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To cite this version:

G. Schumacher, W. Petry, S. Klaumünzer, G. Wallner, G. Weck. DEFECT PRODUCTION BY FAST NEUTRONS AND THERMAL RECOVERY IN AMORPHOUS Pd80Si20. Journal de Physique Colloques, 1985, 46 (C8), pp.C8-603-C8-608. <10.1051/jphyscol:1985896>. <jpa-00225249>

HAL Id: jpa-00225249
https://hal.archives-ouvertes.fr/jpa-00225249
Submitted on 1 Jan 1985

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DEFECT PRODUCTION BY FAST NEUTRONS AND THERMAL RECOVERY IN AMORPHOUS Pd₈₀Si₂₀

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Abstract - Defects were introduced into variously pretreated strips of glassy Pd₈₀Si₂₀ by fast neutron irradiation at 4.6 K. The electrical resistivity was measured during irradiation up to \(2 \times 10^{19} \text{n/cm}^2\) as well as subsequent isochronal annealing up to 483 K. Most of the results can be understood in terms of the familiar concept of vacancy and interstitial-like defects. However, in addition to the well-known process of mutual annihilation an important mechanism for defect relaxation is the disintegration of localized defects into subatomic ones which are distributed among many atoms.

I - INTRODUCTION

Many experiments as well as theoretical considerations suggest that the concept of structural defects in amorphous materials is as useful as in crystals. An established method of defect production in crystalline metals is fast particle irradiation at low temperatures. Fast electrons predominantly displace single atoms whereas fast neutrons mainly produce displacement cascades. In the early stages of defect production (<10⁻¹²s) no essential differences between crystalline and glassy metals are expected because of the high kinetic energies of the knocked-on atoms in comparison to their binding energies. In the subsequent stages of energy relaxation, however, fundamental differences may result from the absence of long range order in an amorphous material since defects need not be strictly localized but can be distributed among many atoms.

It has been shown by positron annihilation in electron-irradiated metallic glasses that holes of nearly atomic size survive frequently /1/ and, to some degree, it makes sense to speak of vacancies in metallic glasses. However, the existence of the corresponding anti-defect, a compressed zone where the knocked-on atom has come to rest, is only inferred indirectly from experiments and it should be noted that computer simulations predict a lower stability of such atomic configurations /2/.

Therefore it is not surprising, that the discussion about the degree of atomic relaxation in the highly defective regions of displacement cascades is still controversial /3, 4/. On the one hand, one expects by analogy with crystalline metals...
large holes due to hole agglomeration within the cascade. On the other hand, pronounced relaxation may take place because of the violent atomic vibrations which tend to eliminate less stable configurations. Therefore it seems to be worthwhile to obtain more information about defects in a metallic glass produced by fast neutrons at very low temperatures.

II - EXPERIMENTAL

In two runs performed at the liquid helium irradiation facility of the research reactor in Munich (FRM) eight glassy Pd$_{80}$Si$_{20}$ samples of different pretreatment (see table 1) have been irradiated at 4.6 K with fast neutrons ($\Phi = 2.9 \times 10^{13}$ n/cm$^2$/s, $E > 0.1$ MeV, flux inhomogeneity across the sample holder < 5%). The flux of thermal neutrons has been about $3 \times 10^{12}$ n/cm$^2$/s which is believed to produce less than 5% of the total damage. The specimens were cut from a melt-spun ribbon, approx. 30 µm thick and 1 mm wide, provided by Vacuumschmelze at Hanau. After each irradiation run an isochronal annealing treatment has been performed up to 483 K with a step width $\Delta T_A/T_A = 0.1$ and a holding time of 5 min below and 10 min above 80 K.

Electrical resistance measurements were used to monitor radiation damage and were done by a standard four-probe technique at 4.6 K. Electrical contacts were made by screws. The resistance was converted into resistivity by setting $\rho_{4.6}(\phi = 0) = 78$ µΩcm for all unirradiated samples. Additionally, the resistivity $\rho_T$ for 1 K $< T < 30$ K was measured prior to irradiation and after annealing at $T_A = 77$ K and $T_A = 287$ K in order to examine the temperature-dependent part of $\rho_T$ for a possible influence of radiation-induced two-level systems. All samples revealed a shallow resistivity minimum at about 13 K but there was no change in the temperature-dependent part within the experimental error of $< 5 \times 10^{-8}$ Ωcm after irradiation and additional annealing. Furthermore, there are arguments that changes in the compositional short range order either play a negligible role in Pd$_{80}$Si$_{20}$ or do not affect its resistivity. Therefore, in Pd$_{80}$Si$_{20}$ $\Delta \rho = \rho_{4.6}(\phi) - \rho_{4.6}(0)$ is a good quantity to monitor radiation-induced changes in topological short range order.

