AMORPHOUS METALLIC MATERIALS

Proceedings of the Second International Conference on

Amorphous Metallic Materials

held in Smolenice, CSSR, May 22-26, 1989

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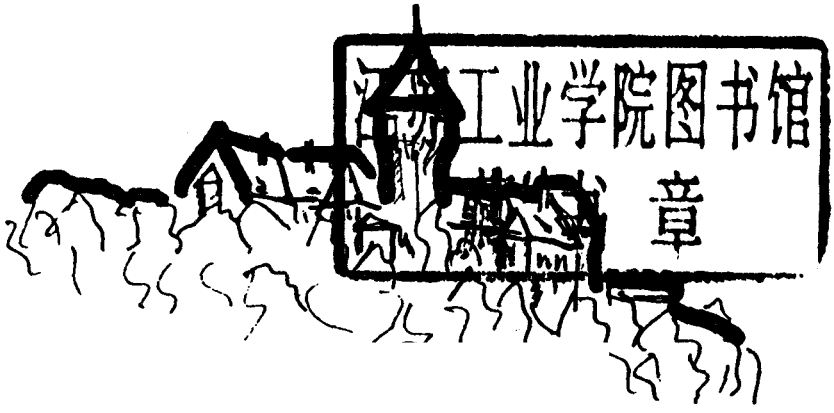

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PREFACE

The Proceedings include invited and oral contributions as well as poster communications presented at the International Conference "Amorphous Metallic Materials II", held at the Smolenice castle in the picturesque region of Small Carpathians (Czechoslovakia) on May 22-26, 1989.
The Conference has been organized by the Institute of Physics of the Electro-Physical Research Centre of the Slovak Academy of Sciences in Bratislava in cooperation with the Union of Slovak Mathematicians and Physicists.
The programme of the Conference has been focused on topics concerning rapidly quenched alloys (mainly on the problems of structural stability, relaxation and crystallization phenomena), however, some contributions from other fields of amorphous or metastable metallic materials (thin layers included) have been presented as well. Much time has been left for informal contacts between participants which numbered 92 from 12 countries.
We would like to thank to all authors for giving their manuscripts available for publication in these Proceedings. About one third of the manuscripts has not been delivered exactly in the camera-ready form as required and had to be retyped and, similarly, some diagrams had to be redrawn. In order to speed up the publishing the editors' adjustments were limited to the minimum (mostly language corrections). We, therefore, take the responsibility for the appearance of unspotted errors.
Finally, we would like to express our gratitude to Trans Tech Publications for publishing these Proceedings.

The Editors

I. INTRODUCTION

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AMORPHOUS METALS IN SLOVAKIA

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It is a great honour for me to have an opportunity to open the scientific program of this conference with an invited paper. This contribution is an invited paper of a special kind-not a report on special monotematic problem, but rather an attempt to present the contribution of Slovak scientists to the field of amorphous alloys. The scientific work in amorphous metals in Slovakia started due to Dr. Duhaj, who has prepared the first samples of amorphous metals in 1971. In the following years he has been able to produce samples of amorphous metals of various compositions and of very good quality, which were studied from the physical point of view in many Slovak scientific institutes and departments of physics of Slovak Universities.

The most original results have been found in the field of structure, phase transitions, electronic states, magnetic properties, transport phenomena and in irradiation and high pressure phenomena.

Allow me to start with the structure of amorphous metals.

1. STRUCTURE

The knowledge of the atomic structure of amorphous systems is a prerequisite for understanding of many of their physical properties. To obtain basic information about their structure, X-ray diffraction has been used to determine the pair correlation functions for Pd-Si [1] and Cu-Ti [2] systems. Besides this, a prepeak in the X-ray diffraction patterns of Ti-Ni-Cu and Ti-Ni-Si systems has been found and its changes after low-temperature annealing have been studied. The change of the prepeak is strikingly pronouced. While in the as-recieved state the prepeak seems to result from the chemical ordering, its changes after annealing may be ascribed to a formation of

small clusters restricted to the nearest-neighbour shell [3].

Dense random packing of hard spheres, single or binary, was simulated on a computer to obtain an insight into the microstructure. The Bennet sequential algorithm has been modified in such a way as to weight the first component of the splitted peak of the pair correlation function. A resonable agreement of density with the improved pair correlation function was obtained [4]. It has been proved that the Bernal-Mason-Finney algorithm simulating hard spheres gas compression leads to models which are fairly homogenous and the atomic density is nearly constant over the cluster and isotropic in the sense that no anisotropy of the pair correlation functions is observed.

A new stochastic method for computer simulation of liquid and amorphous systems has been devéloped and the correctness of the algorithm in the framework of Markovian chain theory has been proved [5]. The generated process rapidly converges to the thermal equilibrium, much faster than in the case of molecular dynamics and Monte Carlo methods. Using this method the shape of the pair correlation function was studied as function of the stiffness of interatomic potential [6].

