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Rheological properties of amorphous alloys and their description on the base of linear viscoelastic theory

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Abstract. It is shown that rheological properties of amorphous alloys may be described by the methods based on linear viscoelastic theory. Application of these methods to the description of tensile deformation of amorphous alloys and stress relaxation in amorphous metallic coatings are considered.

1. Introduction
Amorphous alloys produced by quenching the melt are glasses (metallic glasses). Glasses are viscoelastic materials. Rheological properties of glasses are adequately described by the methods based on linear viscoelastic theory [1]. In this paper we consider results of description rheological properties of amorphous alloys by methods existing in glass science.

2. Deformation of amorphous alloys.
A large number of publications have been devoted to the investigation and model description of the mechanical properties (in particular deformation) of amorphous alloys since the beginning of their industrial application [1,2] up to the present time [3]. However, no unified theory that would completely described deformation of these materials over a wide range of temperatures and loads have been offered. In this paper special case is considered, namely, tensile deformation of amorphous alloys at stresses 10-30 MPa that are two orders of magnitude lower then yielding stress.

Modern commercial amorphous alloys based on iron Fe_{73.5}Si_{13.5}Nb_{9}Cu_{1} (AMAG-200) and Fe_{69.1}Si_{16}B_{10}Nb_{3}Cu_{1}Co_{0.8}Mo_{0.1} (5BDSR) were chosen as the objects of investigation. The alloys were prepared in the form of ribbons 5-10 mm in width and 10-30 μm in thickness. The structural state of the alloys was investigated by XRPD analysis, structural relaxation was investigated by DSC method. Deformation of the alloys was measured on quartz dilatometer in wide range of temperatures.

A detailed analysis of the deformation of inorganic glasses made it possible to separate the deformation of a glass into instantaneous (reversible), delay elastic (reversible), and viscose (irreversible) components and to describe the nonlinear process of deformation relaxation in terms of the equations used in the theory of linear viscoelasticity with the replacement of the real time t by the reduced time ξ. The deformation of the amorphous alloys was described within the mathematical formalism accepted for inorganic glasses by following equation:
where $\Delta l/l$ is the elongation per unit length, $t$ is the time, $P$ is the load, $S$ is the cross-section area of the sample, $J$ is the compliance of the elastic deformation, $J_d$ is the compliance of the delayed-elastic deformation, $\tau_{d,\text{ref}}$ is the relaxation time of the delay elastic deformation at the arbitrarily chosen reference temperature $T_{\text{ref}}$, $b_d$ is the constant characterizing the width of the spectrum of relaxation times of the delayed elastic deformation, $\eta$ is the viscosity, and $\xi$ is the reduced time. $\xi$ is defined by the following expression:

$$
\xi(t) = \int_0^t \frac{\tau_{\text{ref}}}{\tau(t')} dt',
$$

where $\tau$ is the time of structural relaxation, $\tau_{\text{ref}}$ is the time of structural relaxation at $T_{\text{ref}}$. The relaxation time $\tau$ was calculated according to the equations of Tool-Narayanaswamy model of glass transition represented in [5].

The deformation of the amorphous alloys was measured at ten temperatures in the temperature range 573-773 K. The deformation observed at temperatures near the lower boundary of this range consists of instantaneous and delayed elastic components and is reversible. An increase in the temperature leads to the appearance and an increase of the irreversible viscose deformation component. A decrease in the deformation with an increase in time at temperatures near upper boundary of the range 573-773 K is associated with crystallization. When alloys are in amorphous state their deformation is adequately described by eq. (1).

It was found that the activation energy of structural relaxation and crystallization of amorphous alloys are equal to each other. When this equality holds true, the specific reduced time $\xi^*$ should correspond to crystallization of the alloy under any time-temperature conditions in the framework of used model description. The validity of this hypothesis was verifed for AMAG-200 and 5BDSR alloys. Positive results were obtained. The proposed approach to the problem associated with the prediction of crystallization of the alloys, in principle, allows one to specify the reduced time $\xi^*$ to the onset of crystallization in order to transform alloys into nanocrystalline or microcrystalline state.

