



Article Physical Properties of Ti₄₅Zr₃₈Fe₁₇ Alloy and Its Amorphous Hydride

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Abstract: The alloys based on Ti-Zr are considered an excellent candidate for hydrogen storage applications. In this communication, we report the results of Fe substitution for Ni in the well-known $Ti_{45}Zr_{38}Ni_{17}$ compound. The parent and related compounds can be obtained as amorphous powders, transforming into the quasicrystalline phase (i-phase) after annealing. The amorphous $Ti_{45}Zr_{38}Fe_{17}$ phase is transformed into the icosahedral quasicrystalline state, and it is a quasi-continuous process. The i-phase is well-developed close to 500 °C. At higher temperatures, the quasicrystal structure transforms into the other phase: the w-phase (an approximant to the crystalline phase) and another crystal phase with a small addition of the FeZr₃ and the Fe₂(ZrTi)₃. The amorphous $Ti_{45}Zr_{38}Fe_{17}$ phases can be hydrogenated while maintaining the amorphous nature, which constitutes another very fascinating research field for our group. The investigated alloy shows a good capacity for gaseous H₂ at level 2.54 wt.% at elevated temperatures. The ferromagnetic signal of the amorphous TiZrFe comes from magnetic nanocrystallites in the amorphous matrix. After heating, the magnetic signal significantly decreases due to the lack of long-range magnetic ordering in the i-phase of the $Ti_{45}Zr_{38}Fe_{17}$ alloy.

Keywords: hydrogen-storage materials; amorphous alloys; quasicrystalline alloys; magnetic properties; neutron diffraction

1. Introduction

Hydrogen can be a promising energy carrier for future energy economy [1,2], which, of course, involves changes in the transport infrastructure [3,4] and the adaptation of the entire energy system to the properties of hydrogen. One of the most important challenges is hydrogen storage [5]. In this context, the solid-state alloys that allow for reversible hydrogen storage [6] belong to the class of materials that can be suitable for application.

The titanium-zirconium-based alloys are the second largest class of solids, for which quasicrystallinity was found, e.g., TiZrNi [7] or TiZrFe [8–10]. The Ti-Zr compounds are promising candidates for many applications such as biomedical [11–13], filler metal [14], medium entropy alloys [15], bulk metallic glasses [16], dental implant [17], shape memory alloys [18], and high-entropy alloys [19]. The TiZrNi quasicrystal seems to be especially suitable for hydrogen storage due to its large hydrogen uptake capacity [20,21]. In this case, the hydrogen atoms are situated preferentially near Ti and Zr atoms in the quasicrystal lattice.



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Copyright: © 2022 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https:// creativecommons.org/licenses/by/ 4.0/). The chemical-physical properties of the $Ti_{45}Zr_{38}Ni_{17}$ compositions can be changed by substituting other elements such as Ag [22], Pd [23–25], V [26], Co [27], Cu [28], Li [29], Ce [30], Mg [31], and Fe [32] in order to increase hydrogen sorption.

Since the discovery of quasicrystals, magnetic properties have not been studied much due to the lack of translational symmetry required for establishing long-range magnetic order. However, some quasicrystals exhibited spin-glass-like behavior [33]. Recently, the quasicrystals showing both ferromagnetic and antiferromagnetic behavior have been studied [34–38]. The magnetism in the TiZrNi quasicrystals was highly demanded [39]. The ferromagnetic signal for the $Ti_{45}Zr_{38}Ni_{17}$ originated from nickel nano-cluster precipitations in the quasicrystalline alloy [40].

The present work aims at tracking the transformation of the $Ti_{45}Zr_{38}Fe_{17}$ from the amorphous to the quasicrystalline/crystalline phases by the in-situ neutron diffraction technique and monitoring the magnetic properties. Additionally, our goal is to obtain the amorphous $Ti_{45}Zr_{38}Fe_{17}$ alloy with the highest hydrogen capacity.