The model consisting of 256 atoms enclosed in a cube with periodic boundary conditions was used in the analysis. On the basis of Morse potential

$$V(r)=\varepsilon_0\{\exp[-2\alpha(r/r_0-1)]-2\exp[-\alpha(r/r_0-1)]\}\varepsilon(r/r_0)$$

it was pointed out that the shape of the second peak splitting of the pair distribution function very strongly depends on the value of the parameter α. The second sub-peak of the second peak becomes higher as α increases. For $\alpha < 3$ the splitting of the second peak vanishes. For α greater than 10 the second sub-peak becomes higher than the lower r sub-peak of the second peak. To explain this interesting dependence a simple theory has been proposed.

2. PHASE TRANSITIONS

The amorphous to crystalline state transition in metallic glasses is interesting from the view of conclusions on the amorphous state, which can be extrapolated. Besides, understanding of the micromechanism of crystallization is directly connected with the question of stability which determines most of applications.

Especially Fe-B system has been studied in detail [7-9]. It was found that various supersaturated solid solutions are formed with different stechiometry up to Fe_4B, depending on the concentration of B in alloy. In the special case of $Fe_{86}B_{14}$ alloy, it was supposed by various authors that the crystallization occurs via primary crystallization and a fine-grained supersaturated α-Fe phase is formed. Boron has been supposed to diffuse from this phase to the remaining amorphous phase until enriching it to a composition from which Fe_3B can be formed. However, in works of Duhaj and coworkers a different mechanism of this reaction has been found. In the first stage a fine-grained supersaturated solid solution of α'-Fe is formed by relatively rapid crystallisation. The remaining amorphous phase crystallizes later formig α''-Fe phase nucleated on the α'-Fe phase. As there is not a sufficient boron content for the formation of Fe_3B either in α'-Fe or α''-Fe,a transformation of both of these phases into α'''-Fe occurs. Only in this α'''-Fe phase the diffusion of boron takes place and precipitation of very fine lamellae of Fe_3B tetragonal boride oriented in the /111/ direction and probably in the /112/ planes begins.

In ternary systems Pd-Fe-Si /10/, Pd-Ni-Si /11/ and Pd-Co-Si /12/ the crystallization proceeds in a similiar way as in binary Pd-Si.

From the results obtained it was concluded that the formation of phases during the crystallization is conditioned by fluctuations of chemical composition of the melt which freeze-in during the process of rapid quenching .These fluctuations are caused by different binding forces betweeen atoms in the melt and act as embryos or nuclei after solidification. Although

their size can be small at high temperatures, it seems to be sufficient for them to serve as nuclei at annealing temperatures. The "quenched-in" fluctuations need not have structures similar to the phase growing from them, therefore, a certain time is required for the formation of a nucleus of critical size. The formation of the nucleus takes place by rearrangement within the cluster region via a cooperative movement of several atoms, allowing for the free volume. The growth of nuclei will be governed by the interface diffusion.

Using the Johnson-Mehl-Avrami nucleation and growth model of crystallization of amorphous alloys a general theoretical equation for time or temperature dependence of crystallization degree has been derived. Knowing the thermal history of the alloy, the temperature and heats of softening and isothermal and non-isotermal crystallization of glassy systems have been determined [13,14].

According to the viscous flow model the ΔE_A^* vs. T dependence yields the temperature dependence of viscosity [15]. This observation is consistent with the general assumption that during the crystallization of metallic glasses the controlling mechanism is the viscous flow one.

On the basis of dependences of characteristic parameters on temperature it has been concluded that the nucleation and growth of crystalline phases in the investigated amorphous alloys are simultaneous processes but appear with a great temperature and time difference.

Within the framework of the free volume model some volume changes in relaxation and transformation processes are supposed.They can also be observed on macrodimensional scale of samples. In order to study these processes accompanied by changes in the sample volume /dimensions/, e. g. relaxation, magnetostriction, invar effect and flow, a precision dilatometer for both linear heating and isothermal regimes has been constructed [16]. Under linear heating regime the expansion coefficient and its changes during structural transformations have been determined. Besides this, information about kinetics of transformation processes and about important temperature

points were obtained. Under isothermal regimes the authors are able to determine the viscosity and its changes in glassy samples. From the volume changes during crystallization the parameters describing the kinetics of formation of crystalline phases from the glass have been calculated.

3. ELECTRONIC STATES

Using the photoemission measurement method the structures of the valence band of some amorphous metals were investigated. The valence-band spectra were recorded using He I /21,2 eV/ and He II /40,8 eV/ excitations with a resolution of about 0,2 eV deduced from the experimental slope of the Fermi edge.

