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TEM investigation of ZrO_2 in $Zr(Ni_{0.55}V_xMn_{0.45-x})_2$ hydrogen storage alloys

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Abstract

Zirconia particles were found in AB_2 type $Zr(Ni_{0.55}V_xMn_{0.45-x})_2$, $x=0.05$–0.4, hydrogen storage alloys and studied with TEM. Results showed the high temperature tetragonal phase (T) of zirconia coexisted with a monoclinic (M) one at the room temperature. This can be attributed to the shape effect and volume restraint in the T–M transition. The orientation relationship between T and M phases, the morphology and structural aspects of fully transformed M-phase as well as its influence on activation of the alloys were also discussed.

Keywords: Zirconia; Phase transformation; Hydrogen storage alloys

1. Introduction

In the study of Zr-based hydrogen storage electrode alloys, ZrO_2 particles were observed in the metal matrix with noticeable phase transformation, which may lead to the improvement in activation properties and hydrogen diffusivity. In this paper only the phase transformation process is studied and reported. Tetragonal (T) to monoclinic (M) transformation of zirconia ceramics has been an interesting topic to scientists for decades because of the transformation toughening resulted and its martinsitic transformation in nature [1]. In many cases the high-temperature tetragonal phase can be stabilized and maintained to room temperature by some oxide dopants such as Y_2O_3, MgO, CaO and CeO_2 although the phase transition temperature for pure zirconia is very high (~1170°C) [2]. Moreover the T–M transformation mechanism is also believed to be strongly dependent on the environment and microstructure of samples, especially when small ZrO_2 particles are dispersively distributed in a heterogeneous matrix [3,4]. Therefore it is of importance to investigate the influence of the matrix from which the precipitates or the particles nucleate and grow. So far not much work has been done on it [3–6] and none of them was on the transformation of ZrO_2 particles in a metal or alloy heterogeneous matrix.

In this investigation ball-shaped particles of pure zirconia containing untransformed T phase uniformly distributed in the matrix of $Zr(Ni_{0.55}V_xMn_{0.45-x})_2$ Laves phase AB_2 type hydrogen storage alloys were identified and examined by means of common transmission electron microscopy (CTEM), electron diffraction (ED) and high resolution electron microscopy (HREM). The T–M transformation of ZrO_2 in the metal matrix was studied and discussed.

2. Experimental

$Zr(Ni_{0.55}V_xMn_{0.45-x})_2$, $x=0.05$–0.4, Laves phase hydrogen storage electrode alloys were synthesized by arc melting of the pure elements (Zr 99%, Ni 99.9%, Mn 99.75%, V 99.5%) in a water cooled copper hearth under argon atmosphere. All samples were remelted four times and each ingot was inverted before the subsequent melt to ensure homogeneity.

In preparing TEM specimens, thin pieces about 500 μm thick were first cut from cast ingots and then mechanically polished and dimpled down to 20 μm. Ion milling was

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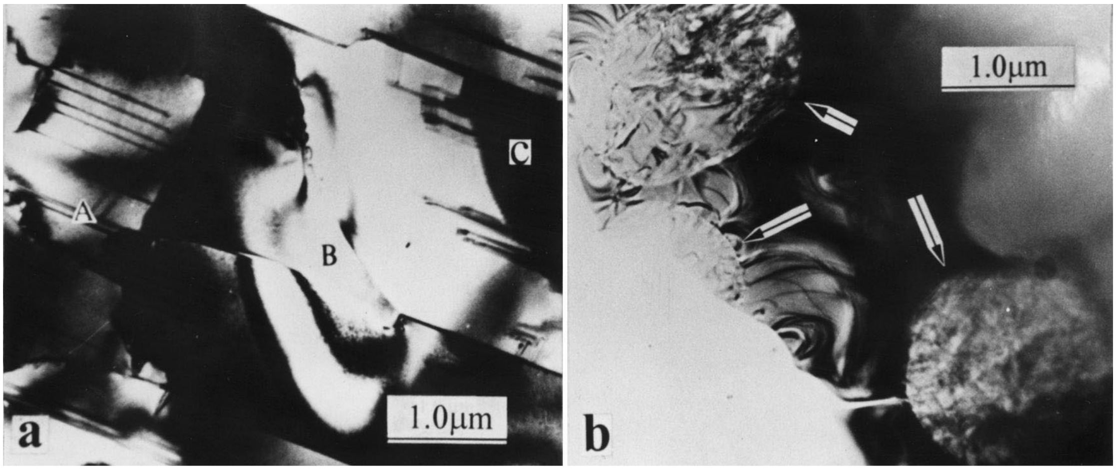

