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# Complex study of H-induced structural rearrangements in FeZr glasses

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**Abstract.** Microstructural changes and relaxation processes were examined in Fe-Zr based rapidly solidified samples. These phenomena occur far below crystallization temperature in the course of heat treatment, or even at room temperature, induced by absorbed hydrogen.

## Introduction

Hydrogen-metal interactions have been widely investigated in the last decades due to its high impact on present and future technologies, such as hydrogen storage [1], sensors [2], microstructural degradation of metal parts [3], [4] etc. Even though several research institutes have examined this field for many years, the exact description of H-Me interactions is still highly incomplete. It is still a great challenge to create an exact computational method for modeling the behavior of hydrogen in metallic surroundings (eg. [5]); the experimental investigation of these processes is also a complex problem. A wide spectrum of examinational methods and some unique, customized measuring systems are invoked as well to understand the atomic interactions.
In our work, we investigate the effects of hydrogen absorption on the microstructure of Fe-Zr melt-spun samples.

## Experimental

Samples were prepared with inductive melting in a cold copper crucible, and melt spun under Ar atmosphere. The resulted ribbon had an average thickness of 20 microns and a width of 0,5 mm. The exact composition is hyper-eutectic: $Fe_{91.88}Zr_{8.12}$ according to XRF (X-Ray Fluorescence) measurement. As XRD (X-Ray Diffraction) results show, the as-quenched samples are fully amorphous. The center of the amorphous peak is at around $2\Theta=34{,}7°$.
The first investigation of the ribbon aims to determine its physical properties. Mass-, geometry- and electric measurements were executed with the following results:

- ribbon thickness: 19-22 μm (average 20 μm), width: 0,513 mm, cross section area: 0,00982 $mm^2$
- density: 6,79 $g/cm^3$ (Fe: 7,87 $g/cm^3$, Zr: 6,52 $g/cm^3$)
- specific resistance: 1684 nΩm (Fe: 96,1 nΩm; Zr: 421 nΩm) (high value due to amorphous structure)

Hydrogen charging was executed in a uniquely designed Sieverts-type apparatus. The system makes it possible to monitor the resistance of the sample continuously during measurements, thus getting indirect information about the interaction of hydrogen atoms with the conduction electrons and – after calibration – the hydrogen content of the sample. The measurement arrangement can be seen on Fig. 1.

Sieverts absorption measurement method is based on the measuring of pressure and temperature in a known volume, thus the amount of absorbed hydrogen can be determined theoretically by the *Ideal gas law.*

Resistance measurements were performed in-situ, on the basis of four point resistance measurement. 50,4 mA constant current was driven through the sample while the voltage drop was measured on a 81 mm long part of the ribbon. For further investigations, measured voltage values were normalized to the initial value, resulting the normalized resistance ($U/U_0 = R/R_0$) rate.