The presence of boron in the $Fe_{82}B_{18}$ alloy is manifested by several changes in the valence band spectrum in comparison with pure iron.

The valence-band spectra of metallic glasses containing nickel do not have such remarkable structures.It is posible to conclude that the interaction betweeen boron valence electrons and iron d-electrons, which is presumably responsible for the broadening of the valence-band spectra, involves shifts of iron and nickel d-bands in the valence band of Fe-Ni-B alloys. Consequently, the respective contributions of iron and nickel are visible in the valence-band spectra. The shift of the boron 1s level to higher energies for high nickel content indicates that the chemical bonding interaction is stronger between boron and nickel than between boron and iron.

The influence of cobalt on electronic states in amorphous $Pd_{80-x}Si_{20}Co_x$ metals was studied, too [18]. The XPS spectra exhibited a broadening of the cobalt 2p-levels in the alloys, while the binding energies remained the same as in the polycrystalline Co. UPS spectra of the valence bands showed a shift of Pd 4d-band to higher binding energies and a cobalt contribution to the density of states above the Fermi level of Pd-Si alloy.

A successfull work was performed in the theoretical calculattion of the density of electronic states in amorphous

metals, e.g. in a-Fe and Fe-B [19, 20]. The main aim was to calculate the partial denities of electronic states in a very fast way.

A complex analysis of the computer simulation of d-electronic states of amorphous systems has been performed in [21].

4. MAGNETIC PROPERTIES

Two basically different systems have been studied so far in some detail: Pd-T-Si /T=Co,Fe,Ni; Si=20 at%/ system with a non-magnetic base and Co-T-Fe-Si-B /T=Co,Ni,Cr,V; Si+B=22 at.% / low magnetostrictive Co-rich system.

Increasing Co or Fe content in the former system, one proceeds from paramagnetic Pd-Si through spin glass and cluster glass to apparently heterogeneous weak ferromagnet at 15 or 20 at.% Co or Fe. Pd-Ni-Si remains paramagnetic up to 40 at.% Ni. The major role in the properties of this system is played by its heterogeneity, i. e. by the existence of T-rich clusters dispersed in relatively T-poor Pd-Si matrix [22]. Very slow and concentration-dependent approch to magnetic saturation, low magnetization, relatively large coercive force, as well as strongly temperature and concentration dependent anomalous Hall effect have been observed. Particular attention has been paid to characterictic discrepancies among the three values of effective magnetization obtained for each composition in three different ways. The explanation of those discrepancies [23] appears to enlighten sufficiently the character of this heterogeneous system. Evaluation of normal Hall effect measurements, considering also the temperature dependence of R_H in Pd-Si still leads to the opinion that the electron transport is not free-electron-like and there are still empty d-states, at least in $Pd_{80}Si_{20}$ [24].

In contrast to Pd-T-Si, the Co-T-Fe-Si-B system comprises generally high grade soft ferromagnets.As-quenched they exhibit initial permeabilities of about 13 000, dc. coercive forces as low as 0.6 A/m, very low core loss and almost zero magnetostriction. Maximum permeabilities and the shape of a B-H

loop /from flat to almost perfectly rectangular/ are easily adjustable by a proper heat treatment [25]. Only the saturation induction /0.55 to 0.8 T/ and generally the stability of as-cast materials are not great.

Some interesting results were found in the research of surface magnetic properties of amorphous metals. Using the Kerr effect method the dependences of the coercive force, the effective anisotropy and magnetoelastic anisotropy on the thickness of etched layers of amorphous Fe-B and Fe-Cr-B samples were studied. It was found that these properties are considerably different from bulk properties [26,27].

The influence of transitive metals on the properties of Fe-B amorphous metals was studied in [28,29]. It was found that transitive metals influence the role of boron in the appearance of magnetic anisotropy. This effect can be generated by quenching in magnetic field or as a consequence of a mechanical deformation.

For soft magnetic applications two systems of amorphous materials have been developed, namely a Co-TM-FeBSi system (nonmagnetostrictive) and a FeCrBSi system (magnetostrictive). These systems can be characterised as a Co - based high permeability (μ_i=30 000 - 40 000) system and a Fe - based low loss ($P_{1.2/50}$=0.20 W/kg) system where the values indicated are achieved by proper heat treatments which improve significantly the stability of these materials as well.

5. TRANSPORT PHENOMENA

The electrical conductivity of metallic glasses is characterised by a high value of residual resistivity and can exhibit the following three typical types of dependences on temperature: slow increase in the whole measured temperature range, slow decrease in the whole measured temperature range, the occurence of a minimum at certain temperature and the occurence of some anomalies on the resistivity - temperature curve having the shape of a certain jump.