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# THE EFFECT OF HYDROGEN TREATMENT ON THE PSEUDO-BINARY HFNI $_{0.35}$ AL$_{1.65}$ LAVES PHASE STRUCTURE

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**Abstract:** Structural changes of the pseudo-binary Hfni $_{0.35}$ Al $_{1.65}$ Laves phase at hydrogen treatment and heating were studied by X-ray diffraction and magnetic phase analysis. The X-ray measurements showed that the Hfni $_{0.35}$ Al $_{1.65}$ compound was amorphized by hydrogenation, and the transformation to an amorphous state took place without the formation of a crystalline hydride phase. At 600 K the sample decomposed into Ni and amorphous phases believed to be equilibrium phases. The existence of ferromagnetic-like behavior of the amorphous Hfni $_{0.35}$ Al$_{1.65}$ phase was detected. The coercitivity was 12.8 kA/m indicating low magnetic hard properties. The magnetic phase analysis was in good agreement with the X-ray measurements. The existence of three ferromagnetic-like phases was shown and the formation of Ni was confirmed.

**Key words:** ternary aluminum - based alloys, pseudo-binary Laves phase, hydrogen treatment, nanocrystalline, amorphous alloys

## Introduction

Laves phases, or AB $_2$ compounds, are a large family of intermetallic compounds that due to their structure may absorb a large amount of hydrogen and could be used as hydrogen storage devices. The Hf-Ni-Al Laves phases also have a perspective as Ni-metal hydride anode materials [1].

Al-based transition metal compounds are successfully developed systems due to their good mechanical properties: low density, high melting point, good wear resistance, high strength and high resistance to creep and oxidation. On the other hand, the Hf-Ni system has attracted much interest in the amorphous state due to the high glass-formation ability [2]. It is known that aluminides of transition elements may demonstrate unpredictable properties in the amorphous state. The topic of amorphization has continued to be of interest to scientists over decades because amorphous and nanocrystalline phases may demonstrate different physical properties than their crystalline analogues that are usually improved for practical use.

There is a number of methods to amorphize crystalline alloys. Hydrogen-induced amorphization (HIA) is good to be used for Laves phases with C14 and C15 structure types (ST), there is a lot of data on this subjecte in the literature [3–5]. Most of these works are devoted to the study of binary Laves phases.

Two pseudo-binary Laves phases in the Hf-Ni-Al system were discovered [6]: HfNi0.6Al1.4 (ST – $MgZn_2$) and Hfni $_{0.35}$ Al$_{1.65}$ (ST – $MgCu_2$). Vast literature on their crystalline structures is available, but it is not about their physical properties. The main purpose of the present work is the investigation of the effect of hydrogen treatment with further heat treatment of the phase-structural state and of the magnetic properties of the HfNi $_{0,6}$ Al $_{1,4}$ Laves phase.

## Experimental

The samples were synthesized via arc-melting of stoichiometric amounts of the constituent Hf, Ni metals and Al pieces (not less than 99.6 wt. %) in a high-purity argon atmosphere. The initial as-cast alloys were hydrogen saturated under the pressure of 3.0 MPa. Then, they were ball-milled in a planetary Fritsch Pulverisette-6 mill with a speed of 600 rpm within 48 hours. We used heptane (95%) and acid oleic (5%) as the medium to prevent interaction of the samples with the balls.

The X-ray powder diffraction data (XRD) of the samples was collected in the transmission mode on a STOE STADI P diffractometer with Cu $K\alpha_1$-radiation ($\lambda = 1.54056\dot{A}$), and a curved Ge (111) monochromator on a primary beam. The preliminary data processing and the X-ray phase analysis were performed using the PowderCell [7] program package. Quantitative Rietveld refinements were performed with the FullProf.2k program [8], applying a pseudo-Voigt profile function. The XRD of the treated alloy was performed in the range from room temperature to 1070 K with $\delta$T=100 K. High-temperature investigations were performed using a DRON-3M diffractometer with Co $K\alpha_1$-radiation ($\lambda = 1.78892\dot{A}$).

The magnetic properties were measured using the Vibrating Sample Magnetometer technique. The temperature dependence of the saturation magnetization in the 800 kA/m magnetic field during the heating and cooling with the rate of 20 K/min was measured.

## Results and discussion

The X-ray diffraction (XRD) pattern for the polycrystalline as-cast and treated alloy is shown (Fig. 1). Unlike the cast alloy, the pattern for the ball-milled alloy exhibits broad peaks in the

range of $10^\circ < 2\Theta < 40^\circ$ indicating that the sample is partially amorphous. This data allows us to suppose that the ball-milled alloy consists of an amorphous matrix with a small amount of the nanocrystalline phase.

