] and NiTi shape memory alloy [6]. The hydrogen effect on Ni-Mn-Ga alloy has been rarely studied. So far only one report has been found [7] dealing with the influence of hydrogen

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charging on existing crack of a polycrystalline sample. Since the best MSM properties are obtained exclusively in Ni-Mn-Ga single crystals having a five-layered modulated (5M or 10M) martensitic structure, the present hydrogen charging studies on a 10M Ni-Mn-Ga single crystal. In this case the influence of grain boundaries can also be avoided.

2. Experimental

A 10M Ni_{49.4}Mn_{27.8}Ga_{22.8} single crystal was employed for hydrogen charging experiments. The bulk sample has a dimension of $0.8 \times 2.3 \times 16$ mm, which was cut along $a$ axis of the cubic phase. In order to study the evolution of microstructure during hydrogen charging by transmission electron microscope (TEM), 3 mm disk were first punched from a 0.2 mm thin sheet and then further thinned by a double jet method using a Struers Tenupol-5. Cathodic hydrogen charging was carried out in 0.5 mol/l $\text{H}_2\text{SO}_4$ solution. For bulk sample 0.25 g/l $\text{NaAsO}_2$ was added for hydrogen recombination, but for TEM foils 0.25 g/l $\text{As}_2\text{O}_3$ used instead. The sample was placed in the center of a circular Pt counter electrode during charging process at room temperature. The current density applied was 0.3 mA/cm$^2$ for the bulk sample and 0.03 mA/cm$^2$ for thin foils.

The crystal structure was determined by X-ray diffraction with Panalytical X’pert MPD, before and after hydrogen charging, to be five-layered 10M martensite. The microstructure evolution during hydrogen charging was investigated in different scales, by optical microscopy Leica DMRX, scanning electron microscopy (SEM) TeScan Mira 3 and transmission electron microscopy Tecnai F20 operated at 200 kV.

3. Results and discussions

The electro-polished surface of bulk sample before hydrogen charging is showed in Fig. 1a. The bulk sample consists one major variant and some traces of second variants (shown as the vertical lines run from top to bottom). The surface is unavoidable sparsely pitted after the electropolishing, which is used as a surface finishing method for the MSM sticks. After 48 hours of cathodic hydrogen charging, corrosion pits cover the whole surface. Pits first start as cross-like formations, then became diamond like shaped by further deepening, and finally evolve into pit clusters which coalescence causing exfoliation of the surface layers. More interestingly, there are fewer pits at and around subgrain/cell boundaries than in the area inside the cell. Cell boundaries are usually not visible after electropolishing, but now their existence is well revealed (see Fig. 1b). Cell boundaries result from dendritic growth during single crystal processing elongated more or less along the cubic axis. The width of the cell is about 200 $\mu$m. Compared to the area near the center of the cell, the cell boundary seems to act as a preferential diffusion path for the hydrogen atoms due to its low misorientation nature [8]. As the hydrogen atoms can move away fast, the surrounding area is depleted from hydrogen atoms resulting in much less pits at and around cell boundary [9]. Furthermore, the number of pits at the boundary is just enough to form a cluster but not to develop into large cracks. The growth of pits is revealed in Fig. 1c starting from a tiny pit, then connected together into a line, and finally resulting in a cracked surface after surface exfoliation. The pit-clusters are aligned along $a$ and $b$ axes of martensite, and the cracks that are gradually formed also align at the same direction and finally develop into large crossed cracks while the polished surface erodes away.

The same microstructural changes as in bulk sample happened also in TEM foils although much faster. After 20 min of hydrogen charging the microstructure changes are dramatic with long cracks appearing. The inset image in Fig. 2a shows the final long cracks, about a few hundred micrometers long, in a foil after 250 min charging. At the end of the long cracks there is a web of cracks consist of alternation cracks along $a$ and $b$ axis of martensite phase, shown in Fig. 2a. Such a web of cracks is found only in thick area, in the thin area near the hole, only large long cracks appear. Those cracks all run along $\{100\}$ planes which indicating that the hydrogen atoms are trapped along $\{100\}$ plane probably due to the fact that the hydrogen atoms are more likely to align themselves along long $a$ or $b$ axis instead of short $c$ axis.

Hydrides are found after hydrogen charging at the sample surface both in bulk sample and thin foils as shown in Fig. 2. The hydrides formed have an irregular particle shape in both cases, but the particles appear to be much larger in thin foil than in the bulk sample.
Fig. 1. (a) Optical microscopic image of bulk sample before hydrogen charging and; (b) SEM image of the same surface after 48 h hydrogen charging; (c) a magnified image showing the pits in more detail.

Fig. 2. (a) Hydrogen induced long cracks ending at cracks web, inset shows the cracks developed in the foil after 250 min charging. Hydrides formed on the surface of charged sample observed by SEM (b) from bulk sample; (c) from thin foil.

Fig. 3. Microstructure after hydrogen charging (a) after 20 min; (b) after 250 min and the corresponding electron diffraction patterns.

The 10M martensite crystal structure after charging was confirmed to be the same as before for the bulk sample. This is also evident from the electron diffraction pattern (EDP) of the foils charged for 20 min or 250 min (Figs. 3a and 3b, correspondingly). In the foils the twinning structure remains unchanged, only hydrides form rapidly on the surface. The hydrides formed after 20 min are quite uniform with dimensions around 50 nanometers and ED pattern
showing a single phase ring pattern, which closely fit to Ni$_2$H (ICDD PDF No. 04-007-1853). After 250 min charging hydrides grow larger having dimensions over 100 nanometers. The ED pattern shows mixed phases, which match two compounds, Ni$_2$H (ICDD PDF No. 04-007-1853) and MnH$_x$ (ICDD PDF No. 04-007-1853), with x in the range of 0.8-0.95.

Twinning stress is the most important property for MSM application. It is believed that the surface state will affect the twinning stress [10]. When the compressive twinning stress in the bulk sample was measured before and after charging (Fig. 4) no visible change in the twinning stress was observed even when the surface become full of pits and cracks. We propose that this is due to the multi twin variant nucleation as the twin interface movement counters the increased obstacles on the surface during the measurement.

![Fig. 4. Twinning stress before and after hydrogen charging.](image)

4. Conclusions

Hydrogen charging will dramatically change the polished surface and promote pitting and crack nucleation in bulk sample, and larger cracks rapidly appeared in thin foil sample. At same time the hydrides are evenly formed on the surface of the charged sample. Twin structure does not change, neither there are visible changes in the density of stacking faults or dislocations in TEM foils. The twinning stress of bulk sample remains unchanged before and after charging even if the sample surface turned to being full of pits and cracks.

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