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AMORPHISATION OF A Pd-Si ALLOY BY IRRADIATION WITH FISSION PRODUCTS

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Introduction

The irradiation of a crystalline solid with particles like electrons, neutrons or ions generally induces point defects which possibly agglomerate in clusters or dislocation loops. Sometimes effects on structure are more important. Irradiation may induce phase transformations. For instance monoclinic zirconia is reported to transform into the high temperature cubic phase when irradiated with fission fragments (f. f.) from ^{235}U (1). Likewise U_2Mo (2) and U_2Ti (3) undergo a phase change. Silica becomes amorphous up on exposure to fast neutrons (4) ; mica also when irradiated with f. f. (5). There is also a metallic alloy which becomes amorphous by irradiation : $U_6Fe + U\alpha$ (6).
To study the amorphization by irradiation we took an alloy that can be obtained amorphous when rapidly quenched from the melt : Pd-Si with 20% atoms of Si (7). This alloy is amorphous up to around 300 or 350°C. Samples can thus be handled at room temperature. The amorphization of this alloy was detected by X-rays diffraction patterns (8) and by electrical resistivity measurements.

Experimental procedure

Samples are obtained by quenching from the melt with an apparatus similar to those used elsewhere (9, 10). A drop of liquid alloy is ejected from a crucible by gas under pressure and smashed between two metal plates driven together at high speed. This amorphous samples are vacuum annealed at about 800°C during 40 hours. This procedure is the simplest one to obtain thin samples. X-ray diffraction patterns then show two phases as reported in the literature : a face centered cubic solid solution of Si in Pd and an orthorhombic phase Pd_3Si ; but in addition there are some lines which do not belong to one or another phase.

Thereafter these samples were irradiated by fast neutrons or fission fragments. In the latter case uranium enriched by 90% ^{235}U is evaporated under vacuum on each face of the samples. The range of fission fragments in $Pd_{80}Si_{20}$ being about 4 μ the thickness of the samples must not exceed 8 μ for the irradiation to be complete. This condition is not required for X-ray diffraction patterns : the patterns are performed with a diffractometer by reflection using Cu Kα radiation and only the two first microns of the sample participate to the pattern owing to the high absorption coefficient of Pd.

Results

- X-ray patterns

A 25 μ thick sample annealed after quenching was irradiated in the reactor Triton (Centre d'études nucléaires de Fontenay-aux-Roses) at about 400 K. In this case uranium was deposited on one side only. Accordingly the sample was irradiated by fission fragments in a range of 4 μ and entirely by fast neutrons.

X-ray patterns were performed after different irradiation times on both faces of the sample. The face not irradiated by f.f. shows no evolution even for doses up to about 4.10^{17} n/cm^2. On the other face diffraction lines of the crystalline phases continuously dissappear while broad rings typical of an amorphous structure appear (fig. 1). These lines disappear without broadening out nor appreciable shift. This shows that amorphization is not the last state of continuous disordering. It rather suggests that a particle leaves behind a small amorphized volume.

An amorphous sample was also irradiated under the same conditions. None change was observed with respect to the sample structure by X-rays, neither partial crystallization nor modification of the short range order.

- Electrical resistivity :

Samples quenched from the melt having different thicknesses (5.0, 6.3, 7.4, 8.4 μ) have been annealed 12 hours at 800°C. On both faces uranium with 90% ^{235}U has been deposited to a thickness of 1 800 A . The irradiation took place in the Fontenay-aux-Roses 20 K facility described

