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THE PHYSICAL PROPERTIES OF METALLIC GLASSES[1]

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After a short summary of the recent research development we give a more detailed report on our investigations of correlations between technological parameters and magnetic properties of metallic glasses.

ФИЗИЧЕСКИЕ СВОЙСТВА МЕТАЛЛИЧЕСКИХ СТЕКОЛ

После краткого обзора новейших экспериментальных результатов подробно описаны проведенные авторами исследования взаимосвязи технологических параметров и магнитных свойств металлических стекол.

I. INTRODUCTION

Metallic glasses represent a new class of materials. We shall use this name after P. Duwez for amorphous metallic alloys prepared by rapid quenching of the melt. These materials have very interesting physical properties (e.g. high fracture strength, excellent soft magnetic behaviour and good corrosion resistance) and promise many applications [1]. The properties of metallic glasses are therefore being studied by many physicists and metallurgists. The main questions are the followings:

— What is the structure of metallic glasses, what is the role of their chemical bonding.

— What are the atomic transport properties including diffusivities and kinetics of structural relaxation, magnetic- and stress- annealing and crystallization.

— What are the main factors which determine these properties.

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To answer these questions requires rather complex investigations. During the past few years, there have been considerable efforts as regards the fundamental understanding of the structure of metallic glasses, their atomic and electronic transport properties and low-temperature behaviour as well as a further exploration of their mechanical, magnetic and chemical properties [2].

II. RECENT RESEARCH DEVELOPMENT OF METALLIC GLASSES

Structure

X-ray, neutron and electron diffraction methods have been frequently used to characterize the structure of metallic glasses. From the measured coherent scattered radiation one can get by the Fourier inversion the reduced radial distribution function

$$G(r) = 4\pi r[\varrho(r) - \varrho_0], \qquad (1)$$

where $\varrho(r)$ is the average density of atoms at the distance r from a reference atom and ϱ_0 is the overall average density.

Investigations of the metal-metalloid containing metallic glasses showed that these have all very similar scattering patterns. The same is true for the metal-metal compositions, but there are some significant differences between the two kinds of metallic glasses. One can get to know much more about these differences from the partial distribution functions which can be determined by a combined X-ray and neutron scattering [3]. In the metal-metal systems the distribution shows random mixing of the constituent atoms while in the metal-metalloid systems the metalloid atoms can never be in close contact. The reason of these different structures is not clear. It is possible that the $s-p$ type bonding of metalloid atoms facilitates preferred bonding between metal and metalloid.

Shortrange order can be examined also by the Mössbauer [4] and the NMR [5] investigations.

Atomic transport properties

Atomic diffusion in metallic glasses has been investigated by Chen and coworkers [6]. They measure the diffusivity of Au implanted in as-quenched and annealed $Pd_{77.5}Cu_6Si_{16.5}$ glasses using Rutherford backscattering measurements. They found that diffusivity depends on the state of the glassy structure. The diffusion constant of the unrelaxed metallic glass ($\sim 10^{-17}$ cm^2 sec^{-1}) can be many orders of magnitude higher than the relaxed one, with a relatively low activation energy $\sim$ 1 eV. The time constant for structural relaxation is at least two orders of

magnitude loger than that for the diffusive process. These two facts can explain many phenomena of aging.

Structural relaxation alters the physical properties, soft magnetic properties become more advantageous because of stress lessening but, the Fe-based glasses, e.g., become brittle. On the other hand, the metal-metal type metallic glasses are not so sensitive to aging, brittleness occurs only at crystallization [7]. The structural changes can be seen by scattering experiments too, the amplitude of oscilations increases in the interference function [8]. Of course, much further research was done besides on structural relaxation and also on crystallization, using magnetic, electronic transport and mechanical properties for the investigations. In spite of that we still do not know the exact mechanism of it.

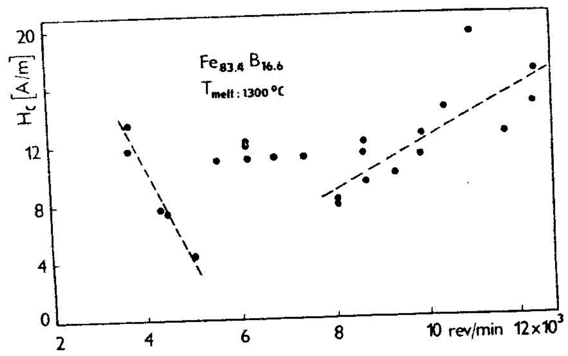

Fig. 1. H_c values measured on samples prepared by different cooling rates.

III. OUR RESEARCH

The physical properties of metallic glasses depend not only upon the chemical composition but also on the quenching conditions and heat treatment. Our purpose was to investigate these phenomena by magnetic measurements. We chose as sample the Fe—B system, which is a simple two-component metal-metalloid alloy and is also suitable for practical applications. The boron concentration varied between 12 and 25 at %. Ir order to investigate the role of chemical bonding we made also a series of alloys of the $Fe_{80}TM_3B_{17}$ type, where TM = Ni, Co, Mn, Cr, V, Ti and some of the $4d$ and $5d$ elements.

