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Brief Reports

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Amorphization mechanism in metallic crystalline solids under irradiation

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The problem of the amorphization mechanism of crystalline materials under energetic irradiation has remained a puzzling one. We show how recent investigations on electron irradiation of metallic compounds give the key to this puzzle through the role of point defects, probably mainly interstitials.

Many solid-state phase transformations affected by irradiation are known, many of them well understood.[1,2] However, the structural transformation from crystalline to amorphous form at a given composition is one of the less well understood, despite its technological relevance. It is the aim of this paper to show that the driving force, and probably also the mechanism of this peculiar transformation, can be elucidated thanks to the latest results obtained on metallic alloys irradiated by high-energy electrons and ions.

The interest in crystalline-to-amorphous transformation was initiated twenty years ago by implantation studies in silicon wafers. Since that time many amorphization models have been proposed along two lines. In the thermodynamical one[3,4] the driving force is provided by some unspecified point defects created by irradiation and stored in the lattice at a low enough temperature.

The crystalline-to-amorphous transition intervenes whenever the free enthalpy of the solid solution of point defects in the crystal has become higher than the free enthalpy of the amorphous "phase." Due to the great complexity of defect creation and thermal evolution in semiconductors, Vook's model[3] of point defects accumulation is fairly crude with respect to the models developed in the case of metallic systems. As we shall see later, more detailed results could therefore probably be obtained on these alloys.

The kinetic approach is based on the notion of the irradiation spike.[5-8] The high-energy core of the cascade is described either as a small liquid droplet[7,8] which, due to the high thermal conductivity, will be superquenched down to the amorphous form, or as spontaneous transformation to an amorphous phase due to the very high defect density.[5,6] This last approach is presently the most widely used to discuss amorphization experiments. Let us now see the consequences of some recent experimental results.

The field of irradiation amorphization of metallic alloys covers three broad experimental areas. The first one corresponds to surface treatment. In that case, the surface of a pure metal, or alloy, which is unable *per se* to amorphize, is irradiated with especially chosen ions, either metalloidic (B, P, Si) or metallic (transition metals, rare earth), the energy of which is generally some tens of kilo-electron-volts.

Briefly the experimental trend in this area is twofold.[9]

(1) All the kinds of substrate-ion couples which are known to give amorphous alloys by a more conventional method, i.e., by ultraquench, give an amorphous surface layer, provided the temperature is maintained low enough to avoid thermal crystallization. This seems to mean that irradiation is a fairly efficient amorphization process, but not enough to allow for the obtaining of *new* materials.

(2) The implant dose needed to complete the amorphization corresponds generally to the buildup of a high enough solute (implant) concentration (i.e., approximately 17 at.% in a transition-metal–metalloid system). In other words, the critical dose is related only to a chemical threshold and does not tell us anything about the amorphization mechanism and the amorphization dose in ready-to-amorphize compounds.

The second kind of irradiation corresponds to amorphization of multiphase systems the mean composition of which belongs to the glass forming range. These systems are generally prepared either by vapor deposition of thin alternate layers of the pure components, or by some ultraquench method. In this case the periodicity of the composition fluctuations is in the range of a few hundred angstroms.

Here also the main classes of glass-forming metallic alloys, transition-metal–metalloid and transition-metal–transition-metal, have been amorphized under irradiation by energetic heavy ions.[9] The critical dose is in the range of some tens of displacement per atom (dpa). But the phases of a suitable composition, if any, amorphize probably at a much lower level.[10] Indeed careful calculations of "ballistic diffusion"[11] show that most of this dpa level is needed only to homogenize the crystalline segregated alloys and tells us nothing about the amorphization process.

It appears then from these results that experiments on well chosen stoichiometric compounds are the best way to study the amorphization process in metallic systems. We have quoted in the Table I the most interesting recent results in ion and electron irradiation of intermetallic compounds.

A lot of compounds have been amorphized (Table I is far from being complete) under ion and electron irradiation,

TABLE I. Characteristics of amorphization of some metallic compounds by irradiation. The fluxes and amorphization thresholds are given, if known, in displacement per atom (dpa/sec or dpa). In the case of electron irradiations the temperatures given here are the temperatures quoted by the authors and therefore probably are underestimated by up to hundreds of degrees (see text), except for Fe_3B.