Table 1 - Sample Characterization

<table>
<thead>
<tr>
<th>Sample No.</th>
<th>RUN</th>
<th>Pretreatment</th>
<th>$\rho_{300}/\rho_{4.6}$</th>
<th>$\Delta \rho_{\text{max}}$ (µΩcm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>P1.1</td>
<td>I</td>
<td>preannealed</td>
<td>1.028</td>
<td>2.97</td>
</tr>
<tr>
<td>P2.1</td>
<td>I</td>
<td>250°C, 1 h</td>
<td>1.029</td>
<td>2.98</td>
</tr>
<tr>
<td>P3.1</td>
<td>I</td>
<td>10$^{-6}$ mbar</td>
<td>1.030</td>
<td>3.13</td>
</tr>
<tr>
<td>P4.1</td>
<td>I</td>
<td></td>
<td>1.037</td>
<td>2.94</td>
</tr>
<tr>
<td>P5.1</td>
<td>I</td>
<td>as</td>
<td>1.031</td>
<td>2.98</td>
</tr>
<tr>
<td>P3.2</td>
<td>II</td>
<td>quenched</td>
<td>1.029</td>
<td>3.80</td>
</tr>
<tr>
<td>P4.2</td>
<td>II</td>
<td></td>
<td>1.028</td>
<td>3.67</td>
</tr>
<tr>
<td>P5.2</td>
<td>II</td>
<td>cold-rolled</td>
<td>1.028</td>
<td>3.57</td>
</tr>
</tbody>
</table>

RUN I: $\Phi_{\text{max}} = 1.1 \times 10^{19}$ n/cm$^2$
RUN II: $\Phi_{\text{max}} = 2.0 \times 10^{19}$ n/cm$^2$
+ prior to irradiation
**III - RESULTS**

Fig. 1 shows $\Delta p$ versus fast neutron fluence $\phi t$ of an as-quenched sample. The resistivity increases of the various samples are slightly different. These differences cannot be fully explained by different neutron fluences at the various sample sites and are, at least partly, due to different starting structures. No clear correlation between the resistivity ratio $\rho_{300}/\rho_{4.6}$ and $\Delta p_{\text{max}} = \rho_{4.6}(\phi t)_{\text{max}} - \rho_{4.6}(0)$ is found (see table 1). At present, we cannot pursue this question because a better evaluation of this problem needs the knowledge of $\rho_{4.6}(0)$ of each individual sample to a high degree of accuracy.

Fig. 2 shows the damage rate $\frac{\Delta p}{\Delta t}$ versus $\Delta p$ for an as-quenched sample. The most obvious feature is the extreme linearity in comparison to crystalline metals /5/. A linear extrapolation to damage saturation $\frac{\Delta p}{\Delta t} = 0$ yields $\Delta p_s = 4.1 \, \mu \Omega \text{cm}$. The same value has been obtained from 80-keV-proton irradiation at 6 K /7/. However, from 3-MeV-electron irradiation at 4.6 K a saturation resistivity of 2.45 $\mu \Omega \text{cm}$ was linearly extrapolated /8/. The latter figure may be too low because an additional curvature in the damage rate cannot be ruled out definitely.

Fig. 3 shows the fractional resistivity recovery $\frac{\Delta p}{\Delta p_{\text{max}}}$ for seven samples versus annealing temperature $T_A$. Additionally, we have depicted schematically the annealing curves obtained after electron bombardment at 4.6 K /8/ and after neutron irradiation of $\text{Pd}_{80}\text{Si}_{20}$ below 7 K /4/. The latter curve was measured with a holding time of 6 min after irradiation with the very low fluence of $1.2 \times 10^{17}$ n/cm$^2$ /4/. The following features are remarkable:

1) There is no distinct annealing stage which points to a pronounced process with a single activation energy.

