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RECOVERY KINETICS AND ORDERING IN IRRADIATED BULK METALLIC GLASSES

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Accumulation and recovery kinetics of radiation damages in $Zr_{46.8}Ti_{8.2}Cu_{7.5}Ni_{10}Be_{27.5}$ and $Zr_{52.5}Ti_5Cu_{17.9}Ni_{14.6}Al_{10}$ metallic glasses was investigated by means of low temperature electron irradiation and electrical resistance measurements. The linear dose dependence of resistance is a manifestation of accumulation of irradiation defects without considerable interaction between them. The recovery spectrum of irradiation-induced electrical resistance was obtained for the 85…300 K temperature range. Two annealing peaks located at T~150 K and ~225 K were resolved. The present data suggest the conclusions that the defect mobility is a thermally activated process, and that the activation energy is not as high as that for vacancies in crystalline alloys. These results are in agreement with the polycluster model of metallic glass structure.

INTRODUCTION

Owing to their unique mechanical and electrophysical properties, including improved radiation resistance, new bulk multicomponent amorphous metallic compounds find an increasingly wide application in various fields of industry, while the research into them becomes more extensive and intensified.

The recent experimental data indicate that the atomic structure of metallic glass is much similar to the structure of supercooled melt. Not being in equilibrium state, the glass is crystallized so slowly that it appears pertinent to use the "freezing" concept for its structure. The main property of the metallic glass structure is the configurational disorder. Correlations in the positional relationship of atoms in the metallic glass quickly disappear as the interatomic spacing increases, and become negligibly small at distances that are equal to approximately ten atomic diameters. It is natural to assume that irradiation cannot increase anymore the structural disorder of the amorphous substance that has already a "perfect disorder". It is just this property that underlies the assumptions about a higher radiation resistance of amorphous alloys.

When planning experimental studies we proceeded from the existence of two most developed theoretical structural models for amorphous solids, namely, the model of random closely packed spheres [1-4] and the polycluster model [5-7]. Each of these structural models implies radically different kinds of primary configuration, lifetime, diffusion length and other properties of point defects. As a result, the kinetics of accumulation and thermal annealing of radiation damages is also expected to be different. Thus, the sensitivity of radiation effects to the structural peculiarities of metallic glass opens up a real possibility for investigating the structure and structural defects in these glasses through investigating the kinetics of accumulation and relaxation of radiation damages. The data obtained in this case may serve as a criterion in choosing this or that structural model of metallic glass.

EXPERIMENTAL

Five-component amorphous alloys of $Zr_{41}Ti_{14}Cu_{12,5}Ni_{10}Be_{22,5}$ and $Zr_{52.5}Ti_5Cu_{17.9}Ni_{14.6}Al_{10}$ compositions that refer to bulk metallic glasses were prepared for the present experiments by the spinning method. The initial structure and the quality of samples were examined and controlled by the use of X-ray diffraction and electron microscopy methods. A typical halo of the X-ray diffraction pattern shows that the as-prepared materials are amorphous.

The method of low-temperature electron irradiation of the above-mentioned metallic glasses with their subsequent isochronal annealing and electrical resistance measurements was used in our experiments The irradiation experiments were carried out at the NSC KIPT Van-de-Graaff accelerator ELIAS. The samples were irradiated with 2.5 MeV electrons in a special two-loop nitrogen cryostat providing the ultrapure liquid nitrogen environment. The temperature of samples under irradiation did not exceed 85 K. After irradiation, the samples were subjected to isochronal annealing at temperatures between 85 and 300 K with a 10 K step. The annealing took 15 minutes at each step. The electrical resistance measurements of the samples were performed by the standard four-probe method using an automated measuring system with two-channel nanovoltmeter Agilent 34420A as the basis. The circuit made it possible to measure simultaneously the current and temperature of the sample and the potential across the sample. To attain better accuracy, 50 to 60 resistance measurements of each sample were made in the temperature range 79…82 K. The obtained results were approximated by the linear dependence, and the resistance value at T=80.5 K was calculated. In this case, the relative error was not

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higher than 5 ppm. These sensitivity and precision are not attained with other research methods. The electrical resistance of the samples was measured before irradiation and after each step of irradiation and isochronal annealing.