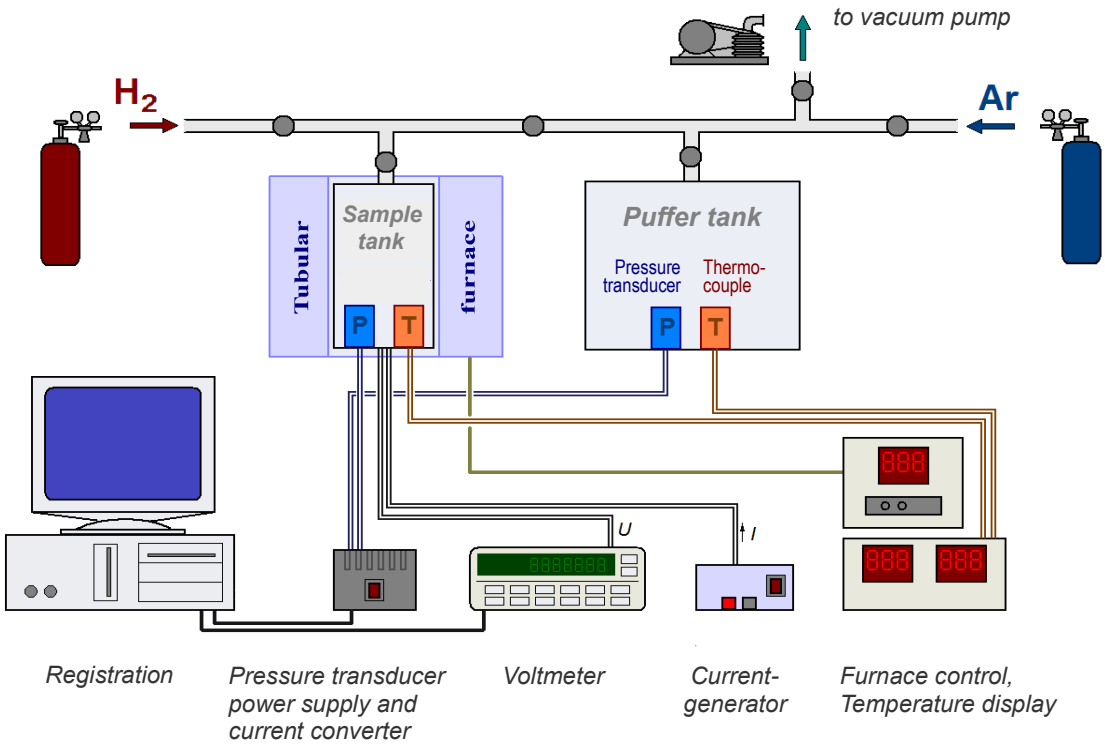


***Fig. 1**: Schema of hydrogen absorption measurement (self-made, combined Sieverts-type apparatus and in-situ resistance measurement)*

Features of the measuring system are the following:

- sample tank volume: 30 $cm^3$, puffer tank volume 150 $cm^3$
- pressure transducer resolution: 0,02 bar
- hydrogen content measurement accuracy in the sample tank: 0,05 mg $H_2$ at 25°C, 0,03 mg $H_2$ at 200°C (according to pressure measurement accuracy)
- resistance measurement: 4-point type, constant 50,4 mA current, 0,0001 mV voltmeter resolution (< 0,001% accuracy for typical samples)
- operating pressure: 0 – 1,5 MPa, operating temperature: ambient – 400°C
- registration of pressure and resistance values to computer (sampling time > 1s)

Samples were hydrogen treated under 10 bar $H_2$ pressure at 25°C and 200°C, while their resistance was continuously registered. For faster hydrogen uptake, the surface of the samples was prepared by etching in 1% HF solution for 10 s in order to remove oxide contaminations. For a detailed description of this method see ref. [6]. Besides hydrogen treated samples, heat treated ones were also prepared accordingly to the thermal treatments during hydrogenations; and only-surface treated samples were investigated too. Thus, the effect of hydrogen absorption could be separated from other impacts.

After H-saturation, heat treatment and surface treatment, samples were examined via DSC (Differential Scanning Calorimetry) measurements to evaluate microstructural relaxation processes.

XRD measurements were carried out after treatments to analyze residual structural changes, namely crystallization status and phase separations (Philips X´Pert X-Ray diffraction apparatus was used).

Measurement results were evaluated with Philips ProFit program. The (volumetric) phase-proportions were determined according to the integral values of fitted peaks, while the half-value width of the fitted peaks indicates the average crystalline size.
Magnetic measurements were also performed on a commercial SQUID-based magnetometer (Quantum Design MPMS XL5) at room temperature to map the changes in magnetic properties due to heat treatment and H-absorption.

**Change of electric resistance.** Dissolved hydrogen atoms act as scattering centers for conducting electrons; hence hydrogen absorption reversibly increases electric resistance. The change of resistance shows a close correlation with hydrogen content, thus measuring electric resistance is a manifest method for monitoring hydrogen absorption-desorption processes [7].
It can be stated, that hydrogenation at low temperature is slower (it takes about 60 minutes to reach saturation) but the amount of absorbed hydrogen is high (manifests itself in high $R/R_0$ value - see Fig. 2/a). The saturation hydrogen content measured at 25°C was 1,2 wt%, H/M = 0,75. (H/M value gives the ratio of hydrogen and metal atoms – it is often used for describing hydrogen absorption properties.)
Fig. 2/b shows the changes in electric resistance of FeZr samples during a heat-treatment cycle (25°C→200°C for 2 hours→25°C) in Ar and H atmosphere. For the latter one, reaching H-saturation (in the heating period) takes about 20 minutes. However, after saturation, changes in temperature do not have significant effect on electric resistance – amorphous alloys usually do not have a thermal coefficient unlike crystalline ones. Moreover, a slight negative thermal coefficient of electric resistance can be suspected according to Fig. 2/b at the cooling period after hydrogenation, as well as during heating and cooling the sample in Ar. The reason for this phenomenon is not thoroughly understood yet.

