

Diffusive phase transformations in metallic glasses

Dmitri V. Louzguine^{1*}

¹WPI Advanced Institute for Materials Research, Tohoku University, Sendai, 980-8577, Japan

*dml@wpi-aimr.tohoku.ac.jp

A large set of experimental results obtained by the author and colleagues related to the diffusion-related effects and phase transformation observed in metallic glasses will be presented and discussed. Structural changes observed in metallic glasses [1] on heating include structural relaxation (leading to densification and hardening of the glass) [2] and devitrification process which includes inverse glass-transition [3] to a supercooled liquid [4] and crystallization [5].

The step-scan mode specific heat capacity of the $\text{Au}_{49}\text{Cu}_{26.9}\text{Ag}_{5.5}\text{Pd}_{2.3}\text{Si}_{16.3}$ and $\text{Zr}_{55}\text{Cu}_{30}\text{Al}_{10}\text{Ni}_5$ metallic glasses exhibited two different slopes within the glass-transition region related to the difference in diffusion coefficients of the alloying elements in these alloys [3].

Three types of diffusive phase transformations observed in the glassy alloys: polymorphous (a product phase has the same composition as the glassy phase), primary (a product phase has a composition different from that of the glassy phase) and eutectic (two or more phases nucleate and grow conjointly) [1] will be discussed. It will also be shown that in some glassy alloys phase separation by binodal or spinodal decomposition precedes crystallization [2].

Primary crystallization involving long-range diffusion and growth difficulties leads to the formation of nanoscale crystalline and quasicrystalline particles [5]. Formation of a nanostructure within the glassy phase leads to enhanced mechanical properties compared to fully glassy and crystalline alloys [2]. It will also be shown that $\text{Fe}_{48}\text{Cr}_{15}\text{Mo}_{14}\text{C}_{15}\text{B}_6\text{RE}_2$ (RE = Y or Tm) alloys are distinct from usual metallic glasses. Their glass-forming ability appears to be limited by the rate of crystal growth, and even rapidly quenched samples contain pre-existing nuclei of the $\chi\text{-Fe}_{36}\text{Cr}_{12}\text{Mo}_{10}$ phase. This phase is formed because RE elements cannot be redistributed fast enough to trigger eutectic crystallization of the supercooled liquid. Calculations based on the diffusion coefficients indicate that slow diffusion of

RE metals at the crystallization temperature does not allow solute partitioning to proceed to completion and trigger eutectic crystallization observed in the RE metals free alloys. Because of these pre-existing nuclei, isothermal crystallization of the $\text{Fe}_{48}\text{Cr}_{15}\text{Mo}_{14}\text{C}_{15}\text{B}_6\text{RE}_2$ glasses occurs without an incubation period. The lack of incubation period, and the particles growth limitation rather than nucleation limitation, are in contrast to the behavior expected for bulk metallic glasses in general. Destabilization of the competing crystalline phases (to be formed by eutectic crystallization) is considered to be the dominant reason for the significantly improved glass-forming ability of these bulk metallic glassy alloys by RE metals. The low growth rate of the $\chi\text{-Fe}_{36}\text{Cr}_{12}\text{Mo}_{10}$ phase, important for the GFA of $\text{Fe}_{48}\text{Cr}_{15}\text{Mo}_{14}\text{C}_{15}\text{B}_6\text{RE}_2$ is related to large, inhomogeneous internal strain in these particles. This strain, related to the large volume difference between the glassy and crystalline phases, is partly reduced but redistributed by the incorporation of slow-diffusing RE element in the crystalline phase.

References

- [1] D. V. Louzguine and V. I. Pol'kin *Bulk Metallic Glasses: Fabrication, Structure, and Structural Changes under Heating*, Russian Journal of Non-Ferrous Metals, **57**, 25–32 (2016).
- [2] D. V. Louzguine-Luzgin, I. Seki, T. Wada, A. Inoue, *Structural Relaxation, Glass Transition, Viscous Formability, and Crystallization of Zr-Cu-Based Bulk Metallic Glasses on Heating* Metallurgical and Materials Transactions A, **43**, 2642-2648 (2012).
- [3] D. V. Louzguine-Luzgin, I. Seki, S. V. Ketov, L. V. Louzguina-Luzgina, V. I. Polkin, N. Chen, H. Fecht, A. N. Vasiliev, H. Kawaji, *Glass-transition process in an Au-based metallic glass*, Journal of Non-Crystalline Solids, **419**, 12–15 (2015).
- [4] D. V. Louzguine-Luzgin, L. V. Louzguina-Luzgina, H. Fecht, *On limitations of the viscosity versus temperature plot for glass-forming substances*, Materials Letters, **182**, 355–358 (2016).
- [5] D. V. Louzguine-Luzgin, A.I. Bazlov, S.V. Ketov, A.L. Greer and A. Inoue, *Crystal growth limitation as a critical factor for formation of Fe-based bulk metallic glasses* Acta Materialia, **82**, 396–402 (2015).