The samples were prepared by the melt spinning technique as long ribbons of about 20 μm × 2 mm dimensions. The temperature of the melt was measured by the optical method, the cooling rate was regulated by the revolution speed of the disc. The amorphous state was checked by X-ray diffraction and the concentration was measured by the atomic absorption method.

Investigations were carried out on samples prepared with various cooling rates quenched from different melt temperatures in the as-quenched state, after stress-relief and magnetic annealing and after annealing under tensile stress.

For measurements we used an static magnetometer for *coercive force* and *magnetization* measurements which we applied also for the determination of *magnetic anisotropy*. The *magnetic aftereffect* was investigated by measuring the initial magnetic susceptibility as a function of time after demagnetization using a mutual induction bridge. *Magnetostriction* was measured by the opto-mechanical method, which gave the possibility of studying the magnetostriction under very small external tensile stress.

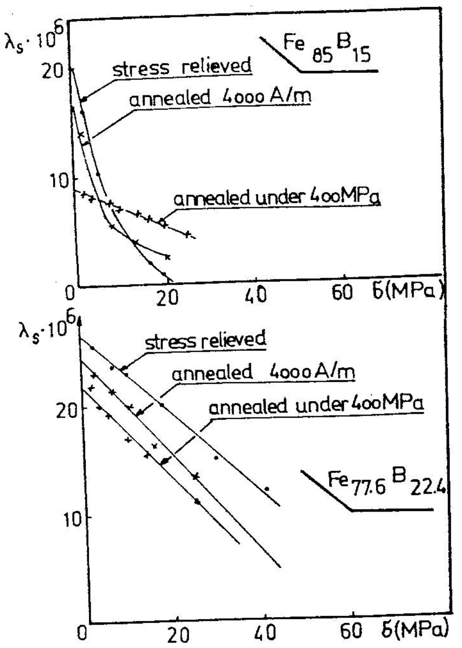

Fig. 2. Effect of annealing on $\lambda_s(\sigma)$, a) measured in $Fe_{85}B_{15}$, b) measured in $Fe_{77.6}B_{22.4}$. T_{melt} = 1770 K, disc speed 6210 rev/min. –.– after stress-relief annealing, – × – after heat treatment in a 4000 A/m magnetic field, – + – after heat treatment under tensile stress of 400 MPa.

IV. RESULTS AND DISCUSSION

Fig. 1 shows the coercive force measured on as-quenched samples prepared with different cooling rates [9]. The cooling rate was in this range proportional to the revolution speed of the disc. One can see that at low speeds the coercive force decreases with increasing speed. At lower speeds the ribon already cannont be prepared in the amorphous state. In the high-speed range the coercive force increases with increasing speed. In this range the increase can be explained

supposing that at a higher cooling rate more stresses are frozen in. Measuring the coercive force on slowly heated (~ 1.7 °C/min) samples we got a decreasing curve in the low temperature part (T_{room} ∸ 500 K), which may be connected with the relaxation of internal stresses. This decrease is steeper in samples prepared with a higher cooling rate. This also supports our previous supposition.

The coercive force is also sensitive to melt overheating: in samples quenched from higher temperature the coercive force is smaller.

The influence of the cooling rate on the saturation magnetostriction was also investigated: a higher cooling rate results in lower saturation magnetostriction, which also verifies that a higher cooling rate causes more quenched in tensile

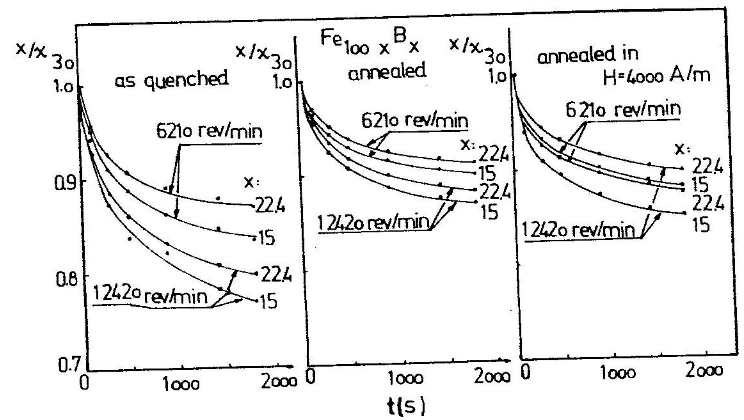

Fig. 3. Time dependence of relative susceptibility on samples containing 15 and 22.4 at % B prepared by –.– 6210 rev min^{-1} and –□– 12420 rev/min. quenched from 1770 K. a) as-quenched, b) after stress-relief annealing, c) after annealing in a 4000 A/m magnetic field.

stresses (the saturation magnetostriction in these metallic glasses always decreases with increasing applied tensile stress).