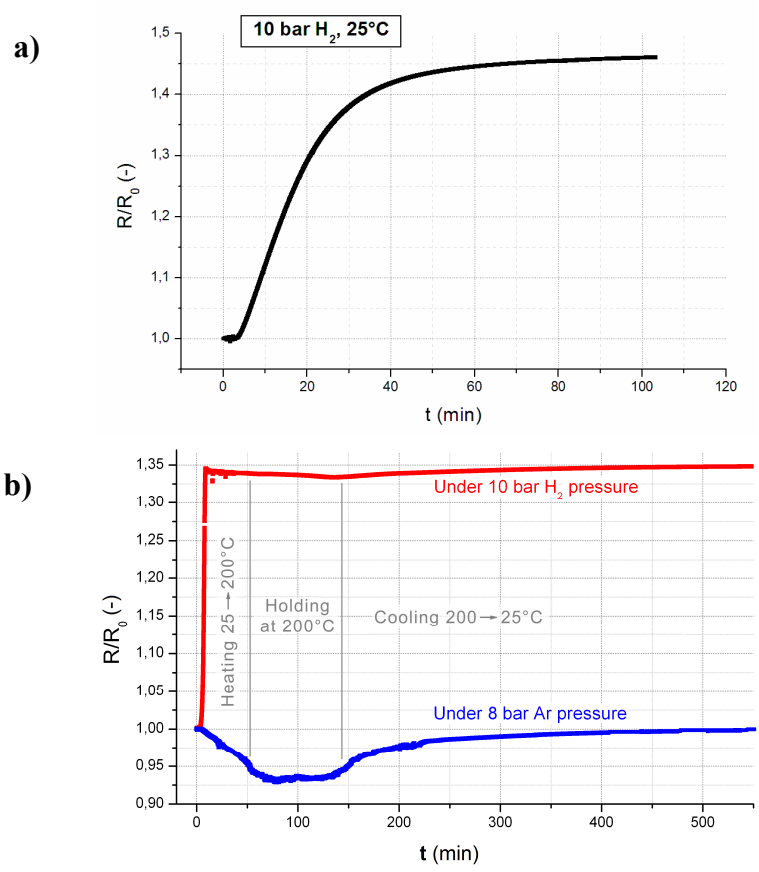


***Fig. 2**: Change of resistance during hydrogenation at 25°C (a), hydrogenation and heat-treatment at 200°C (b)*

**DSC measurements.** On Fig. 3. the results of DSC measurements were plotted. As it can be seen, heat treatment for 2 hours even in Ar or H results in a structural relaxation – however, glass transformation temperature (Tg) of the sample is 290°C, and the onset temperature of crystallization ($T_{x1}$) is above 300°C when heating at a rate of 20K/s – according to DSC traces.

A conspicuous effect of high temperature hydrogenation is the drastic increase of second heat release (see fig. 3/b). The source of this effect – besides crystallization – is the hydride phase formation: as hydrogen solubility in amorphous phase is much higher than in crystalline phase, during crystallization the majority of solved hydrogen instantly forms a $ZrH_2$ phase.

The result in Fig. 3/d is interesting too: a destabilization of amorphous state due to H-absorption can be suspected even at as low temperature as 25°C – where all thermal impact can be excluded.

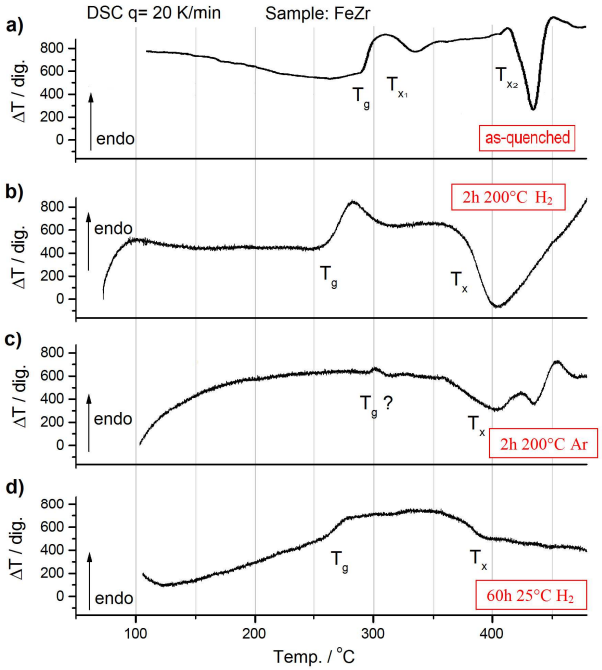


***Fig. 3**: DSC measurement results*

**XRD measurements.** Fig. 4. shows the most important results: as it can be seen, the as-quenched (only etched) samples were totally amorphous. Heat treatment in Ar at 200°C for 2 hours results in the appearance of crystalline traces. Crystallized fraction is estimated to be 0,5% with an average grain size of 40-50 nm. The formed phases are $Fe_2Zr$ and some FeH in hydrogenated samples.