2. Experimental

The $Ti_{45}Zr_{38}Fe_{17}$ nanopowders were synthesized by mechanical alloying (MA), which was performed in the Frisch Pulverisette 7 planetary mill. Commercially available titanium (99.9%), zirconium (99.9%), and iron (99.9%) powders were used as starting materials. A mixture of the starting elements corresponding to the chemical composition of the $Ti_{45}Zr_{38}Fe_{17}$ was placed in stainless steel vials (45 mL), which contained stainless steel balls (14 mm in diameter). An initial mass of the powder mixture before MA was 8.5 g, with the ball-to-powder weight ratio equal to 8:1. The vials containing the powder mixture and balls were evacuated by a rotary pump and then refilled with argon gas (99.999%) in a glove box. Then, gaseous argon was pumped out several times in order to extract all spurious gases from the operating atmosphere. The final argon pressure was maintained at 0.1 MPa. The ball acceleration was 15 g, while the maximum alloying time was 40 h. To avoid a temperature increase during MA, alloying periods of 0.5 h were alternated with rest periods of 0.5 h. After the first 20 h of milling, the vials were opened in a glove box and the powder was mixed. Then, the powder was subsequently alloyed for 20 h under an argon atmosphere.

The morphology of the amorphous nanopowder was studied using FEI Versa 3D scanning electron microscope (SEM). The differential scanning calorimetry (DSC) measurements were conducted under an argon gas flow at a heating rate of 5 K/min^{-1} .

The sample was tested using neutron diffraction to check if transformation from the amorphous to the crystal structure occurred. The amorphous phase was hydrided. Hydrogen gas was introduced at a pressure of 4 MPa, and the reaction chamber was heated to 163 $^{\circ}$ C to initiate hydrogen uptake. The X-ray powder diffraction (XRD) patterns were collected before and after the hydrogenation of the amorphous sample to check its quality. All the above steps were performed following the procedures reported in Ref [27].

Magnetization as a function of temperature from 127 °C to 927 °C was measured using a LakeShore Model 7407 vibrating sample magnetometer (VSM) equipped with an oven under an argon atmosphere (6N) heating rate of 5 °C/min⁻¹ in the presence of a magnetic field of 1 Tesla. The sample was mounted with Thermeez 7020 ceramic putty on a quartz rod. The characteristic and Curie temperatures were estimated as the maximum of the first derivative of the curve.

3. Results and Discussion

Figure 1 presents the submicrometer agglomerates of primary <100 nm particles, which were observed in the amorphous specimen.



Figure 1. The SEM images of the amorphous Ti₄₅Zr₃₈Fe₁₇.

The phase changes for the amorphous $Ti_{45}Zr_{38}Fe_{17}$ during the heating in the temperature range from 200 °C to 800 °C recorded with the DSC are shown in Figure 2.



Figure 2. The DSC curve for the $Ti_{45}Zr_{38}Fe_{17}$ amorphous powders was obtained by MA for 40 h.

The broad exothermic shoulder is visible between 200 $^{\circ}$ C and 700 $^{\circ}$ C. The energy introduced by mechanical alloying is released during heating, which is visible in the DSC shoulders.

Between 325 °C and 515 °C, the structure changes from amorphous to quasisrystalline with some addition of the crystal phases such as the FeZr₃ and the Fe₂(ZrTi)₃. The minor peak appears at about 515 °C, which indicates that the quasicrystalline phase is fully formed.