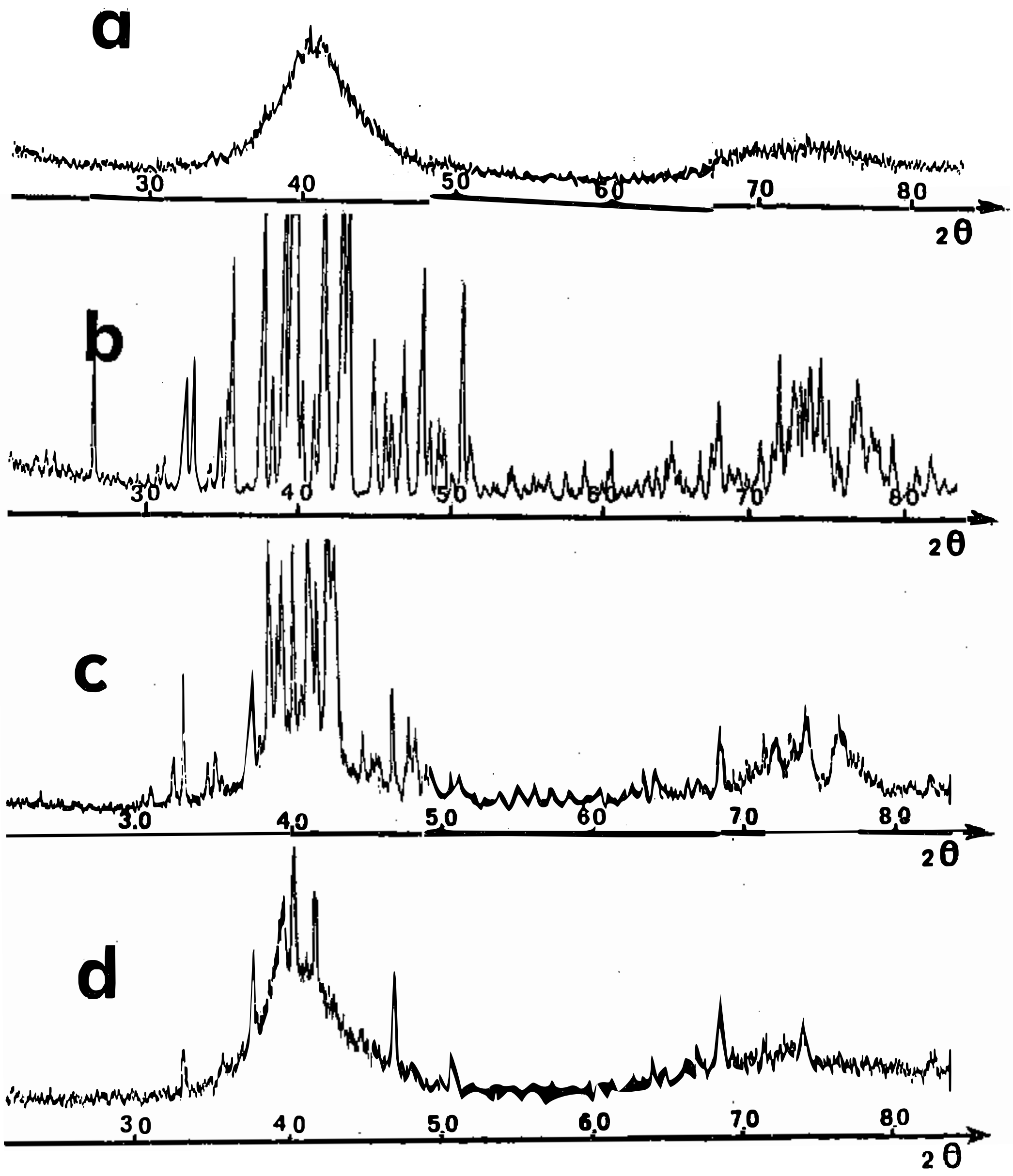
FIG. 1

a/ Quenched amorphous

b/ Annealed 40 h. at 800 °C

c/ Irradiated by $1.8.10^{13}$ f.f./cm^2

d/ Irradiated by $5.6.10^{14}$ f.f./cm^2



elsewhere (11). The instantaneous flux was 1.3 x 10^{13} th. neut. cm^{-2} s^{-1}. The results for these four samples are given in figure 2. Let us indicate that the resistivity ratio of the quenched amorphous state to crystalline state is about 9 at 20 K.

These curves show that

a. - For three of them we observe a definite maximum. Such a feature is exceptional if we consider that in metals the electrical resistivity varies monotonously during irradiation.

b. - For fluences greater than 9 x 10^{13} f.f./cm^2, the increase in resistivity is linear with increasing fluence. This may be not true for the 8.4 μ sample.

c. - The resistivity values for a fluence greater than 2.5 x 10^{14} f.f./cm^2, increase with increasing thickness.

d. - More precisely if one substracts from the resistivity changes the linear extrapolated increase, asymptotical values are obtained which are proportional to the different thicknesses.

e. - The broad resistivity peak appears clearly for the 5.0 μ sample, somewhat less for the 6.3 μ one, becomes a plateau for the 7.4 μ one and cannot be seen for the 8.4 μ one.

f. - The peak value is reached the more quickly the thinner the sample is.

Discussion

The sample thickness is seen to be an important parameter in the $\Delta\rho/\rho_0$ vs dose curves.

Since the source of particles lies on the whole sample, the flux is isotropic at the entrance of the sample but the damage is not homogeneous in the sample thickness. This fact complicates the interpretation.

