VARIABLE LATENT VACANCY MECHANISM OF DIFFUSION IN AMORPHOUS METALS

Supplement to Sci. Rep. RITU, A, March, 1980

VARIABLE LATENT VACANCY MECHANISM OF DIFFUSION IN AMORPHOUS METALS

M. Kiritani

Department of Material Physics, Faculty of Engineering Science

Osaka University, Toyonaka, Osaka 560, Japan

ABSTRACT

A model which is pertinent to describle the characteristics of atomic diffusion in amorphous metals is proposed. The process corresponding to the thermal equilibrium generation of diffusion carriers such as lattice vacancies in crystalline metals is sought in the thermally reversible change of already existing vacancy like positions to the state of easier activation for their motion. Discussions on the temperature dependence of diffusion speed is given from the proposed variable latent vacancy mechanism.

INTRODUCTION

The elucidation of dynamic structure of amorphous alloys, typically the atomic diffusion in the amorphous phase, is required to understand their structure change such as relaxation within amorphous and their crystallization, and it helps in establishing the most prousible model for their static structure.

Simply because of the lack of well defined atomic lattice positions in amorphous structure, the established concept of the equilibrium formation of diffusion carriers in crystalline metals at high temperature which mainly comes from the requirement to increase the configurational entropy at high temperatures, can not be applied; namely the amorphous structure itself is in the state of high configurational entropy. The effort to find the direct analogy to crystalline material may lead to the misunderstanding of the essential characteristics of the material.

The present authors have found the existence of a strong temperature dependence of the crystallization of amorphous alloys by electron radiation induced diffusion, which can not be expected in crystalline metals.[1] In crystalline materials, the motion of diffusion carriers such as lattice vacancies and interstitial atoms, which moves with rather well defined

fixed activation energy, can not have temperature dependence in their motion if the motion is carried out solely by the athermal collision process with incident high energy electrons. The authors reached to the concept of the variation of motion activation energy of already existing diffusion carriers with temperature. In this paper a qualitative explanation of these latent carrier model for diffusion in amorphous phase will be presented.

PROPOSED MODEL

Some Characteristics of Diffusion in Amorphous Phase

Relaxiation phenomena such as the irreversible change of mechanical and magnetic properties after the production of amorphous alloys can be attributed to the rearrangement of atoms by rather short range motion of each component atoms. These processes are thought to proceed until the excess diffusion carriers which have quenched-in during the preparation process exhaust. On the other hand there are various indications for the existence of long range diffusion through amorphous phase, and several examples will be quoted in below.

Figure 1 shows an intermediate stage of the crystallization of $Fe_{85}B_{15}$ amorphous thin films. A simultaneous appearance of pure iron crystallites along the surface, larger patterns in the figure, and Fe_3B crystallites in the foil, small round particles in the figure, have been observed. The former is iron rich and the latter is iron poor in composition compared with that of amorphous matrix, and there should exist a long range transport of constituent atoms through amorphous phase between these two different type of crystals, because two types of the crystallites are not distributed nearby each other but separated rather randomly.

Figure 2 shows the progress of the crystallization of a $Au_{35}Si_{65}$ amorphous thin film prepared by vaccum deposition. Pure silicon crystals