2) The relative resistivity recovery does not depend significantly on the pretreatment. The sample mentioned in Ref. 4, which was preannealed at 360° C for 3 h, is presumably partly crystallized and should not be taken into account.

3) There seems to be a smooth transition from the annealing of radiation-induced defects to intrinsic relaxation, which starts at about 400 K for as-quenched samples and which does not exist in the preannealed specimens for all temperatures covered by our experiment.

4) After electron irradiation the resistivity recovery starts at 10 K /8/ whereas after neutron bombardment appreciable recovery begins at about 50 K.

5) In the high fluence regime ($\phi t > 1 \times 10^{18}$ n/cm$^2$) the fractional resistivity recovery is independent of fluence. However, the resistivity recovery of $\text{Pd}_{80}\text{Si}_{20}$ of Ref. 4 is clearly shifted to higher annealing temperatures in comparison to our results. Three explanations are possible. i) The unirradiated original metallic glasses are widely different in structure and thus not directly comparable. Concerning the amorphous material at a fixed composition this explanation is not very likely because different pretreatments have no significant effects on the recovery behaviour (see point 2). However, small deviations from the nominal composition $\text{Pd}_{80}\text{Si}_{20}$ may influence the location of the recovery curves as can be concluded by comparison of the annealing data of $\text{Pd}_{80}\text{Ni}_{2}\text{Si}_{18}$ and $\text{Pd}_{80}\text{Si}_{20}$ /4/. Unfortunately, a closer sample characterization cannot be done since we are lacking in data. ii) The differences in the recovery curves after neutron irradiation are merely due to the different annealing programmes. However, if we allow for reasonable attempt frequencies ($10^7$ to $10^{14}$ Hz) for atomic jumps an analysis of the recovery curves yields a broad distribution $p(E)$ of activation energies $E$ and the difference of 4 min in the holding times between Ref. 4 and this work is not sufficient to bring both curves into agreement. iii) The shift reflects a real fluence effect and points to differences in $p(E)$ between low and high fluence neutron irradiation.

We believe point iii) the most probable one, although i) and ii) cannot be ruled out with certainty.
Fig. 1 - Resistivity increases $\Delta \rho$ of as-quenched $\text{Pd}_{80}\text{Si}_{20}$ irradiated at 4.6 K with fast neutrons.

Fig. 2 - Damage rate versus resistivity increase $\Delta \rho$ of the sample of Fig. 1. Note the excellent linear dependence of $d\Delta \rho/d\Phi$ on $\Delta \rho$.

Fig. 3 - Fractional resistivity recovery for various $\text{Pd}_{80}\text{Si}_{20}$ glasses (a.q. = as-quenched, c.r. = cold rolled, ann. = annealed at 250°C, 1 h in vacuum, compare Table 1). The fractional recovery after a low fluence neutron irradiation /4/ (---) and after electron irradiation /8/ (---) is additionally depicted.
IV. DISCUSSION

For the further discussion we adopt tentatively an oversimplified position. We assume relatively well-localized defects which behave similar to those in pure crystalline metals, i.e. we assume vacancy-like and interstitial-like defects which can recombine and thus mutually annihilate. This concept has been applied successfully for the interpretation of the behaviour of the electrical resistivity /7/ and positron annihilation /1/ after irradiation with light particles. According to this concept the damage rate is given by /9/

\[
\frac{d\rho}{dt} = \sigma_d \rho_F \xi [1-2\varphi a \frac{\Delta\rho}{\rho_F}]
\]  

(1)

where \(\sigma_d\) denotes the total displacement cross-section for fast neutrons, \(\rho_F\) and \(\varphi a\) describe the resistivity per unit concentration and an average recombination volume of individual defects, respectively. For \(Pd_{80}Si_{20}\) \(\rho_F\) is about \(4.10^{-4}\) Qcm /7, 8/. \(\xi\) is roughly 0.3 in crystalline metals and takes into account the recombination of close-lying defects due to large vibrations of atoms within a displacement cascade /9/. Point 4) suggests that a similar mechanism is also present in amorphous \(Pd_{80}Si_{20}\). With these numbers we obtain good agreement between eq. (1) and the experimental data of Fig. 1 if \(\sigma_d = 3.810^{-24}\) cm² and \(\varphi a = 49\) atomic volumes are inserted. The value for \(\sigma_d\) is unusually high in comparison with crystalline metals but cannot be evaluated further since the minimum threshold energies for displacements are unknown for \(Pd_{80}Si_{20}\). The average recombination volume \(\varphi a\) is the same as for light-ion bombardment, reflecting merely the identical saturation resistivities. This is a surprising result, since many effects contribute to damage production in cascade-producing irradiation which are absent in light-ion bombardment /9/.