Compound	Irradiation characteristics	Temperature/dose	Ref.	Remarks
Zr_3Al	Ar^+; 0.5–2 MeV	30 K/1.5 dpa 300 K/30 dpa	12	No amorphization above 300 K Unknown flux, but between 10^{-3} and 10^{-4} dpa/sec
	N^+; 0.5–2 MeV	30 K/14 dpa	12	
	Electrons; 1 MeV; 10^{-3} dpa/sec	130 K/44 dpa	13	Amorphization detected, not complete
Fe_3B	Ni^+; 4 MeV; 5×10^{-3} dpa/sec	300 K; <0.15 dpa	14	
	Ar^+; 4 MeV; 7×10^{-4} dpa/sec	300 K; ~0.3 dpa	14	
	Electrons; 1 MeV; 10^{-3} dpa/sec	~130 K; ~0.4 dpa	15	Given temperature is probably correct
NiTi	Ni^+; 50–200 keV $\sim10^{-3}$ dpa/sec	~300 K; <0.4 dpa	16	
	Electrons; 2 MeV $\sim2\times10^{-3}$ dpa/sec	100 K; 0.1 dpa 200 K; 0.2 dpa	17	No amorphization above 300 K

which leads us to believe that probably all glass-forming systems are able to amorphize during such irradiation, if due care is taken against the beam heating. Beam heating is in fact a very severe limitation in irradiation experiments, particularly in electron irradiation. Glass-forming systems are always very bad electrical and thermal conductors. Therefore the high fluxes needed to amorphize the crystalline compounds generally produce a temperature rise in the beam which is high enough to induce thermal recrystallization of the previously formed amorphous phases, if any. A due account of this beam heating is very rarely taken. Our own measurements and calculations show that in typical glass-forming systems the beam heating in high-voltage electron microscopy could be as high as several hundred degrees. This is, for example, the case of high-voltage electron microscopy irradiations of Zr_3Al (Ref. 13) where a beam heating of up to 200 K occurs at 300 K, and of NiTi (Ref. 17) where a beam heating of up to 600 K occurs at 200 K as deduced from the experimental conditions given by the authors and from comparison with our own measurements.[18] In the following discussion the given temperatures are corrected for this effect, especially for electron irradiation (but not in the Table I).

The results displayed in Table I show clearly the following general trends. First, the metallic glass forming compounds are able to amorphize under irradiation by energetic particles, ions, or electrons, at a low enough temperature. Second, the critical amorphization dose expressed in normalized displacement per atom is very low, down to one atom over ten, and does not seem to depend strongly on the nature of the particle at a given dose rate. Third, this critical dose seems to be sensitive to dose rate, decreasing as the dose rate increases, and is very sensitive to temperature above some temperature threshold.

In fact, this third point has to be more explicitly stated. As we see in the Table I, the temperature dependence is firmly grounded, and a discussion will be given later. The dose rate effect on the critical dose, a slight decrease of the dose needed as the dose rate increases, is a more subtle effect.

In Table I we have quoted, following the authors, the normalized dpa and dpa/sec, as given by the modified Kinchin and Pease formula valid for heavy particle irradiation (Ref. 19):

$$Nd = 0.8\frac{E_{\text{nuc}}}{2Ed}\ .$$

E_{nuc} is the part of the primary energy lost in elastic collision, total energy minus any inelastic part, and Ed is a mean threshold energy for permanent atomic displacement. E_{nuc} is generally calculated following the treatment of Winterbon, Sigmund, and Sanders.[20] Clearly Nd represents the number of Frenkel pairs created during the slowing down of the primary particle, but not the number remaining after any thermal annealing, during the irradiation itself if the defect mobility is high enough at the irradiation temperature. That this formula is well obeyed is now well established, if the energy and the mass of the primary particle are not too high, nor too different from the mass of the target atoms.[21,22]

It is difficult however, to calculate theoretically a well-defined value for the Ed parameter,[22] especially for concentrated, ordered alloys. Nevertheless, Ed can be considered in a given target as an adjustable but characteristic parameter, which once chosen is well suited for comparing different irradiations. Under these restrictions the validity of the above formula is probably within a factor of 2.[22]

Therefore we are allowed here to compare validly Ni^+ and Ar^+ irradiation on Fe_3B. The difference in dose rate was near a factor of 10, which is well outside the calculated uncertainty.

