# SURFACE DAMAGE EFFECTS IN METALLIC GLASSES BY HELIUM, HYDROGEN AND ARGON ION BOMBARDMENT

by

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DEDICATED TO THE MEMORY OF

MY BELOVED FATHER

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# ABSTRACT

Blistering, flaking and bubble formation in metallic glasses $Fe_{40}Ni_{40}P_{14}B_6$, $Fe_{40}Ni_{38}Mo_4B_{18}$, $Fe_{40}Ni_{40}B_{20}$, $Fe_{80}B_{20}$, $Ni_{64}Zr_{36}$, $Ni_{33}Zr_{67}$ and $Ni_{60}Nb_{40}$ due to helium, hydrogen and argon ion bombardment has been studied. Irradiations were performed at room temperature and normal incidence. Helium blistering and bubble formation is examined as a function of relevant irradiation and material parameters. The effect of projectile energy (50-150 keV), total dose ($1\times10^{16}$-$1\times10^{19}$ ions/cm$^2$), dose rate (10-100 μA/cm$^2$), thermal crystallization, cold-work (30% thickness reduction), composition and post-irradiation annealing (473-873 K) was studied. The results on metallic glasses are compared with similar results reported for crystalline materials. The similarities and differences are outlined and discussed. It is found that metallic glasses are more resistant against helium blistering. The critical doses for blistering and/or flaking in metallic glasses are higher, by about a factor of 2, as compared to their crystalline counterparts. The precipitation behaviour of helium in metallic glasses is very similar to that reported for metals. Except $Ni_{33}Zr_{67}$, all other metallic glasses used in this study remained amorphous after ion irradiation.

Possible mechanisms of helium trapping in metallic glasses are examined. A molecular dynamics computer simulation study of displacement damage in an amorphous

Lennard-Jones solid is reported. It is shown that the vacancy and the interstitial type defects are produced dynamically due to the displacement of atoms from their local positions. Helium trapping in metallic glasses is envisaged to occur at such vacancy type defects (atom-sized-holes) during energetic ion irradiation. Using rate theory, it is shown that the collapse of compact atom-sized-holes into distributed free volume lowers the rate of He-V complex formation in metallic glasses relative to that for crystalline materials.

Hydrogen and argon ion irradiations were performed at 100 keV. The precipitation of implanted hydrogen into bubbles and eventually blistering of the bombarded surface is observed in metallic glasses, for the first time. The resistance of metallic glasses against hydrogen blistering is found to be nearly 3 times higher as compared to their crystalline counterparts. Blistering due to argon ion bombardment was observed in a limited dose range of $1\times10^{17}$-$1\times10^{18}$ ions/cm$^2$. At higher doses, blisters disappeared with concurrent roughening of the bombarded surface. Erosional features like cones or pyramids were not observed for metallic glasses. Argon blisters also disappeared on room temperature aging for about 100 days or more. Post-irradiation annealing at 673 K and 873 K resulted in blister formation, exfoliation and pin-hole formation. There was no evidence of solidification of implanted argon into bubbles in metallic glasses. In contrast, solid argon bubble formation was observed in an fcc metal, Ni, for similar irradiation conditions.

# P R E F A C E

The behaviour of inert gases particularly helium in metals is of interest both in nuclear material engineering and fundamental research in condensed matter physics. Helium has extremely low solubility in metals and therefore it tends to precipitate in the form of gas bubbles. The precipitation of helium into bubbles in nuclear materials leads to several technological problems. Helium induced effects in reactor materials are broadly classified into two categories: bulk effects and surface effects. Helium produced by $(n,\alpha)$ reaction in the bulk of materials can lead to helium embrittlement and can influence the swelling behaviour and the phase stability of reactor structural alloys. Helium produced by D-T reaction in a fusion device can bombard the first wall surfaces and cause surface damage effects such as blistering and flaking. The reason for blistering and flaking is the precipitation of implanted helium into bubbles in the near-surface region of the material. However, these can lead to serious first wall erosion and plasma contamination problems in magnetically confined fusion devices. In view of this, numerous simulation studies of helium ion bombardment induced blistering and flaking have been reported on various crystalline materials. In addition, helium ion implantation experiments have been performed to study the basic properties of helium in metals and the processes of helium bubble nucleation and bubble growth. Similar studies were not made on amorphous materials whose disordered atomic structure could lead to important differences from crystalline materials. With the availability of rapid quenching techniques, it has become possible to obtain alloys of many metals in the amorphous state. Such amorphous metal alloys, known as metallic glasses, exhibit highly desirable combination of physical, mechanical and chemical properties and some of these glasses can also be of technological interest for nuclear applications. In this context study of helium precipitation into bubbles, blistering and flaking in metallic glasses is of both basic and practical interest, particularly when a comparison with their crystalline counterparts is made. Some of these aspects are investigated in this thesis.

Metal-metalloid glasses $Fe_{80}B_{20}$ , $Fe_{40}Ni_{40}B_{20}$ , $Fe_{40}Ni_{40}P_{14}B_6$ and $Fe_{40}Ni_{38}Mo_4B_{18}$ were choosen because of their easy availability from their commercial suppliers. In addition, these glasses also provide a good series in composition to study the possible influence of replacing the metal and/or metalloid atoms by another similar atoms (Fe by Ni or Mo and B by P). However, it was realized that metal-metal glasses will have better prospects for reactor applications because they generally have a higher crystallization temperature and lower neutron capture cross-section (since metalloid B is not present). With these considerations in mind the work was extended to metal-metal glasses. Metallic glasses $Ni_{64}Zr_{36}$, $Ni_{33}Zr_{67}$ and $Ni_{60}Nb_{40}$ were choosen. Both Ni-Zr and Ni-Nb glasses have good neutronic properties, are thermally stable to reasonably high temperaturesand have excellent mechanical properties. A detailed and systematic study of helium ion irradiation induced blistering, flaking and bubble formation in both metal-metalloid and metal-metal glasses has been performed as a function of various relevant irradiation and metallurgical parameters. In addition to helium, hydrogen and argon ion irradiations were performed to study the influence of ion species related parameters on induced damage in metallic glasses. The results on metallic glasses are compared with similar results reported for crystalline materials. Possible mechanisms of damage production and gas trapping in metallic glasses are also discussed.

The organisation of the thesis is as follows: the thesis is written in five chapters. Chapter 1 provides an introduction to the field of gas ion implantation induced surface damage in metals. In Chapter 2, a brief discussion of structure, defects and diffusion in metallic glasses is given. A molecular dynamics computer simulation study of displacement damage in an amorphous Lennard-Jones is presented. The results are then used to develop a model of helium trapping in metallic glasses for energetic ion irradiation. Chapter 3 deals with the experimental details. An analysis of damage and implantation profiles for ion irradiations of metallic glasses employed in this study is also given. In Chapter 4, our experimental results of helium, hydrogen and argon ion irradiations of metallic glasses are presented. Chapter 5 provides a discussion of experimental results. The thesis is concluded with a summary which brings out the salient features of the present work and the conclusions drawn from this study. Possible further studies are also indicated. A summary of irradiation studies reported so far on metallic glasses is given in the appendix.

CONTENTS

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