What is easily understood in an two-defect-species model is the particle and fluence dependence of the damage recovery. Electrons produce predominantly isolated defect-anti-defect pairs which are not far from one another due to the low energy recoils. Hence, only small activation energies are needed to induce thermally activated recombination. During fast neutron irradiation a high energy transfer initiates a displacement cascade in which interstitial-like and vacancy-like defects are effectively separated. In particular, close-lying defects which would be stable under electron bombardment, recombine immediately /9/. Thus higher annealing temperatures are needed to produce the same fractional recovery as in the electron-irradiated glass. With increasing neutron fluence, however, cascade overlap reduces the mean distances of the defects again and the recovery curve is shifted now to lower annealing temperatures. Nevertheless, recovery after fast neutron irradiation will always start at higher annealing temperatures in comparison to electron irradiation due to the close-pair instability mentioned above.

However, the following facts fit hardly into the picture of localized defects:

1) The effective separation of interstitial-like and vacancy-like defects should produce significant agglomeration of defects of the same kind. Hence one would expect larger holes (vacancy agglomerates) in a cascade-damaged glass than in an electron-irradiated material. However, positron-lifetime experiments indicate the contrary /1, 3/. To our opinion the interpretation given in Ref. 3 is not convincing. Provided it would be correct, we would expect a significant increase in positron lifetime with increasing fluence which is not observed in Ref. 3 although the fluence range covers the regime from isolated cascades near to damage saturation /10/.

2) The insignificant influence of pretreatment on irradiation and annealing behaviour might be understood if we would assume negligible interaction between radiation-induced defects and otherwise produced structural modifications. But with this assumption, the smooth transition from the annealing of radiation-induced defects to intrinsic relaxation is merely fortuitous.

3) There is now growing evidence, that radiation-induced defects in metallic glasses do not migrate appreciably /1, 3, 11/ which is mysterious for localized defects.
The easiest way to overcome these difficulties is to allow for a non-localization of the defects. We still retain two defect species which can mutually annihilate but each species can also relax by disintegration. At low temperatures we think mutual recombination for the most important process. Since free migration does not occur, only close-lying defect-anti-defect pairs can recombine. At higher temperatures disintegration of localized defects becomes more and more important and holes of atomic size are believed to be unstable. Thus, appreciable amounts of radiation damage can affect the electrical resistivity without being visible in the positron lifetime. When a defect is distributed among so many atoms that it becomes indistinguishable from intrinsic density fluctuations it is meaningless to differentiate between recovery of radiation-induced defects and intrinsic relaxation and a smooth transition is observed experimentally.

The vibrations of the atoms within a cascade during neutron bombardment can be visualized as a thermal spike. The consequence is that defects within the cascade are expected to be weaker localized than after electron irradiation. This explains the shorter positron lifetimes. Moreover, the term "agglomeration" of defects of the same species can now only mean a density fluctuation which is more pronounced than fluctuations in the original material.

Free migration of localized defects does not occur because they are already delocalized before appreciable migration appears.

IV - CONCLUSIONS

The main conclusion of this paper are:

i) The experimental results can be well understood if vacancy-like and interstitial-like defects are assumed.

ii) Close-lying pairs consisting of a defect and an anti-defect are unstable during neutron irradiation in Pd₈₀Si₂₀.

iii) Defect and anti-defect can mutually annihilate like in crystals but they can also relax by disintegration. The latter process is not possible in crystals and prevents the free migration of defects in metallic glasses.

iv) The resistivity damage rate in glassy Pd₈₀Si₂₀ has the same simple mathematical form as in crystals.

Here a final remark should be added. In crystalline metals pₑ is nearly the same for isolated Frenkel defects as for clustered Frenkel pairs allowing a straightforward interpretation of Eq. (1). A delocalization of defects within a displacement cascade as proposed in this paper, however, makes the use of a single pₑ for neutron, electron, and light-ion bombardment somewhat doubtful. Further work must be done to clarify this problem.

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