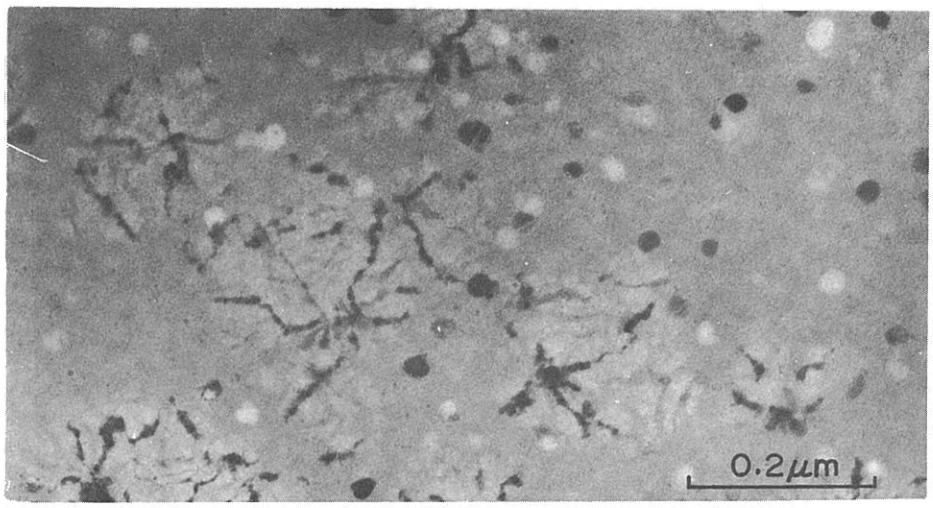


Fig. 1 An intermediate stage of the crystallization of $Fe_{85}B_{15}$ amorphous alloy,* showing the appearance of two different types of crystallites. Annealed at 260°C for 25 minutes.

* Specimen supplied by Prof. T. Masumoto of Tohoku University.

have grown into a large scale observed as white area at the center, but there is no indication of the composition gradient in the amorphous phase radially from the crystal-amorphous interface. This observation indicates the existence of a fast long rage diffusion of gold atoms through amorphous phase.

The third example is of metal-metal amorphous of $Mg_{70}Zn_{30}$. Figure 3 shows the suppression of the nucleation of small high density crystallites in the vicinity of larger crystals which have grown prior to the overall crystallization. This observation indicates the possibility of the change of amorphous phase near the large crystals by the diffusion of unbalanced component atoms expelled from or absorbed to the large crystals.

Above examples, especially the first two, are suggesting, in addition to the existence of a long range diffusion, the existence of a strong tendency in these amorphous phase to homogenize their own constituent atom compositions whenever any local reaction to break the homogenity takes place. It might be stated that these amorphous alloys exist as metastable

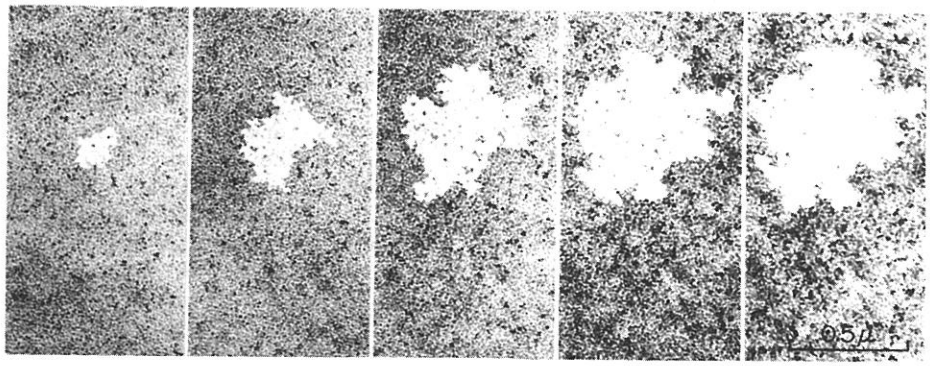


Fig. 2 The growth of silicon crystals in a $Au_{35}Si_{65}$ amorphous film under electron irradiation at room temperature.