Investigating the correlation between magnetic properties and heat treatments we measured the saturation magnetostriction after stress-relief annealing, after heat treatment in the magnetic field and under tensile stress [10]. The $\lambda(\sigma)$ curves are shown in Fig 2. Annealing under tensile stress reduces very strongly the saturation magnetostriction in both 15 and 22.4 at % boron containing alloys. On the other hand stress-relief and magnetic annealing produces the same value of λ_s in $Fe_{85}B_{15}$, in which we could get only a small induced anisotropy [11]. In higher boron containing samples the magnetically induced anisotropy was greater and also λ_s in samples annealed with and without the magnetic field are different. This proves that ordering processes influence the magnetostriction.

Also the magnetic after-effect was investigated in samples prepared with various cooling rates in as-quenched and heat treated states. The results are summarized in Fig. 3. The effect increases with the increasing cooling rate, indicating that the mobility the boron atoms is also influenced by the preparation conditions.

The correlation of magnetically induced anisotropy and parameters of preparation can be seen in Fig. 4 [12]. The result is curious: at a lower melt temperature a slower cooling rate gives a higher induced anisotropy but here at 1770 K in the hypereutectic concentration range the situation is opposite. We show also the corresponding results of magnetic after-effect measurements according to which a lower cooling rate leads to a higher mobility of boron atoms. It is possible that this higher mobility lowers the induced anisotropy.

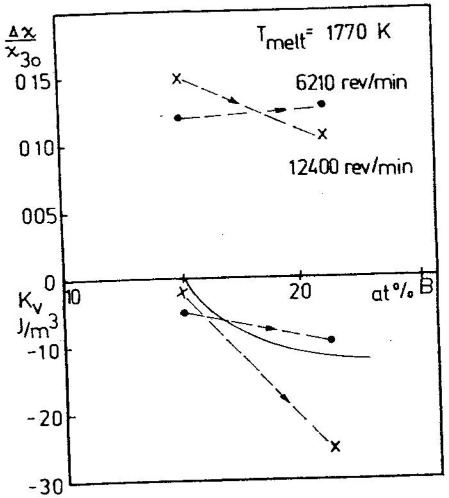

Fig. 4. Time dependence of relative susceptibility on samples containing 15 and 22.4 at % B prepared by –.– 6210 and –□– 12420 rev/min. quenched from 1770 K. T_{meas} = 330 K a) in as-quenched state, b) after stress-relief annealing, c) after annealing in a 4000 A/m magnetic field.

The role of chemical bonding was examined in the $Fe_{80}TM_3B_{17}$ metallic glasses by thermomagnetic investigations [13]. Alloying with TM metals in most cases decreased the coercive force compared with the binary $Fe_{83}B_{17}$ alloy. Only Ti, Pt and Cu caused an increase. In the case of these alloys clustering or the tendency towards the two-phase nature of the melt is highly suspected. The thermomagnetic curves (heating rate 1.7 K/min) for $Fe_{83}B_{17}$, $Fe_{80}Co_3B_{17}$ and $Fe_{80}Ni_3B_{17}$ are quite similar, the thermal stability of the magnetic system is the highest for the Co containing alloy. In Fig. 5 we show the thermomagnetic curves for $Fe_{80}W_3B_{17}$ and $Fe_{80}Ti_3B_{17}$. Such TM elements with high affinity to boron cause a pronounced separation of the amorphous Curie temperature from the crystallization temperature. The relatively low magnetization of the crystallization products is also specific to these curves. In general we can say that there is an inverse connection between

the magnetic and the thermal stability. Those TM-elements which raise the thermal stability, lower the Curie temperature compared with that of $Fe_{83}B_{17}$. Saturation magnetization at room temperature is increased by those elements which are to the right of iron in the periodic system and decreases by Mn, Cr, V, proportional to the relative valency between iron and the element in question.

We investigated also the crystallization of Fe—B alloys be magnetic measurements and by using a transmission electron microscope [14]. In the hypereutectic concentration range various mechanisms of crystallization were observed heating the samples by the electron beam in the chamber of the microscope. This may be connected with some chemical microinhomogeneities in the amorphous materials.

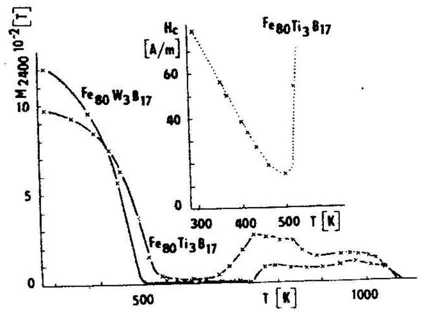

Fig. 5. Thermomagnetic curves for $Fe_{80}W_3B_{17}$ and $Fe_{80}Ti_3B_{17}$ alloys. Heating rate 1.7 K/min.

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