RESULTS AND DISCUSSION

As it follows from our first experiments, the irradiation of bulk metallic glasses by high-energy electrons to a dose of ~$7 \cdot 10^{19}$ e^-/cm^2 does not cause any appreciable structural change that can be detected by common methods of X-ray diffraction and electron microscopy. It is evident that here one must use the method providing a much higher sensitivity to primary radiation damages than the above-mentioned methods do. For this reason we have used low-temperature electrical resistance measurements to study the kinetics of accumulation and annealing of radiation damages in bulk metallic glasses.

DOSE DEPENDENCES OF ELECTRICAL RESISTANCE

Dose dependences of electrical resistance of the samples irradiated with 2.5 MeV electrons are presented in Fig. 1. The data show that the electron irradiation really changes the electrical resistance of metallic glasses. It means that irradiation generates atomic replacements and displacements that result in the resistance changes. The linear dependence of R_{irr}/R_o on the dose is a manifestation of accumulation of irradiation defects without considerable interactions of the cumulative damages.

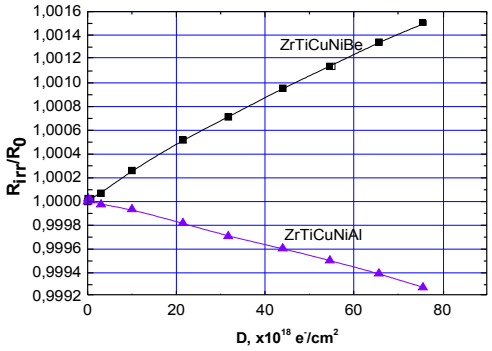

Fig. 1. Dose dependences of relative electrical resistance for ZrTiCuNiBe and ZrTiCuNiAl irradiated with 2.5 MeV electrons at 85 K

The remarkable feature of the present data is that the $R_{irr}(D)$ line for ZrTiCuNiBe has a positive slope, while for ZrTiCuNiAl glass we have $dR_{irr}/dD<0$. The main compositional difference of the glasses under study is the presence or absence of Be atoms. It is just this difference that causes the observed dramatic changes in R_{irr} (D). The origin of the observed difference in the slopes, $dR_{irr}(D)/dD$, for different glasses can be understood as follows.

In the Be-containing glass, the interstitials of Cu-Be or Ni-Be dumbbell types have the lowest energy formation of all possible interstitial compositional configurations. The same phenomenon is well known for all crystalline alloys, where atoms of the host metal and the undersize impurities form stable interstitial dumbbells with a low diffusion activation energy. Due to this fact, the segregation of undersize atoms on the sinks takes place. Accordingly, the $R_{irr}(D)$ increase with increasing irradiation dose can be explained as a result of Be segregation on intercluster boundaries, just as in the crystals [8, 9].

In the ZrTiCuNiAl bulk glass, the interstitial dumbbell formation is questionable. In this case no undersize impurities are segregated at the boundaries, and therefore, electron scattering at the boundaries does not increase too much. But this property cannot account for the decrease in electrical resistance under irradiation and during the following annealing. This feature can be explained as a result of irradiation-induced atomic replacements that lead to short-range ordering of the alloy. The ordering process enhanced by electron irradiation can take place in both the cluster body and at the intercluster boundaries. This process does not need a long-range diffusion (as Be atoms do within ZrTiCuNiBe glass). Of course, the short-range ordering-induced decrease in the resistance is accompanied by the increase in resistance due to the conducting electron scattering on the irradiation-generated defects and heterogeneities. The observed result shows that the last process is weaker than the first one, in other words, the short-range ordering is a dominant process.

RECOVERY KINETICS IN IRRADIATED METALLIC GLASSES

The recovery curves of irradiation-induced electrical resistance changes on isochronal annealing of ZrTiCuNiBe and ZrTiCuNiAl bulk metallic glasses are shown in Figs. 2 and 4, respectively. The first derivatives, dR/d T, are presented in Figs. 3 and 5.