Fig. 1. The typical microstructure of ZrNiVMn hydrogen storage alloys showing C15, C14 Laves phases and Zr_9Ni_{11} coexist as indicated by A, C and B respectively (a), and zirconia particles were found in the alloys (b).

applied for the final thinning of the samples under 3.8 kV. CTEM, ED and EDS experiments were carried out on a Philips CM12 electron microscope operated at 120 kV, and HREM images were taken from a JEOL JEM 2010 TEM with the point to point resolution of 1.9 Å operated at 200 kV.

3. Results and discussions

Fig. 1a shows a typical TEM bright field (BF) micrograph for the matrix of $Zr(Ni_{0.55}V_xMn_{0.45-x})_2$ alloys. C15, C14 Laves phase and tetragonal Zr_9Ni_{11} coexist in the specimen as indicated by A, C and B, respectively. Their structural features, crystalline relationships as well as their influence on electrochemical properties of the alloys were studied in detail and will be published elsewhere soon [7]. Fig. 1b shows some spherical particles with an average diameter of 1–2 μm distributed rather dispersively in the matrix as indicated by arrows. X-ray energy dispersive spectrometer (EDS) analyses revealed that only Zr with Z≥11 was existing, which implied that they could be either pure zirconium or zirconium oxide. To examine their reciprocal space, series tilting ED experiments were subsequently performed, from which the resulting composite ED patterns (Fig. 2) showed that it composed at least of two sets of different phases. Through carefully analysis, the pattern was successfully indexed by coincidence of T with twinned M phases of zirconia. As no other metal elements but Zr was shown in our EDS analyses for all the particles, the existence of pure zirconia was confirmed then. During TEM observation one noticed that the morphology and microstructure of ZrO_2 particles changed rapidly, and that the thin part of ZrO_2 particles, for instance in areas near a hole, always displayed fully transformed M pattern (region A of Fig. 3). However the thick regions are often composed of T and M mixed phases (region B of Fig. 3). Fig. 4a is the TEM image of a single ZrO_2 particle taken in a relatively thick region, where dense planar defects and strain field contrasts can be seen

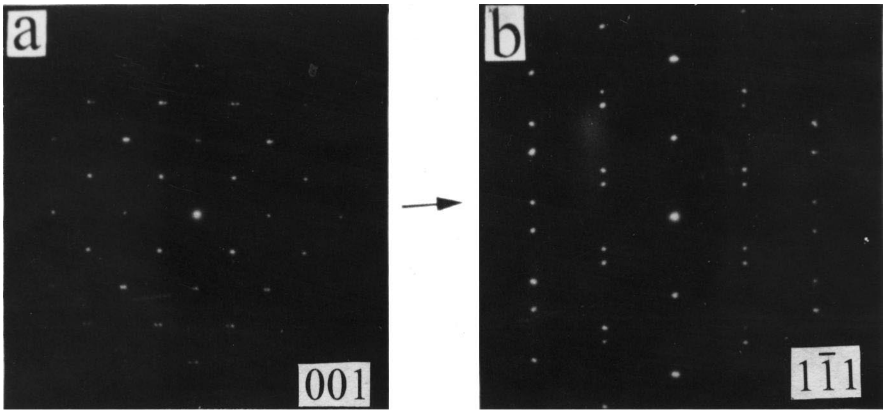

Fig. 2. Composite ED patterns for zirconia particles showing it consists of both T and twinned M phases.