The quantitative comparison with the electron irradiations is probably less convincing in the details. However, the observation remains valid, namely, that amorphization takes place roughly at the same dpa level with ion and electron irradiation at a given temperature and dose rate. This result has already been stressed by Howe and Rainville.[12(a)]

Note that irradiation appears here to be a fairly powerful tool for amorphization since neither of the compounds of the Table I can be amorphized easily by standard ultraquench methods.

First of all the experimental evidence of amorphization by electron irradiation in many, if not all, ready-to-amorphize metallic compounds clearly rules out the specific role of cascades. Electrons of only 1-MeV energy do not produce collision cascades by only isolated Frenkel pairs in NiTi or Zr_3Al. All models which invoke thermal effects[8] and ultrafast quenching in displacement cascades are invalidated for this kind of experiment. The same conclusion has been reached by Ruault, Chaumont, and Bernas[23] by *in situ* electron microscopy during heavy ion irradiation of silicon. Their observations clearly show that amorphization proceeds also *between* zones of strong contrast due to individual ion impacts.

One can then ask if two (or more) amorphization mechanisms are competitively operating during heavy particle irradiations of these metallic alloys, one due to isolated defects, and the other effective in the densest part of the cascade. If the existence of the first one is clearly established by electron experiments, the second one is much more difficult to show directly. Indeed the size of the amorphous zone created by each particle impact remains largely an *ad hoc* parameter, the value of which has no simple relation with the length scale (range, straggling, etc.) of cascade theory. A more detailed study of the structure of the damaged zone could answer this question. However, in the presence of two different unrelated mechanisms, one must explain why the critical dpa dose would be roughly the same for electron and heavy particle irradiations.

A second unclear point, up to now, was the role of electronic processes in amorphization of metallic compounds. One knows that some covalently bounded compounds like silicon dioxyde are amorphized by low-energy electron irradiation,[24] the radiolytic defect formation[25] being the mechanism responsible for the amorphization.[26]

The same process has been invoked by Lesueur[27] in the Pd-Si alloy to explain the very low amorphization threshold in fission fragment irradiation experiments [approximately 5×10^{-1} dpa (Ref. 9)]. However, the result displayed in Table I shows that such a low threshold seems to be common in metallic glass-forming alloys. The same results show also that the amorphization dose correlates much more closely with the dpa level than with the electronic losses. For example, in the case of Fe_3B (where the temperature given by the authors is probably correct) Ar^+ ions and electrons at the same dpa/sec level need roughly the same critical dose, despite very different electronic losses. Also it appears that contrary to the variation of the cross section for ionization damage, the amorphization is possible with high-energy electrons (HVEM), but not with low-energy electrons (conventional 100-keV transmission electron microscopy).

In the same way 4-MeV Ni^+ and Ar^+ ions have nearly the same electronic losses (in Lindhard's theory), but the former has three times higher nuclear losses and a more than two times smaller critical dose. It appears then that the electronic processes, if they might eventually create defects as in a covalent medium (this fact remains to be proved), have no direct specific effect upon amorphization in metallic systems.

Neither "spikes" nor electronic processes uniquely produce the crystalline-to-amorphous transition, the situation is therefore very akin to the one of radiation-induced precipitation in metallic crystalline alloys. We know in this case that the dose rate is a control parameter of the thermodynamical state of the alloys, segregated or homogeneous. Two driving forces have been invoked. In the first case the homogeneous alloy is destabilized thanks to a kinetic process. The elimination of radiation-created point defects induces point defect fluxes to sinks which by a defect-solute coupling mechanism leads to solute segregation.[1]

In the second case, the thermodynamical one, a small part of the energy of the incident particle is stored in the lattice, either in the form of point defects or in the form of an ordering, i.e., a chemical energy.

However, in the case of crystalline alloys, most, if not all, radiation-induced transformations appear to be of the first kind, due to the very small concentration of point defects, and therefore to the small energy, which can be sustained in a crystal in the temperature range where defect mobility is high enough to allow for macroscopic fluxes of matter.[2] This role of the mobility shows through a double boundary. A high-temperature one, above which no precipitation takes place due to a too small defect concentration, and another at a temperature below which the mobility is too small to give rise to a significant solute drag. The picture is very different in our case of crystalline-to-amorphous transition: the transformation appears to be easier, the lower the temperature. An upper boundary is even reported above which no transformation takes place. This boundary is clearly related to the absence of mobility of the defects as the critical dose is closely correlated with the mobility of, probably, interstitials.[12]

Even at the fairly high temperature of 775 K no feature of point defect elimination by a mechanism of high mobility, like cavities, dislocation loops, or networking, is observable in Zr_3Al alloy[13] under electron irradiation. The same result has been found in NiTi,[28] unlike, for example, FeAl and NiAl alloys which do not amorphize under irradiation. The first possibility, as given above, is then probably ruled out.