The fission fragments can be divided in two parts : heavy fragments with an atomic mass of about 139 are emitted with an energy of 65 MeV and light fragments with an atomic mass of about 95 are emitted with an energy of 90 MeV. They penetrate into the solid with this energy and constitute initially highly charged (around 20 +) particles. First they are slowed down essentially by electronic collisions. Then when their energy

FIG. 2

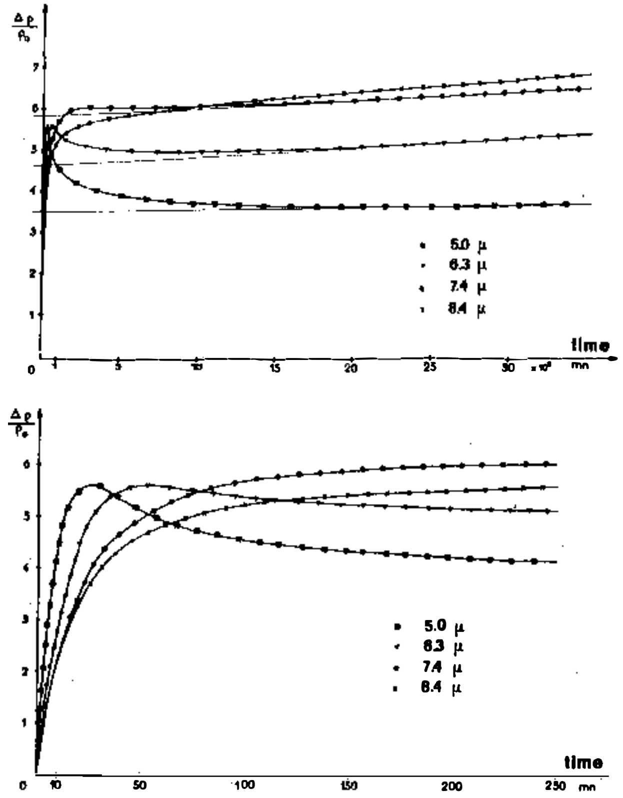
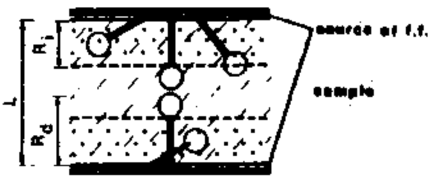

$\frac{\Delta\rho}{\rho_0}$
1
2
3
4
5
6
7
5.0 μ
6.3 μ
7.4 μ
8.4 μ
time
0
1
5
10
15
20
25
30
x10³
mn
$\frac{\Delta\rho}{\rho_0}$
1
2
3
4
5
6
5.0 μ
6.3 μ
7.4 μ
8.4 μ
time
0
10
50
100
150
200
250
mn

FIG. 3


source of f.f.
sample
L
R_i
R_d

has been enough reduced, the atomic collision cross section becomes greater and they produce displacement cascades.

Four processes can be considered :

a. - The energy loss by electronic excitation at the beginning of the path is dissipated in the lattice as thermal vibrations. The studied alloy though a conductor has a much lower conductivity than a good metal, so that the volume concerned by the thermal spike is small and the increase in temperature is high. The melting point can then be reached in a very short time. This thermal spike would then be followed by a rapid cooling. It would be somewhat like a rapid quench from the melt.

b. - If the heating in the thermal spike flows more efficiently, then the reached temperature is smaller. So instead of heaving a quench an annealing could take place, as it is pointed out in metals irradiations, and thus induce a change of short range order in a previously damaged volume.

c. - The displacement spike created at the end of the particle path can break interatomic bonds. In metallic alloys which can be quenched, amorphous partially covalent and thus oriented bonds probably exist particularly in Pd-Si alloy. When these bonds are broken during irradiation they cannot re-orient themselves if irradiation takes place at a temperature much lower than the crystallization temperature of the amorphous state.

d. - This displacement spike could also induce a heating in the neighbourhood of this spike and therefore produce an annealing.

The unusual shape of the resistivity curves involves that two phenomena at least play a part in the damage process : the first one produces an increase in resistivity while the second one produces a decrease in resistivity. In the thickest samples the latter is masked by the former, but in the thinnest samples the second phenomenon appears clearly.

Let us call R_i the range of the thermal spike, R_d the range of displacement spike, and L the thickness of a sample. R_d is the maximum range, 4μ in the studied alloy and R_i is inferior to R_d (fig. 3). So in all our samples the whole volume is concerned by the processes c or d since $L \leqslant 2 R_d$, while the volume concerned by processes a or b is in proportion greater when the samples are thinner, like $\frac{2 R_i}{L}$. It is then likely that the process c produces the amorphization, that is to say the increase in resistivity, while the process b induces the relative decrease in resistivity, that is to say a change of the short range order.

Nevertheless other experiments should be performed to test this hypothesis. We shall irradiate a thin sample (2 or 3 μ) with a parallel flux of fission fragments in which case overlapping of processes a or b and c or d will not occur. This can be done if the source of particles is removed to some distance away from the sample. Furthermore shields of different thicknesses between the source and the sample will allow to slow down the fission fragments more or less before entering the sample. So the effect of displacement spike and of thermal spike could be separated.

Conclusion

The irradiation of a Pd-20 at % Si alloy by heavy ions induces amorphization. We suggest that the displacement spikes are responsible for this amorphization. Further experiments are now going on to test this hypothesis and, more precisely, to separate the apparently competing influences of the thermal and of the displacement spikes.

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