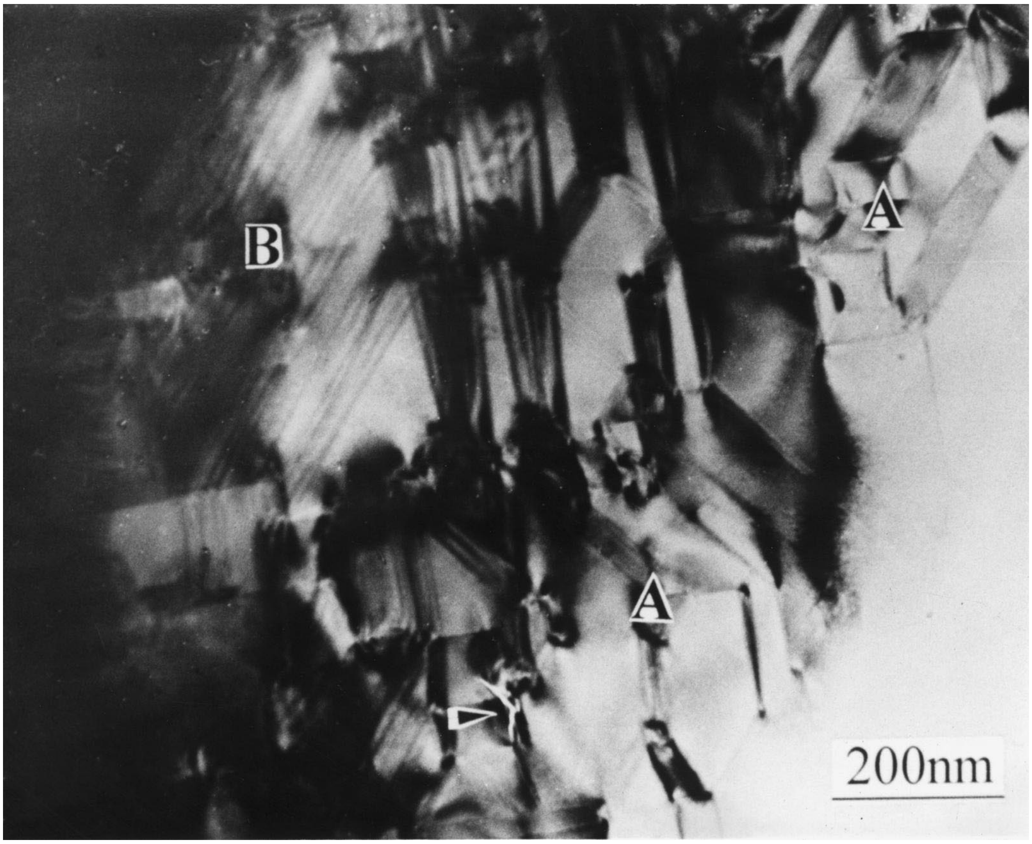

Fig. 3. TEM micrograph with a higher magnification of a zirconia particle showing M phase in the thin region (A) and T+M phases in thick part (B) of the particle; note that dense planar defects in B area and microcracks (indicated with an arrow) were observed.

inside the particle, specially in the interface regions of the particles and the matrix, which was undergoing phase transition at that moment. The corresponding ED pattern of the particles confirmed again the presence of untransformed T phases (Fig. 4b). Microcracks in the interface, indicated by the arrow in Fig. 4a, is due to the stress