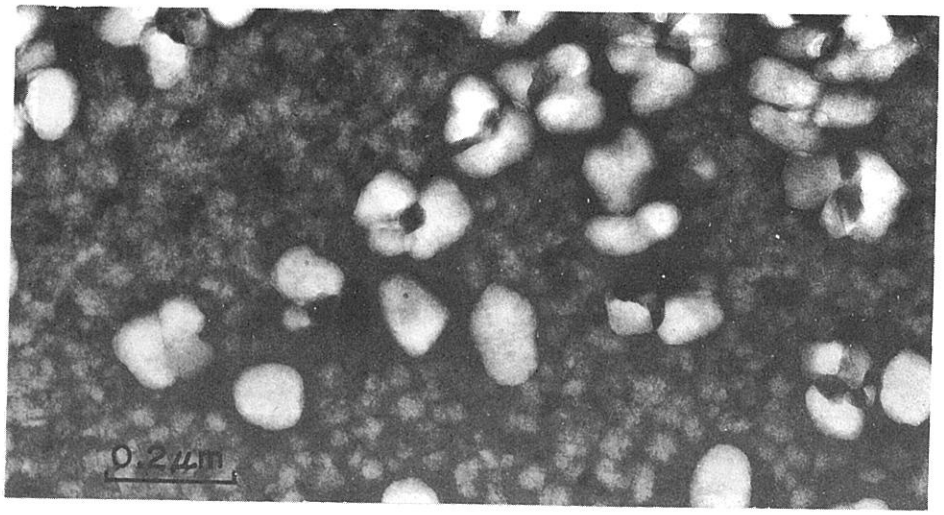


Fig. 3 An intermediate stage of the crystallization of $Mg_{70}Zn_{30}$ amorphous alloy,** in which two steps of crystallization is observed.

** Specimen supplied by Prof. T. Mizoguchi of Gakushuin University.

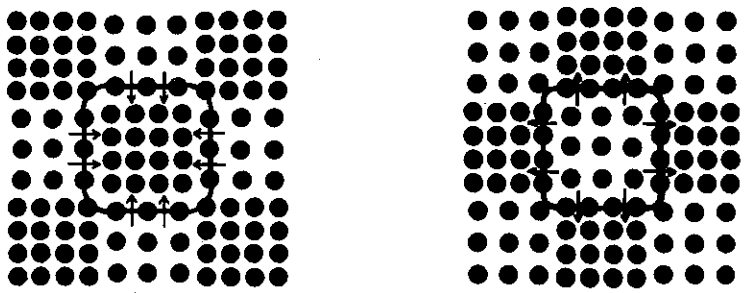
equilibrium phase. Based on the acceptance of equilibrium phase of amorphous and being initiated to understand the temperature dependence of radiation induced crystallization, the following discussion will be given on the characteristics of the diffusion in amorphous phase by proposing a model of diffusion carriers.

Static Model at Zero Temperature

Regardless of the difference of the standpoint of static model of atomic structure such as dense random packing, micro-crystalline, or dislocation, the amorphous structure is believed to be composed of the three dimentional pile-up of opposite nature of small volumes --- volumes under compression and volumes under expansion. The size of volume unit should be as small as atomic dimension because the definition of compression-expansion should be made as follows. An atom is under compression when the distance to its neighbouring atoms is shorter than the distance which would be maintained if the packing of the similar nature extended longer distance from the atom. Simply as illustrated in Fig. 4 (a), atoms feel compression if they are surrounded by less compactly packed shells. Opposite situation leads to the expansion as in Fig. 4 (b).

For the convenience of explanation, let us imagine the Bernal's polyhedron. The above nature of small volumes is not uniquely assigned to each of the different type of polyhedron, because the situation is not defined solely by the arrangement of nearby atoms but essentially affected by a wider surrounding circumstances. In another word, even the same unit polydedron essentially has different size, and if the hole probability is measured experimentally as in the work by Suzuki et al., the size of holes should show rather continuous distribution even when the structure is composed of rather well defined small number of packing units.

The two differently natured volumes are the cause and effect to each other and can not exist separately. A schematic fractional distribution of the volume against the sense and degree of strain may be given as in Fig. 5 (a) for the simplest case of the equal total volume of the compression and expansion. If one side occupies more volume than the other, the distribution of the other side extends to higher strain as in Fig. 5 (b) to satisfy the balance of total internal strain. If we observe local relation of the distribution of the compressed and expanded volumes, we should find the highly expanded part as A in Fig. 5 (a) should be situated near to the highly compressed part A' in the figure.



(a) Compression (b) Expansion

Fig. 4 An atom or a small volume feels compression or expansion stress from its circumferences.

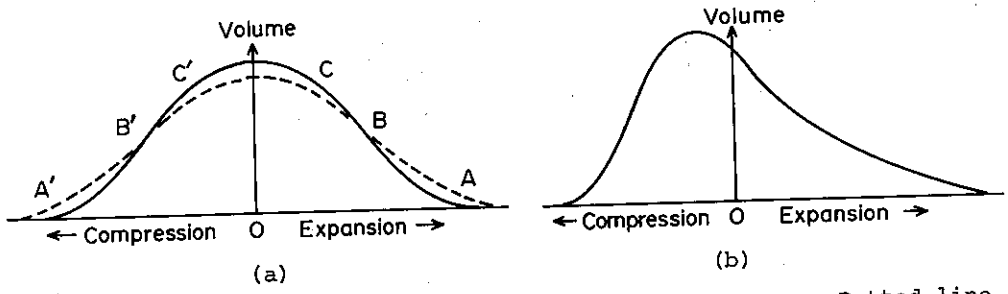


Fig. 5 Distribution of local strain in amorphous structure. Dotted line shows the distribution in freshly prepared material before relaxation.