Figure 3 shows the evolution of the neutron diffraction patterns for the amorphous structure during heating. As is apparent from Figure 3a, broad maxima at about 60° of 2θ

is changing due to the start of thermal diffusion above roughly 300 °C. The change is connected with the gradual forming of crystalline and quasicrystalline (i) phases. The maxima broadens splitting into small reflections that at 500 °C develop rapidly into well-defined reflections of icosahedral and metastable FeZr₃ [41] phases. Also at this temperature, the Fe₂(ZrTi)₃ phase appears roughly at 40° of 20. The DSC results are consistent showing maxima at 325 and 515 °C, which is understandable as the DSC measurement has a much higher temperature ramp than neutron diffraction measurements. The i-phase can be evidenced by several well-defined reflections, which appears at about 53.5°, 58.8° of the 20 angle. The results of the neutron diffraction experiment show the quasi-continuous character of the transition from the amorphous phase to the quasicrystalline phase. The icosahedral structure of the Ti₄₅Zr₃₈Fe₁₇ starts to evolve into the w-phase above 525 °C. At higher temperatures (750 °C), an additional transition from the w-phase into the cubic phase was evidenced. The transitions at 525 °C and 750 °C are not strongly reflected in DSC as both are not associated with the significant rearrangement of the constituting atoms.



Figure 3. The transformation from the amorphous to the crystal phase for the $Ti_{45}Zr_{38}Fe_{17}$ alloy as seen by neutron diffraction (**a**); the in-situ neutron diffraction patterns at some chosen temperatures (**b**).

The pattern for the cubic phase can be indexed in the same crystal phase as the wphase. The reflections are in similar positions; however, the primary reflections become significantly narrowed. The cubic phase is stable while cooling down to room temperature. It is worth noting that the $Fe_2(ZrTi)_3$ phase is stable to the highest investigated temperature of 900 °C and is also present after the cooling of the specimen.

The magnetic properties measured in the temperature range of 127 °C to 927 °C for the amorphous $Ti_{45}Zr_{38}Fe_{17}$ powder are shown in Figure 4. A systematic decrease in the magnetization of $Ti_{45}Zr_{38}Fe_{17}$ is observed as a function of increasing temperature, and the transition of the ferromagnetic phase into the paramagnetic phase is observed. The amorphous phase changes its structure into some crystal phases during the first heating.

The amorphous phase is not expected to be magnetic. The magnetic properties of the amorphous material originate probably from small amounts of the magnetic nanocrystals not successfully observed by neutron diffraction. The characteristic temperature with the Curie temperature (T_C) was defined as the peak position in the dM/dT-T curve, as shown in Figure 4b. It is equal to 267 °C/300 °C, 352 °C, 468 °C, and 737 °C, respectively. From 127 °C to 267 °C/300 °C, a slight increase in the magnetic signal was observed, which can be explained by the ordering of the magnetic moments of the magnetic nanocrystallites in the amorphous matrix under the influence of magnetic field. The transformation of the amorphous phase started above 300 °C. The temperature value 352 °C obtained from the

VSM measurement is correlated with the value of 325 °C derived from the DSC measurement, in the results of which one can observe the evolution of the amorphous phase to the i-phase. The formation of the quasi-phase is noticed both as peaks in the DSC (515 °C) or the VSM (468 °C) measurement, which can be additionally confirmed by the neutron diffraction at the temperature of 500 °C. The start of the formation of the i-phase is observed probably at 468 °C, and the end is observed at 515 °C. The Curie temperature (737 °C) is observed during the transition of the amorphous phase into the crystalline phases and during the subsequent heating of the crystalline phase. This temperature is close to the value of 770 °C known for pure iron [42]. This means that apart from an occurrence of the similar crystalline phase close to the w-phase, the sample also contains a small number of iron atoms that have not reacted.



Figure 4. The temperature-dependent magnetization at 1 T for the amorphous phase (**a**); the derivative of the temperature-dependence used for the determination of the characteristic temperature (**b**); the thermal evolution of the magnetic coercivity (**c**); and the isothermal magnetization curves (**d**) before (red) and after heating (blue).