As one can see, the unit cell dimension from both the as-cast and ball-milled samples fully suggests isotypism with Hfni $_{0.35}$ Al $_{1.65}$ (the $MgCu_2$ structure type). In the XRD, the HfNi $_x$ Al $2-x$ as-cast sample data was completely indexed in a cubic lattice of the Laves phase (C14) Hfni $_{0.35}$ Al $_{1.65}$ with the cell parameter a=7.34453(10) Å. The lattice parameter from the milled alloy is 7.35883(82) Å. Such small difference between parameters gives us a reason to think that the compound does not react with hydrogen. Most probably we received highly dispersed powder after the treatment, which is confirmed by the decreasing intensity of the X-ray diffraction peaks and their increasing width.

The half-width of these peaks in the XRD of the ball-milled sample is equal to $1^\circ$ $2\Theta$, while in the as-cast state it is $0.1^\circ\Theta$. Such change indicates the reduction of the size of the coherent-scattering regions (CSR). The value of the CSR was 100 $\dot{A}$ in the ball-milled alloy (for comparison, it was 800 $\dot{A}$ in the as-cast sample). The level of microstrains in the crystallites in the initial state is small ($\varepsilon = 26.54 \times 10^{-4}$), but it increases in the course of phase transitions when the alloy is milled, and then it is $105.65 \times 10^{-4}$.

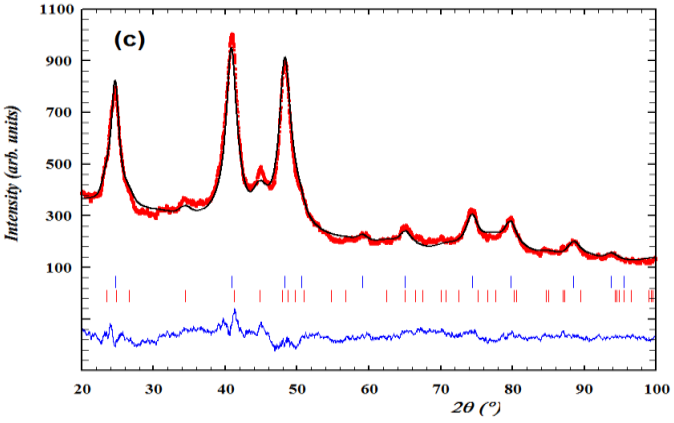


Fig. 1: X-ray diffraction patterns of initial (a) hydrogen-treated (b) and heated (c) Hfni $_{0.35}Al_{1.65}$ samples after cooling. The vertical blue bars indicate the calculated Brag positions for a cubic structure of the Hfni $_{0.35}Al_{1.65}$ phase described by the $Fd\bar{3}m$ space group, the red bars – the hexagonal structure of HfNi $_{0.6}$ Al $_{1.4}$. The solid line derives from Rietveld refinement. $Y_{obs}$-$Y_{calc}$ is the intensity difference between experimental data and Rietveld calculations.

The magnetic state of Hfni $_{0.35}$ Al $_{1.65}$ is observed to be substantially modified after hydrogen treatment. The sample demonstrates ferromagnetic like behavior. The magnetic hysteresis loops were measured from -300 kA/m to 300 kA/m at room temperature (Fig. 2). The saturation magnetization of the sample takes the value 3.5 A$\times$ m$^2$/kg. The coercitivity is 12.8 kA/m. This value characterizes it as a low magnetic hard material. We suppose that the ferromagnetic characteristic belongs to the amorphous phase.

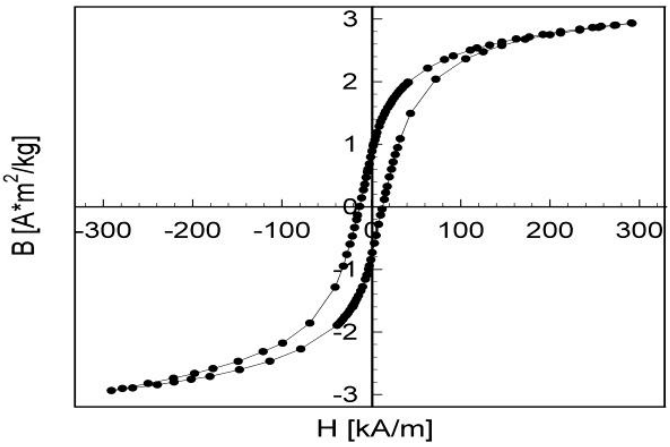


Fig. 2: Magnetic hysteresis loops of HfNi $_{0.35}$ Al $_{1.5}$ sample after hydrogen treatment.