Multi-Component Diffusion

The diffusion, the displacement of the position of atoms, may takes place within the expanded region or by the motion of atoms from cpmpressed part to expanded. The latter process might lead to the change of the distribution of the volumes in Fig. 5 towards the elimination or cancellation of two opposite extreme parts of compression and expansion, and this should correspond to the relaxation phenomena observed commonly in freshly prepared amorphous alloys.

However, the above relaxation can not proceed beyond a certain limit at which the motion of an atom from the compressed region to the dilatation can not lead to the cancellation of the opposite sign of strain but merely excanges the position of different natures, or at most it changes the spacial distribution in a little larger scale keeping the total distribution unchanged. The diffusion keeping the shape of the distribution as the solid line in Fig. 5 can be called self-diffusion under equilibrium in the amorphous structure.

The activation energy required to displace an atom is not single valued but it should have a distribution as illustrated in Fig. 6 (a) or as in Fig. 6 (b) if the energy is separated from each other according to the classification of neighbouring configurations. Each group in Fig. 6 (b) may be assigned to each of the group of packing unit (as to the Bernal's polyhedron) but has some width owing to the difference of the packing of the surrounding volume. Extra populations may exist at smaller energy in freshly prepared specimen as shown with dotted lines in the figures, and they disappear by finishing their role in the process of relaxation.

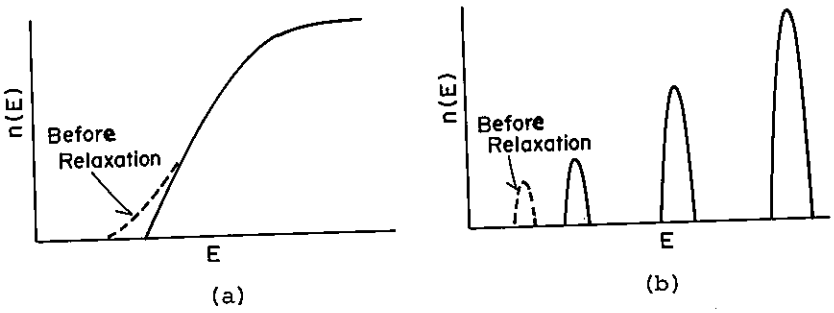


Fig. 6 Distribution of motion activation energy of diffusion carriers.

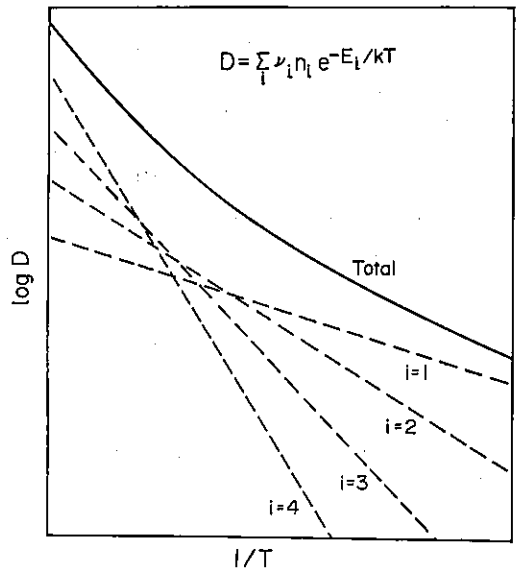


Fig. 7 Temperature dependence of the diffusion speed in multi-component diffusion system.