In the second one we have to determine the form under which the energy responsible for the transformation is stored. We want to show that this is probably not the ordering energy. In fact, the free enthalpy difference between the amorphous and crystalline form of these compounds is typically of the order of some 10^{-2} eV per atom.[29] Such an order of magnitude can be accounted for by a modest ordering energy if the alloy is completely disordered by the irradiation before being amorphized. This is indeed the case of Zr_3Al[12] as well as of NiTi.[17] However, this is not the whole story since Zr_3Al can be completely disordered either by ion or electron irradiation up to at least 600 K under a dose[12,13,17] of approximately 1 dpa, but the amorphization is only very partial under electron irradiation at approximately room temperature[13] for the very high dose of 44 dpa. Under ion irradiation the amorphization becomes impossible above 300 K, whereas complete disordering is obtained up to 700 K.[13] The ability to amorphize is clearly more closely related to point defect mobility than to disordering. The driving force for the transformation is then provided by energy stored in point defects as proposed for silicon[3,4] and Zr_3Al.[12]

Many results are in favor of this point of view. First of all, the beginning of amorphization is preceded by a clear increase of diffuse scattering,[13] which could be due to a large concentration of stored point defects. Also the critical dose in Zr_3Al appears to be correlated with interstitial mobility[12] since the critical dose begins to increase dramatically at a temperature related to interstitial mobility.[13] In thin foils amorphization appears to be limited to regions thick enough to allow for point defect storage in the lattice and not for escape to the surface.[16]

Data on defect mobility in metallic compounds are very scarce, so it is not possible to assess our interpretation more firmly on a quantitative basis. Nevertheless, it is now fairly well established that interstitial mobility is greatly reduced in most alloys with respect to pure metals. This fact has been completely elucidated in AgZn,[30] in Fe-Cr-Ni solid solutions,[31,32] and in ordered FeAl alloys.[33]

This last case is especially relevant to our case of strongly ordered systems. It has been proven by Rivière and coworkers that the long-range mobility of interstitial defects is shifted up to 500 K (pure iron, 120 K) with a migration enthalpy of 1.35 eV (pure iron, 0.25 eV).[33] This result has been recently confirmed by Mukai, Kinoshita, and Kitajima[34] and Guillot, Rivière, and Beaufort-Richard.[35] In the case of vacancy mobility the effect is less severe since the migration enthalpy in the same alloy is 1.06 eV[36] (with respect to 1 to 1.3 eV in α iron).

The free enthalpy difference between the crystalline and amorphous forms of these kinds of metallic compounds is of the order of some hundredths of an electron volt, so we see easily that at point defect saturation the typical spontaneous volume of recombination allows a high enough defect density to explain the energy difference between the two forms. The question remains whether Frenkel pairs as a whole are needed or if only one of its elements could be sufficient. However, in some ordered crystalline alloys, like FeAl and NiAl, very large concentration of structural vacancies can be introduced by departure from stoichiometry, without producing a spontaneous amorphization. The role of the interstitial is then probably crucial. Its strong effect on the elastic constant of crystals could probably provide the softening of the lattice which allows for the transformation. The same reason explains why amorphization starts earlier along dislocations and grain boundaries.[37] These are distorted parts of the crystal where transformation is able to take place at a lower defect concentration. Finally, our model can easily explain the observation of Brimhall, Kissinger, and Charlot[28] that intermetallic compounds which undergo a crystal-to-amorphous transition under irradiation have a narrow concentration range. In fact these kinds of compounds, like FeAl or NiAl, very likely accommodate departure from stoichiometry by a large concentration of structural vacancies.[38,39] It is easy to understand that a large vacancy concentration, structural or thermal, can prevent the buildup of a large enough interstitial accumulation to initiate the crystal to amorphous transformation.

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