A higher degree of crystallization with about 2% crystallized phase was observed at the 200°C hydrogen-treated sample. Crystalline phase is the same as at the heat-treated sample. However, the average crystalline size is around 10 nm which confirms that the presence of hydrogen facilitates the homogenous nucleation.

As DSC results implied, hydrogen treatment even at 25°C destabilizes the amorphous phase and dissolved hydrogen content induces phase separation: Weak peaks of crystallization can be observed on Fig. 4/b, however, crystalline size is under 10 nm and crystallized fraction is lower than 0,3% (the same phase as formerly). *We should remark that – due to the small peak intensities – the determination of crystallized fractions and crystalline sizes could be quantitatively inaccurate.*

According to DSC results, it can be expected that the crystallized fractions – even at heat treated or at hydrogenated samples – are too small compared to the changes in heat flow. The reason for this paradox is presumably due to the initiatory steps of crystallization (relaxation, cluster formation) which concern the whole volume of the sample but has no demonstrative effect on XRD results.

Another microstructural change can be noticed from these results: according to different treatments, the amorphous peak shifts differently. Its position correlates with the average atomic distances. It can be concluded that heat treatment results in a densification caused by the structural relaxation,

which manifests itself in the shift of the amorphous peak by about 1 degree towards higher values. On the contrary, the absorbed hydrogen atoms expand the original atomic structure resulting a shift of the amorphous peak towards lower angles by a value of 0,5-1°. This effect occurs at both the high- and low temperature hydrogenated samples.

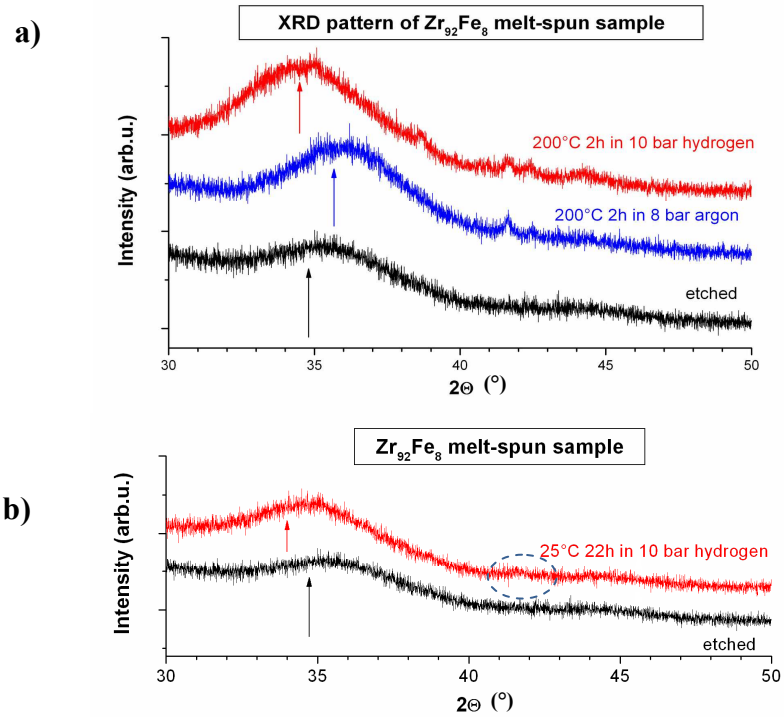


***Fig. 4**: XRD measurement results*

**Magnetic measurements.** As can be seen on the Fig. 5, hydrogen treatment significantly influences the magnetic properties of samples too. The change of the saturation magnetization directly confirms changes both in the microstructure and in the arrangement of the iron atoms, as it is described above. These changes can be derived from the position of Iron on the Bethe-Slater curve, resulting that small changes in interatomic spacing between Iron atoms result in huge changes in exchange interaction.

Fig. 5/b indicates that saturation magnetization shows a maximum among the differently treated samples, which is the result of two simultaneously enacting processes: the structural relaxation and the crystallization.