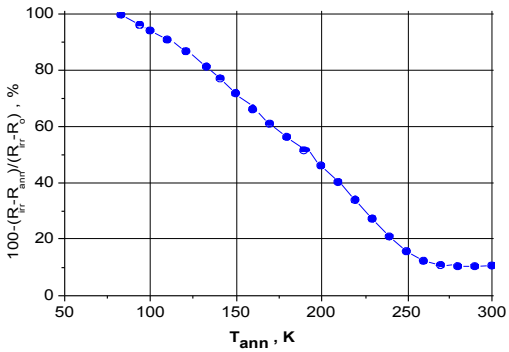

Fig. 2. Recovery of irradiation-induced resistance changes of ZrTiCuNiBe irradiated with 2.5 MeV electrons at 85 K to a dose of $7.5 \cdot 10^{19}$ e^-/cm^2. Here R_o, R_{irr} and R_{ann} are the electrical resistances before irradiation, after irradiation and after annealing at $T = T_{ann}$, respectively

As it is clearly seen from Figs. 3 and 5, two annealing peaks located at T~150 K and T~225 K are resolved for ZrTiCuNiBe glass. The only difference of the recov-

ery result for the ZrTiCuNiAl bulk MG is a shift of the first peak towards ~130 K. It is necessary to note that in this case there is no real recovery, but a further decrease in resistance occurs during annealing. This feature can be attributed to a continued short-range ordering in the previously irradiated alloy.

From the location of annealing stages (peaks in Figs. 3 and 5) the effective activation energy of relaxation processes can be estimated as $E_{eff}(eV) = 3 \cdot 10^{-3} x\ T_{peak}(K)$ [10]. As a result, we have for ZrTiCuNiAlBe: E_{150K} = 0.46 eV and E_{225K} = 0.69 eV and for ZrTiCuNiAl: E_{135K} = 0.40 eV and E_{225K} = 0.69 eV. Accordingly, the activation energies responsible for the relaxation stages do not exceed 1 eV.

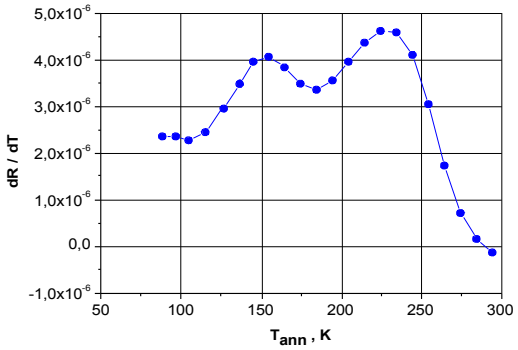

Fig. 3. Recovery spectrum of irradiation-induced resistance changes for ZrTiCuNiBe irradiated with 2.5 MeV electrons at 85 K to a dose of 7.5·10[19] e⁻/cm²

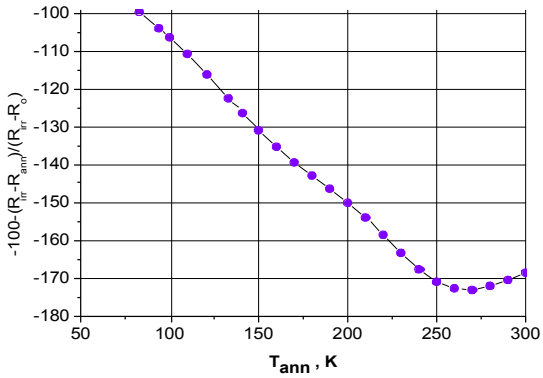

Fig. 4. Recovery of irradiation-induced resistance changes of ZrTiCuNiAl irradiated with 2.5 MeV electrons at 85 K to a dose of 7.5·10[19] e⁻/cm²

