## Enthalpies of formation and glass-forming ability of $(Sc_{1-x}TM_x)Fe_2$ ( $0 \le x \le 1$ , TM – transition metal) alloys

Andrzej Musiał, Zbigniew Śniadecki

Institute of Molecular Physics, Polish Academy of Sciences, Poznań, Poland.

The enthalpies of formation of intermetallics, solid solution, and amorphous phase in  $(Sc_{1-x}TM_x)Fe_2$  ( $0 \le x \le 1$ , TM – group 4 and 5 transition metals) alloys are calculated and compared with existing literature data. The desired alloys are intended to be amorphous precursors for further crystallization of Laves phases (crystalline grains embedded in an amorphous matrix). The general aim is to improve the mechanical properties and cycling behavior of composites designed for caloric applications. Enthalpies of formation of intermetallic phases are the most negative, but the formation of glassy structure cannot be neglected for off-stoichiometric compositions and for ternaries with large differences in atomic radii and significantly negative values of mixing enthalpies (especially those containing Zr and Hf atoms).

Keywords: glass-forming ability; Laves phases; caloric effects

## 1. Introduction

A method based on the semi-empirical Miedema's model and geometric approach [1] was used to calculate the enthalpies of formation of various phases in  $(Sc_{1-x}TM_x)Fe_2$  ( $0 \le x \le 1$ , TM – group 4 and 5 transition metals) alloys. Designed compositions are planned to form a glassy state and can be then treated as precursors for the crystallization of Laves phases with appropriate stoichiometry. The goal is to form crystalline grains in an amorphous matrix. Such composites can be beneficial in improving mechanical properties and preserving magneto- or barocaloric performance of such materials during prolonged and cyclic application of magnetic field or pressure [2].

## 2. Results and discussion

The formation enthalpies of amorphous alloys and their solid solution counterparts are compared to those of respective intermetallics. Additionally, the normalized entropy change and the glass-forming ability parameter were determined. An exemplary ternary contour map of enthalpy of formation of amorphous phase  $\Delta H^{\text{am}}$  in Sc-Zr-Fe system is shown in Figure 1. Compositions maintaining a constant 2:1 ratio of Fe to Sc and Zr atoms, specific for Laves phases, are marked with grey dots.

The results were obtained for various TM substitutions: Zr, Hf, Nb, V, Ta, and Ti. As expected, for stoichiometric binary compositions with 1:2 ratio of TM to Fe (*e.g.* ZrFe<sub>2</sub>), enthalpies of formation of intermetallic phases are the most negative, but we cannot neglect the formation of glassy structure for off-stoichiometric phases. In turn, large differences in atomic radii and significantly negative values of mixing enthalpies (especially in Zr- and Hf-containing compositions) are the key factors when evaluating the possible formation of the amorphous phase in ternaries. For example,  $\Delta H^{\rm am}$  calculated for Sc<sub>0.2</sub>Zr<sub>0.8</sub>Fe<sub>2</sub> is equal to -12 kJ/mol and is more negative than the enthalpy of formation of the solid solution.



Figure 1: Compositional dependence of formation enthalpy of amorphous phase  $\Delta H^{am}$  of Sc-Zr-Fe system.

It has been proven that in Zr-Fe binary [3], the amorphous phase can be easily formed (using rapid quenching) close to the eutectic point (lowest melting temperature), and, in this case, calculated thermodynamic parameters are not decisive. Nevertheless, due to additional substitutions (growing entropy connected with increasing atomic radii differences) formation of a glassy state can be promoted, and calculated contour maps of enthalpies can serve as a guide. One has to bear in mind that in rapid quenching, kinetic factors play an important role also, but in other methods (e.g., mechanical alloying), determined values can be utilized more directly.

## References

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Acknowledgements: This work was funded by the National Science Centre, Poland, under the OPUS call in the Weave programme 2023/51/I/ST11/02562