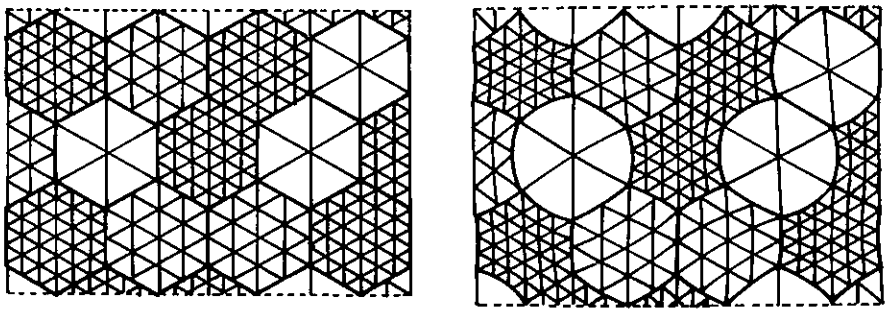
In general the population at smaller activation energy is smaller and it increases towards the larger values.

Under the above circumstances the total diffusion is carried out by multiple component, and its main part is carried out with smaller energy component at lower temperatures and with larger energy components at higher temperatures as schematically illustrated in Fig. 7. The apparent activation energy observable in low temperature region should be larger than the average value of the energy of active diffusion component at that temperature and it should be smaller at higher temperature.

Reversible Change with Temperature

At elevated temperatures, the mutual relation between the compressed and expanded volumes may not kept unchanged. Macroscopic concept of thermal expansion under high pressure can primitively be applied to understand the qualitative change with temperature. Experimental observations, though not for amorphous materials, showed smaller thermal expansion under high hydrostatic pressure.[3] Although no data is available for the thermal expansion under negative pressure, one can expect larger expansion. When one consider the typical small volume of the central part of Fig. 4, the center of (b) tends to expand more than that of (a) at high temperature. If these (a) and (b) are tightly joined each other the part in (a) may shrink rather than expand at higher temperature by the pressure from the larger expansion of the surrounding highly expanded volumes.

This situation is typically illustrated in Fig. 8. The lattice-like structure in the figure is solely for the easiness of the illustration, and the spacing of the density of lattice-like structure merely represents the sense and degree of the local internal strain; the dense and coarse lattice represent the compression and dilatation, respectively. The configuration



(a) Low temperature (b) High temperature

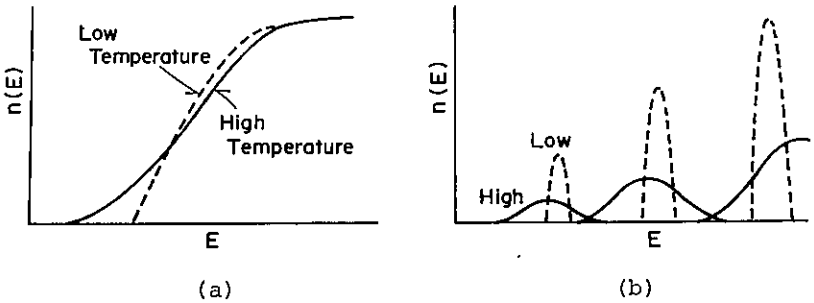
Fig. 8 Model illustration of the variation of compressed and expanded volumes with temperature.

expected at high temperature is illustrated in such a way that the difference from the low temperature is larger for the part at which the two volumes of more different nature are joined each other. Same type of the local volume at low temperature changes into different shape and volume according to the difference in the surrounding volumes.

When we apply the above concept of local expansion at high temperatures down to atomic sizes, the variation is equivalent to the activation of already existing diffusion carriers, latent vacancies, to easier state for their motion at high temperatures. This process is reversible with temperature and have some analogous meaning as the formation of thermal equilibrium generation of diffusion carriers in crystalline metals at high temperatures.

Diffusion with Variable Vacancies

When the above variation of the latent vacancy size with temperature is taken into account, the diffusion in amorphous phase is carried out with diffusion carriers whose motion activation energy changes with temperature, and this situation should be taken into account in addition to the diffusion with multi-component. Although the additional expansion of the originally expanded small volume might be not large, it makes the displacement of atoms related to this volume appreciably easy because the potential at the saddle point which is determined from the steep part of



(a) (b)

Fig. 9 Variation of the distribution of motion activation energy with temperature.