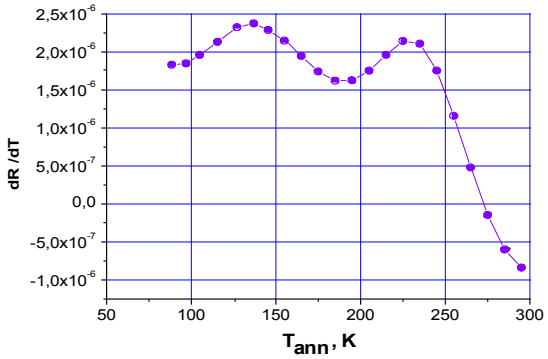

Fig. 5. Recovery spectrum of irradiation-induced resistance changes for ZrTiCuNiAl irradiated with 2.5 MeV electrons at 85 K to a dose of 7.5·10[19] e⁻/cm²

The relaxation kinetics of interstitial and vacancy complexes in the crystals within the mentioned temperature range, as a rule, has a similar characteristic activation energy. It is worthy of note that in crystalline Zr-based alloys the diffusion migration energies are higher than 1 eV [11].

The observed annealing stages present the most important result of the undertaken recovery experiments. They show that stable point defects – vacancies and interstitials – do exist in the metallic glasses under study.

CONCLUSION

The present data show that the point defects are stable in metallic glasses and the defect mobility is a thermally activated process. The activation energy of defect migration in metallic glasses is lower than that in crystals. This experimental result allows us to conclude that (i) the structural model of densely random-packed spheres is irrelevant to bulk metallic glasses under study; (ii) the results are in accord with the polycluster structure of ZrTiCuNiBe and ZrTiCuNiAl bulk metallic glasses. These results were partially reported at 2007 MRS Fall Meeting [12].

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КИНЕТИКА ВОЗВРАТА И УПОРЯДОЧЕНИЕ В ОБЛУЧЕННЫХ ОБЪЕМНЫХ МЕТАЛЛИЧЕСКИХ СТЕКЛАХ

Ю. Петрусенко, А. Бакай, И. Неклюдов, В. Борисенко, Д. Баранков, А. Астахов, М.-П. Махт

Исследована кинетика накопления и отжига радиационных повреждений в металлических стеклах $Zr_{46.8}Ti_{8.2}Cu_{7.5}Ni_{10}Be_{27.5}$ и $Zr_{52.5}Ti_5Cu_{17.9}Ni_{14.6}Al_{10}$ с использованием метода низкотемпературного электронного облучения и измерений электрического сопротивления. Линейная дозовая зависимость электросопротивления свидетельствует об аккумулировании радиационных дефектов без существенного их взаимодействия. Определены спектры возврата радиационно-индуцированного электросопротивления для температурного интервала 85…300 K, выделены два пика отжига при температурах T~150 и ~225 K. Полученные данные позволяют сделать вывод о том, что подвижность дефектов является термоактивированным процессом с энергией активации, не превышающей значений энергии миграции вакансий в кристаллических сплавах. Эти результаты согласуются с поликластерной структурной моделью металлического стекла.

КИНЕТИКА ВЕРТАННЯ ТА УПОРЯДКУВАННЯ В ОПРОМІНЕНИХ ОБ'ЄМНИХ МЕТАЛІЧНИХ СТЕКЛАХ

Ю. Петрусенко, О. Бакай, І. Неклюдов, В. Борисенко, Д. Баранков, О. Астахов, М.-П. Махт

Досліджена кінетика накопичення та відпалу радіаційних пошкоджень в металічних стеклах $Zr_{46.8}Ti_{8.2}Cu_{7.5}Ni_{10}Be_{27.5}$ та $Zr_{52.5}Ti_5Cu_{17.9}Ni_{14.6}Al_{10}$ з використанням методу низькотемпературного електронного опромінення та вимірів електричного опору Лінійна дозова залежність електричного опору свідчить про акумулювання радіаційних дефектів без суттєвої їх взаємодії. Визначені спектри вертання спричиненого опроміненням електричного опору для температурного інтервалу 85...300 K та вірізнені два піки відпалу з температурами T~150 та ~225 K. Отримані дані дозволяють зробити висновок про те, що рухливість дефектів є термоактивованим процесом з енергією активації, що не перевищує значень енергії міграції вакансій в кристалічних сплавах. Ці результати узгоджуються з полікластерною структурною моделлю металічного скла.