The temperature behavior of the treated sample in vacuum was observed for a detailed study of the hydrogen effect on the structure state. The XRD pattern was recorded for each 100 K. No significant changes were observed up to 673 K, therefore only one diffractogram is presented. The heating (Fig. 3a) shows gradual decreasing of X-ray diffraction intensity peaks that indicate further grinding of nanocrystalline grains, related to the motion of the compound caused by hydrogen. It has been shown [9] that the thermal expansion coefficient of the unit cell of this phase is equal to $7.44\times10^{-5}$ K$^{-1}$ at room temperature that is notably larger than for $MgCu_2$ and linearly increases with temperature.

At 873 K an amorphous halo in the range of $2\Theta$ from $35^\circ$ to $45^\circ$ can be seen which does not coincide with the angles for the Laves phase. Small reflexes at $52^\circ$ and $61^\circ$ are in good agreement with the crystalline Ni reflex. Thus, the mixture of nanocrystalline and amorphous Hfni $_{0.35}$ Al $_{1.65}$ Laves phase transforms to an unknown amorphous phase and crystalline Ni.

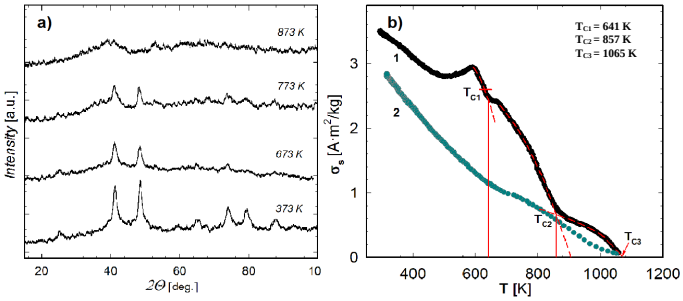


Fig. 3: XRD pattern (Co-K$\alpha_1$-radiation) of hydrogen treated $HfNi_{0.35}Al_{1.5}$ sample at heating (a) and temperature dependence of saturation magnetization of treated Hfni $_{0.35}$ Al $_{1.65}$ alloy (b): 1 – heating and 2 – cooling (2)

The temperature dependence of specific saturation magnetization of the sample demonstrates a decrease on heating that is natural for ferromagnetics (Fig. 3b).

## Conclusions

Structural changes upon heating were investigated by XRD and magnetic phase analysis to clarify the influence of hydrogenation on the pseudo-binary Laves phase Hfni $_{0.35}$ Al $_{1.65}$. Hydrogen absorption in the crystalline state, followed by heating in vacuum, induced the formation of the amorphous phase and its decomposition to an amorphous phase and crystalline Ni with a further increase in the temperature. We were able to confirm it by the magnetic phase analysis. Ferromagnetic-like properties of the Laves phase $HfNi_{0.35}Al_{165}$ with transition to amorphous state were discovered.

## Literature

[1] Reilly J., Adzic G., Johnson J., Vogt T., Mukerjee S., McBreen J. The correlation between composition and electrochemical properties of metal hydride electrodes. *Journal of Alloys and Compounds*, 293-295:569–582, 1999.

[2] Buschow K.H., Beekmans N.M. Formation, decomposition and electrical transport properties of amorphous Hf-Ni and Hf-Co alloys. *J. Appl. Phys.*, (50):6348, 1979.

[3] Ishikaway K., Ogasawaraz N., Aoki K. Hydrogen-induced amorphization in the C14 Laves compound $NdMn_2$. *Phil. Mag. Lett.*, 84(4):207–214, 2004.

[4] U-In Ch., Yong-Gyoo K., Jai-Young L. General features of hydrogen-induced amorphization in $RM_2$ (R = rare earth, M = transition element) Laves phases. *Philosophical Magazine B*, 63(5):1119–1130, 1991.

[5] Aoki K., Masumoto T. Hydrogen-induced amorphization of intermetallics. *J. Alloys and Compounds*, 231(1-2):20–28, 1995.

[6] Markiv V.Y. *Metall*, volume 6, chapter The Hf-Ni-Al System, pages 113–115. Izv. Akad. Nauk SSSR., 1969.

[7] Kraus W., Nolze G. *PowderCell for Windows (version 2.4).* Federal Institute for Materials Research and Testing, Berlin, 2000.

[8] Rodriguez-Carvajal J. Recent developments of the program FULLPROF, Commission on Powder Diffraction (IUCr). *Newsletter*, (26):12–19, 2001.

[9] Mudryi S.I., Shved O.V. *Material Sciences*, 52(2):76–80, 2016.

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