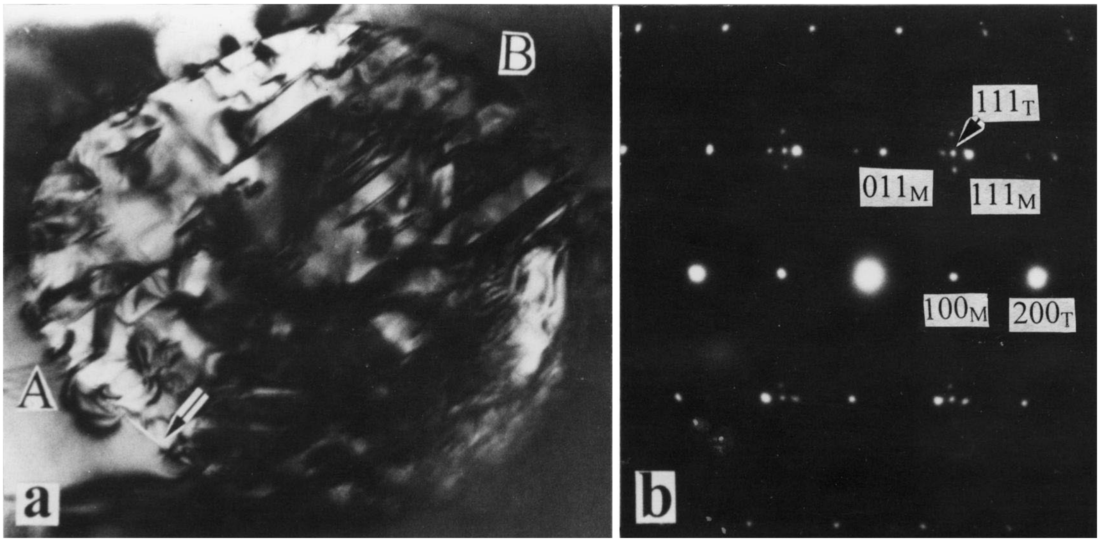

Fig. 4. A single zirconia particle undergoing T–M phase transformation induced by beam radiation, note that full of defects inside the particle and the strain field contrasts seen everywhere specially in the interface region A and B.

caused by volume change (5% expansion and 8% shear) during T–M transformation [8]. From ED patterns of Figs. 4b and 2, the following crystalline orientation relationship between T and M phase can be deduced: $(100)_M//(100)_T$, $[001]_M//[001]_T$, and also $(010)_M//(100)_T$, $[001]_M//[001]_T$. The latter relationship can be obtained by exchange of reciprocal vectors $[100]^*_M$ and $[010]^*_M$ and is consistent with ED pattern of Fig. 2a, where the reflections of both the rows of [100]* and [010]* split into pairs due to the slight difference in d_{100} and d_{010} of the M phase. The presence of untransformated high temperature T phase at room temperature indicates that the T–M transformation process was retarded in the alloys, which can be attributed to the shape of the particles and the volume restriction of matrix with the following reasons: (1) T phase particles in spherical or ellipsoidal shape are more stable at relative low temperature than the particles with facets, and the smaller particles are more stable in the T–M transformation [5,6]. (2) No other oxides have been found as stabilizers in the zirconia particles. (3) The observed T–M transition has been exposed to beam radiation. (4) M phase exists in thin regions and T phase in thick regions. According to above analyses we infer that the zirconia particles in question were formed during the melting stage due to the easiness of oxidation of zirconium. They were all in spherical shape as small droplets due to the surface tension. The small particles distributed dispersively in the matrix because of several inversions of the sample during melting. After solidification particles of high temperature T phase were imbedded in the matrix and their subsequent phase transformation was retarded owing to their shape and the volume constriction of the matrix during cooling down to room temperature. Therefore the following conclusion can be made that all zirconia particles in bulk samples of the alloys under investigation must come from high temperature T phase. The T phase started to transform into M phase only in thin specimen and subjected to beam radiation. The thinner the part of T phase, the more easily the transition happened.

