ELECTRONIC STRUCTURE, STABILITY AND ELECTRON TRANSPORT PROPERTIES OF SOME METALLIC GLASSES

by

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TO MY PARENTS

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ABSTRACT

The electronic structure, stability and electron transport properties of Pd-Ge and Cu-Zr metallic glasses, which represent two major classes of glassy metals, have been studied with Auger electron spectroscopy (AES), X-ray photoelectron spectroscopy (XPS), differential thermal analysis (DTA), electron microscopy (EM) and X-ray diffraction (XRD) techniques and by measuring the electrical resistivity and thermoelectric power over a wide temperature range. The objective was to look into: (i) the role of cooling rate and characteristic features of the equilibrium phase diagrams on glass formation, (ii) the influence of topological disorder on the electronic structure of d-sp and d-d type alloys, (iii) the role of electronic structure and alloy chemical factors, like charge transfer and difference in the electronegativity of the constituents, towards the stability of the glassy structures, (iv) applicability of the diffraction model over the models which have been proposed to explain the high resistivity and its anomalous temperature dependence in these materials and a correlation between the alloy stability and occurence of a negative TCR, and (v) the mode of atomic transport below and above the glass transition temperature and the kinetics of crystallization.

A vacuum melt spinning technique was designed and fabricated in the laboratory and ribbons of Cu-Zr and Pd-Ge alloys were made. On melt spinning of Cu_xZr_{1-x} and Pd_xGe_{1-x} alloys a complete glassy structure is observed for x = 0.72 to 0.335 in the former and x = 0.8 to 0.775 for the later system. The gun-quenching leads to glass formation for x = 0.72 to 0.20 in Cu-Zr and 0.75 to 0.825 in Pd-Ge alloys. These observations, when combined with the characteristic features of the equilibrium phase diagrams, show that glass formation in a two phase region is decided by the cooling rate whereas at the stoichiometric compositions the structure and stability of the stoichiometric compound play a deciding role. The glass transition and crystallization temperatures, which increase linearity with Cu content in Cu-Zr alloys and show maximum at the eutectic for

Pd-Ge system, are dependent on the degree of frozen in disorder. The quenched-in disorder also decides the activation energy for transformation of these glasses. The extensive use of XRD, ED and DTA has shown that the glass to crystalline transformation is polymorphous or eutectic decomposition type.

In glassy Cu-Zr alloys, the d-bands of Cu and Zr show a shift towards higher and lower binding energies respectively. The full width at half maximum of the constituent bands is related to the short range order in the glass, A Gaussian shape of the bands suggest a homogeneous distribution of the constituents in the structure. The shifts in the constituent bands arise mainly from a change in the alloy Fermi level. A comparative study of the valence band structure of the glassy and crystalline alloys do not show any change in the density of states at the Fermi level. A shift in the $M_{45}VV$ Auger, symmetry of Pd $3d_{5/2}$-$3d_{3/2}$ spin orbit doublet and some modifications in the valence band of the glassy alloy suggest a filled Pd '4d' shell in the glass. Since the magnitude and sign of the core level shifts do not support a flow of charge from Ge to Pd, the observations have been understood in terms of an intra-atomic charge transfer in Pd.

Electrical resistivity measurements on Cu-Zr and Pd-Ge ribbons show high residual resistivity ($>100\,\mu\Omega$ cm). The TCR is small and positive for $Cu_{65}Zr_{35}$, $Cu_{70}Zr_{30}$ and all Pd-Ge alloys. For remaining melt-spun Cu-Zr glasses, the TCR is negative. The room temperature thermopower of Pd-Ge glasses is negative whereas for glassy Cu-Zr alloys the TEP is positive. In both the cases, the thermopower varies linearly with temperature. High value of the resistivity, nature of the TCR and thermopower of these alloys have been compared with the predictions of the diffraction model, electron configuration interaction, electron mean free path condition and s-d scattering by a detailed study of electron atom ratio, structural data a(q) and photoemission results. It has been shown that the overall transport can be understood, fairly well, in terms of the structural disorder scattering (the diffraction model).

For Pd-Ge system, crystallization temperature of the eutectic glass ($Pd_{80}Ge_{20}$) is the highest. This behaviour is understood in terms of maximum packing of the structure. The lower degree of ionization of the Ge, as shown by XPS studies, however, requires a significant deviation from the ideal Polk model for the structure of transition metal-metalloid glasses.

For Cu-Zr alloys our studies show that a high viscosity of the melt and a mutual competition between a number of low melting point stoichiometric compounds to nucleate and grow during solidification leads to structural chaos and thus, the disordered structure of the liquid is frozen. The subsequent stability of the structure which increases with Cu concentration is decided by the activation energy for atomic transport.

We have extended the melt-spinning technique to prepare silicon ribbons. Our preliminary studies on the microstructure and growth morphology of the ribbons show some interesting features of the rapid solidification process.

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