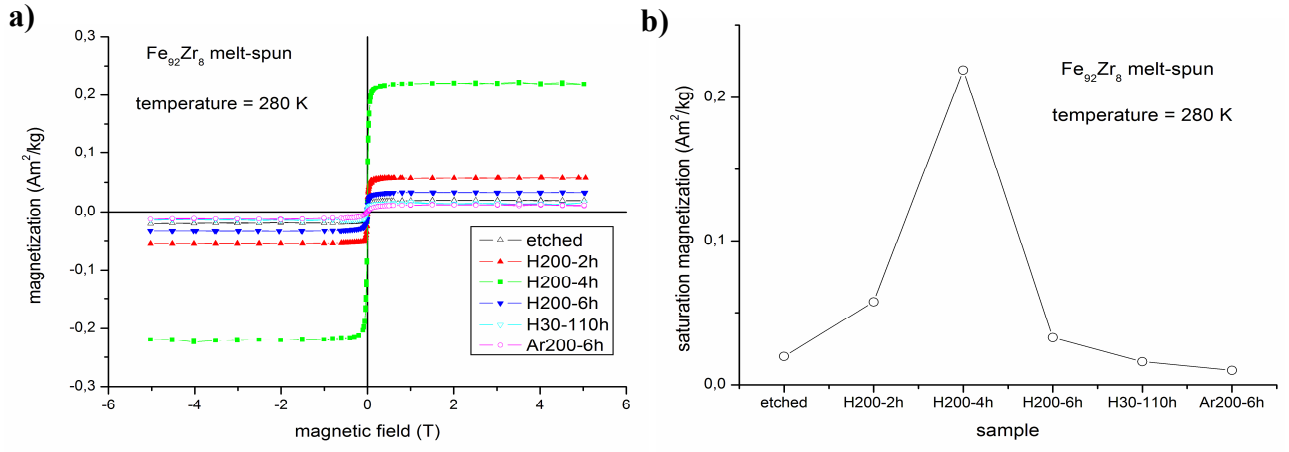


***Fig. 5**: Magnetization curves (a) and saturation magnetization (b) after various treatments. (H or Ar means treated in hydrogen/argon; 200 and 30 means the temperature of the treatment in °C; 2h, 4h etc. means its duration in hours.)*

## Conclusions

FeZr-based melt-spun samples were treated in Ar and H at room temperature and at 200°C for different durations. Subsequent measurements proved that hydrogen treatment (even at room temperature) induces a structural relaxation and a small-scale crystallization at these samples – manifests itself in XRD and also in magnetic measurement results. Heat treatment at raised temperature speeds up these processes – even in Ar atmosphere, but more expressively, when treated in hydrogen. However, crystallization temperature of these samples is over 300°C according to DSC results.

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## References

[1] Louis Schlapbach, Andreas Züttel: Hydrogen-storage materials for mobile applications, Nature Vol. 414, ISSN: 0028-0836, 2001, pp. 353-358.

[2] Sumiaki Nakano, Shin-ichi Yamaura, Sakae Uchinashi, Hisamichi Kimura, Akihisa Inoue: *Effect of hydrogen on the electrical resistance of melt-spun $Mg_{90}Pd_{10}$ amorphous alloy*, Sensors and Actuators B Vol. B 104, ISSN: 0925-4005, 2005, pp. 75-79.

[3] W.P. Chen, J.Q. Qi, Y. Wang, X.H. Wang, Z.W. Ma, L.T. Li, H.L.W. Chan: Hydrogen-induceddegradation in NiCuZn ferrite-based multilayer chip inductors, Materials Letters, Vol. 59, Issue 13, ISSN: 0167-577X, 2005, pp. 1636-1639.

[4] K.-J. Kurzydlowski, E. Lunarska: Hydrogen degradation of steels under long-term in-service conditions, Environment-Induced Cracking of Materials, ISBN: 978-0-08-044635-6, pp. 349-361, 2008.

[5] M.Pozzo, D.Alfè: Hydrogen dissociation and diffusion on transition metal (= Ti, Zr, V, Fe, Ru, Co, Rh, Ni, Pd, Cu, Ag)-doped Mg(0001) surface, International Journal of Hydrogen Energy Vol. 34., ISSN 0360-3199, 2009, pp. 1922-1930.

[6] S. Balla, B. Vehovszky, A. Bárdos, M. Koval'aková: *The study of H-absorption-desorption Process in $Ni_{67-X}M_XZr_{33}$ Glassy Alloys Monitored by in-situ Resistance Measurements*, Journal of Physics: Conference Series vol.144, 012012 (doi: 10.1088/1742-6596/144/1/012012), ISSN 1742-6596, 2009.

[7] József Garaguly: Invesitgation of hydrogen absorption-desorption *in amorphous alloys via in-situ resistance measurements*, Doctoral thesis, BME Faculty of Transportation, Research Institute for Solid State Physics and Optics – Hungarian Academy of Sciences, Budapest, 1998.