TEM examination also revealed that the fully transformed M-phase contains abundant twins with different variants. Fig. 5 is a TEM BF image taken in the thin region of a zirconia particle with M phase near [001] zone axis and the specimen was nearly in the zero tilt position. A notable feature of the image is that almost all the twinning planes stand edge-on (parallel to the beam direction). It implies that the twinning direction (along the c axis) is also parallel to the foil normal of the specimen. Apparently this phenomenon is not just a coincidence because the thinnest direction along the foil normal is the easiest direction to avert the matrix restraint and hence the direction of shear in T–M transformation, accompanied with twinning of the M phase. So it gives another evidence for the volume restriction retaining the T phase in the alloys. Here $[001]_M//\langle 001\rangle_T$ can be deduced from the orientation relationship of T and M phases, which is consistent with

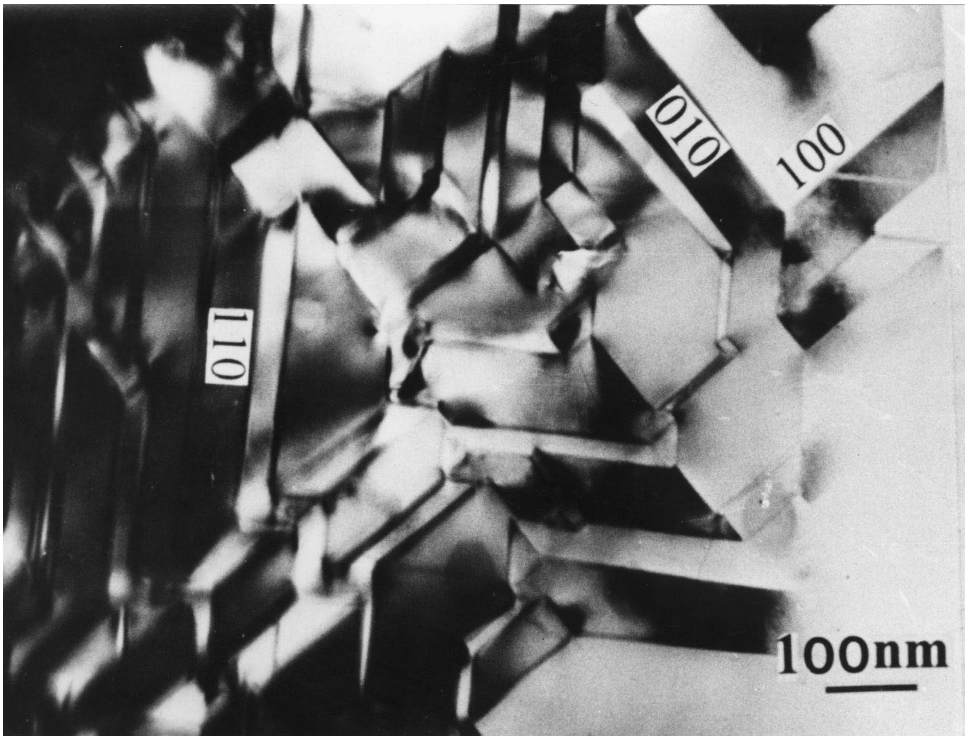

Fig. 5. A fully transformed region of M phase where abundant twins with different variants were observed with beam direction along $[001]_M$, the twinning planes were indicated upon trace analyses.

our ED analyses shown in Figs. 2 and 4 before. Trace analyses confirmed that the twinning planes are $(100)_M$, $(010)_M$, $(110)_M$, $(\bar{1}10)_M$ as indicated in Fig. 5. According to above analyses a geometry relationship for T–M phase transformation and twinning is established as follows: the direction of shear in the formation of M from T is along the **c**-axis, i.e. $[001]_M//[001]_T$. On this account a pair of twinning variants can be produced by exchanging $\mathbf{a}_M$ and $\mathbf{b}_M$ with $-\mathbf{a}_M$ and $-\mathbf{b}_M$, while keeping $\mathbf{c}_M$ unchanged. This model is strongly supported by the observed crystalline orientation between T–M transformation and the twinning planes with indexes of (100) and (010) between the variants. Similar model can be established for the other pair of variants with twinning plane of (110) and $(\bar{1}10)$, just by exchanging $\mathbf{a}_M$ with $\mathbf{b}_M$ and keeping **c** direction of T and twinned M phase parallel to each other. Fig. 6 shows a HREM image of a twinned M phase with the twinning plane (100) or (010). Strains and defects can be observed in the interface areas between twins possibly due to the lattice misfit resulted from the slight difference of d_{100} and d_{010}.