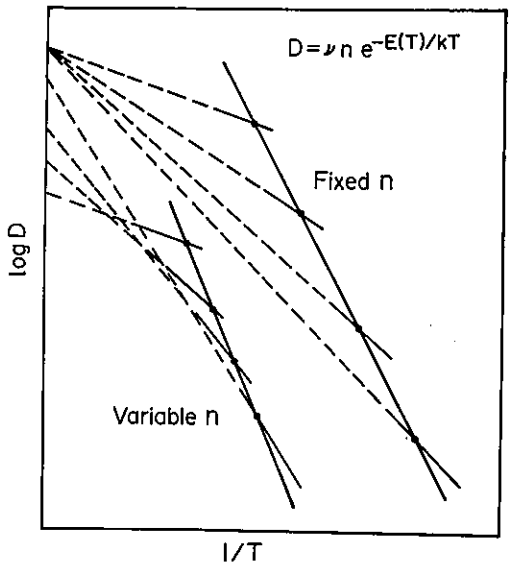


Fig. 10 Temperature dependence of the diffusion speed in variable energy diffusion system.

interatomic potential is expected to be lowered appreciably by a slight increase of the atomic distances at the saddle point.

The population distribution of diffusion carriers analogous to Fig. 6 (a) was shown for this case of variable vacancies in Fig. 9, in which the tails to the smaller activation energy extends toward the smaller energy at higher temperatures or the groups at smaller energy shifts to smaller energy side along with the sidening of its distribution, and the groups at larger energy may shift to the higher energy side.

Let us figure out the nature of temperature dependence of diffusion speed from the above variation of activation energies. With these variable vacancies, diffusion takes place with smaller activation energy at higher temperature. This does not mean that the apparent variation of the diffusion speed at higher temperature becomes slower at higher temperature, but rather contralily the gradient of the diffusion speed becomes steeper at higher temperature superficaially showing the increase of apparent activation energy of diffusion. This situation is schematically illustrated in Fig. 10, in which the contribution from only one component is given to avoid the confusion. Dotted lines in the figure is extended from each temperature with a fixed activation energy at the temperature. In one of the two examples in the figure the number of the diffusion carrier was simply supposed to be fixed. In reality the number of the activated latent vacancies to the state of smaller activation energy should be smaller than those at low temperature, and this case is shown in the figure as the case of variable n. In both cases, the resultant diffusion speed has drawn with a straight line but htis has no meaning and they should be curved generally.

CONCLUDING REMARKS

One can not deny the existence of wider distribution of interatomic distances in amorphous structure than in crystals, and this lead to the

concept of multi-component diffusion in the amorphous material. The discrete formation of diffusion carriers at high temperatures was not necessiated in the diffusion process in the amorphous structure, and the vacancy-like positions always existing in the sturcture may play roles as diffusion carriers.

Thermally reversible change of the local atomic arrangement caused by the spacial inhomogeneity in the structure was proposed to play roles in the temperature dependent activation process of diffusion. The amorphous materials whose diffusion carriers have a strong variable nature with temperature may be called 'soft amorphous', and the material whose diffusion carriers are not affected much by temperature may be called 'hard amorphous'. The evidence for the existence of real soft amorphous is not well established, but indications are already observed in the experiments quoted at the early part of this paper. More suitably designed experiments to measure the diffusion in amorphous materials are desired on one hand, and efforts to establish a more quantitative model such as with molecular dynamics analysis are required on the other.

REFERENCES

1) M. Kiritani, T. Yoshiie and F. E. Fujita: Proc. Third Int. Conf. Rapidly Quenched Metals, Brighton 1978 (The Metals Society, London) II-308.
2) K. Suzuki, F. Itoh, M. Hasegawa, T. Fukunaga and T. Honda: Proc. Fifth Int. Conf. Positron Annihilation, Lake Yamanaka 1979 (Japan Institute of Metals) p. 861.
3) M. S. Anderson, E. J. Gutman, J. R. Packard and C. A. Swenson: J. Chem. Solids 30 (1969) 1587.

ACKNOWLEDGEMENT

The author is grateful to Professors T. Masumoto and T. Mizoguchi for their kind supply of amorphous specimens. He is also thankful to Mr. K. Nunogaki for the use of his experiamental result prior to publication.