### 3. Aging of amorphous alloys.

Amorphous alloys have an extremely non-equilibrium structure and a high crystallization ability. For such materials investigation of aging is of grate importance. Aging of material is considered to mean a change in operating properties with time. For glasses, the aging process is similar to annealing processes, because the system in both cases tends to a minimum energy due to the structural transformations. However, the analysis presented in [6] with the use of a large amount of experimental data on aging of silicate glasses, demonstrated that aging at room temperature differs substantially from the structural relaxation at temperatures in the glass transition range. In particular, the aging time for glasses at room temperature is considerably shorter than the aging time estimated by extrapolating the regularities of structural relaxation to the temperature range below the glass transition range.

Commercial amorphous alloys Fe$_{77}$Ni$_{1}$Si$_{9}$B$_{13}$ (2NSR) and Fe$_{61}$Co$_{20}$Si$_{5}$B$_{14}$ (24KSR) were chosen as the object of our investigation. These alloys are one-phase and two-phase glasses, respectively. Deformation of amorphous alloys was measured after storage for seventeen years at room temperature. The deformation after storage was compared with the deformation after production (quenching). The differences in the behavior of deformation after storage were detected. The experimental data of deformation and XRPD analysis demonstrate that after storage alloys undergo structural transformation associated with crystallization. Analysis of own experimental data along with the data of [7,8] lead to following conclusions: activation energy of crystallization at temperatures below the
glass transition range is much lower than that in the glass transition range; the time-temperature
dependence of the onset of crystallization is shifted downward along log(t) axis by 1-1.5 orders of
magnitude. We estimate further behavior of the alloys on the upper boundary of the so-called climatic
temperatures 193-423 K. For 2NSR alloy crystallization may expected to occur after several ten years,
for 24KSR - after several years. Method of AFM registers the early stage of crystallization and may be
considered as a method of control aging process.

4. Stresses in amorphous metallic coatings.
The number of parameters that effects on service properties of coatings is high (according to the
estimation, this number is more than fifty). However, one of the principal parameters affecting the
strength and properties of coatings is considered to be the magnitude of stresses in coating-substrate
system.

We performed the calculations of stresses for two plasma-sputtering coatings on metallic substrates
on the assumption that the initial materials for coating production were amorphous alloys AMAG-200,
5BDSR. Such coatings may be used for wear and corrosion protection, and for magnetic screening.

Our investigation [9] showed that the structural relaxation in amorphous coatings having different
chemical nature and produced by different techniques (plasma sputtering, plasma melting, chemical
deposition) occurs similarly to that in rapidly quenched glasses [10]. If we consider plasma sputtering
coatings deposited on metallic substrates as a glass-to-elastic body seals, well developed procedures
can be used to calculate stresses in such seals [11]. We performed a test for the suggested approach by
the example of calculation of stresses in chemically deposited nickel-phosphorus amorphous coatings ,
and obtained quite satisfactory results [12].

To calculate stresses it is necessary to have dilatation curves of coating and substrate. Dilatation
curves of metallic ribbons were measured on quartz dilatometer. The method of measurements is
described in [13]. Dilatation curves were used for definition the kinetic parameters of the glass
transition model. Once the kinetic parameters were identified, dilatation curves may be calculated for
any time-temperature regime.

Stresses were calculated in coatings on eighteen metallic substrates. It has been found that stable
coatings may be obtained on iron, nickel, cobalt. It was shown how different factors affect stresses.
The influence of following factors was investigated: the difference between thermal expansion of
coating and substrate; the thickness ratio of coating and substrate; regimes of annealing.

5. Conclusions
Results of this work allow considering method of calculation properties of amorphous alloys in
viscoelastic approximation as an effective method for searching optimum regimes of their production,
annealing and operation.

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