In contrast to ceramics heterogeneous matrix, metals and alloys usually have larger thermal expansion coefficient than their oxides, or in other words, compressive stress rather than tension would be imposed on the ZrO_2 particles in an alloy matrix after cooling down from high temperature. Obviously the compressive stress gives another restriction to the T–M transformation in addition to the shape factor of the particles. Only when both restraints released, the T–M transformation could be started.

ZrO_2 does not store hydrogen and is considered as an impurity in Zr-based hydrogen storage alloys. However, the volume change (5% expansion) and the shear strain (8%) during T–M phase transformation is thought to have a positive effect on the first stage of activation for the hydrogen storage alloys. After pulverization the matrix restriction to the T–M phase transformation is released, the strain and the microcracks generated in the matrix around zirconia particles would provide more activated sites and channels for diffusion of hydrogen atoms.

4. Conclusions

Spherical zirconia particles with a diameter of 1–2 μm in $Zr(Ni_{0.55}V_xMn_{0.45-x})_2$, $x=0.05$–0.4, hydrogen storage alloys were found to be a high temperature tetragonal phase at the room temperature, which is attributed to the shape effect and volume during T–M transformation. The orientation relationships between T and M phases for the particles are $(100)_M//(100)_T$, $[001]_M//[001]_T$, and also $(010)_M//(100)_T$, $[001]_M//[001]_T$ and the twinning planes are $(100)_M$, $(010)_M$, $(110)_M$, $(\bar{1}10)_M$. The strain and microcracks produced during phase transformation are thought to provide more activated sides and channels for

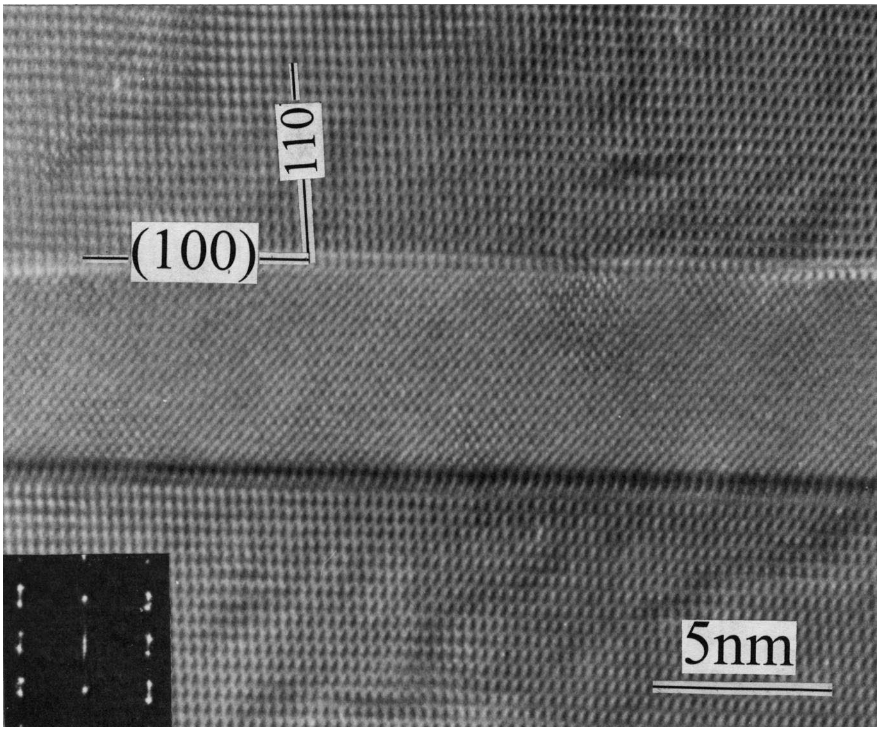

Fig. 6. A HREM image of a twinned region of zirconia M phase, the twin plane is determined to be (100) or (010), inset shows the corresponding ED pattern.

the hydrogen diffusion into to matrix in the first stage of activation.

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