Figure 4c,d show the evolution of the magnetic coercivity vs. temperature and the magnetization vs. magnetic field curves measured at 20 °C before and after heating. The high values of the magnetic coercivity ($H_C = 46.5 \text{ mT}$) and the magnetic saturation (Ms) ($M_S = 4.9 \text{ emu/g}$ at 1.5 T) are observed before heating; they can be associated with magnetic nanocrystals dispersed in an amorphous matrix. The abnormal behavior of the magnetic coercivity between 328 °C and 480 °C is related to the changes in the structure. It is correlated with the earlier results of the DSC and neutron diffraction measurements. After heating, the magnetic coercivity and the magnetic saturation change significantly ($H_C = 9.6 \text{ mT Oe}$, $M_S = 0.3 \text{ emu/g}$ at 1.5 T).

The amorphous phase with some nanocrystals showed ferromagnetic properties. In the i-phase formation, most of the ferromagnetic behavior disappears due to a lack of long-range magnetic order in the quasicrystal structure. The w-phase and the new c-phase showed a weak magnetic signal, which came from the small addition of unreacted iron, which was confirmed by the Curie temperature after annealing.

After introducing hydrogen into its structure, the TiZrFe alloy remains amorphous. It creates an exciting opportunity to observe and research the behavior of hydrogen in the amorphous matrix.

Bringing hydrogen into an amorphous alloy leads to the creation of simple nanocrystalline hydrides. The hydrogen atoms are bonded to their particular constituents. The diffraction patterns for the base and hydrided alloy obtained from the XRD measurements are typical for amorphous materials. The broad central maxima observed for the hydrided sample are shifted toward the lower angles than for the base alloys (see Figure 5a), which can result from an increase in the mean metal–metal distances. Interestingly, we optimized the thermodynamic conditions so that formations of simple hydrides are not observed, which is favorable at higher temperatures or pressures.



Figure 5. The diffraction patterns for the amorphous phase before (black) and after (olive) hydrogenation (**a**); hydrogen mass absorption vs. time for the amorphous TiZrFe (**b**).

The isothermal hydrogen absorption kinetic curves for the TiZrFe compounds are shown in Figure 5b. Precisely at 163 °C, the investigated alloy can readily absorb hydrogen under initial 4 MPa H₂ pressure and reach a hydrogen storage capacity of about 2.54 wt.%. The activation process energy for hydrogen atoms at some hydrogen storage alloys is a long process [43]. Hydrogen atoms must pierce the oxide layer surface of the nanoparticles before creating metal hydrides during the activation process. In the initial hydrogenation process, hydrogen atoms must penetrate the previously formed hydride layer to hold the hydrogenation reaction. Hydrogen atoms diffuse rapidly into the amorphous matrix from grain boundaries and phase interfaces between the amorphous phase and nanocrystals, which keep accelerating the hydrogenation process rate. After some time related to the processes mentioned above, the reaction is described with a single exponential function. It is probably related to hydrogen diffusion into the grains (bulk diffusion) after creating possible diffusion paths through the surface.

4. Conclusions

The amorphous phase is stable below 300 °C, and it is slowly evolving into the quasicrystal phase above this temperature., The i-phase structure is well formed close to 515 °C, with the addition of the FeZr₃ and the Fe₂(TiZr)₃. The TiZrFe compound demonstrates the quasi-continuous character of the transformation from the amorphous into the quasicrystalline (+some other crystals) phase. The structure of the Ti₄₅Zr₃₈Fe₁₇ is evaluated from the i-phase to the w-phase above 500 °C, close to 600 °C, at which temperature the reflections of the w-phase observed in the XRD diffraction patterns are

well developed with some amount of the $Fe_2(ZrTi)_3$ with the $FeZr_3$. The ferromagnetic signal of the amorphous TiZrFe comes from magnetic nanocrystallites in the amorphous matrix. The Curie temperature is close to 740 °C, and it shows a small number of iron atoms that have not reacted. The amorphous phase with a hydrogen capacity exceeding 2.54 wt.% is still stable after the hydrogenation process, which is exciting for the materials designed for hydrogen storage.

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