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A Geometrical Relaxation Model on Structure Change and Kinetics during Low-Temperature Annealing of Amorphous Metals*

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Synopsis

The atomic scale structure relaxation in melt-quenched amorphous metals has been simulated in a computer using a geometrical relaxation model of the dense random packing of hard spheres. The atomic arrangement and kinetics during the geometrical relaxation has been compared with the experimental behaviors on the low-temperature annealing of amorphous alloys.

I. Introduction

The highly disordered state of atomic arrangement is frozen in as-melt-quenched amorphous metals. On the low-temperature annealing the frozen-in structures relax toward a lower energy state with less disordered atomic arrangement, which still remains in the amorphous structure. This stabilization process is usually called the low-temperature structure relaxation and often leads to the drastic change in mechanical and magnetic properties of amorphous metals.

The atomic scale structure change due to the low-temperature relaxation was originally observed in the computer simulation of the energetic relaxation of the dense random packing of hard spheres (DRPHS) by Heimendahl⁽¹⁾ and Barker *et al.*⁽²⁾. Recently Egami and Ichikawa⁽³⁾ have made a combined study between the structural and kinetic behavior of the low-temperature structure relaxation in a melt-quenched amorphous alloy using energy dispersive X-ray diffraction.

The energetic relaxation of the DRPHS assembly has been shown, by Yamamoto *et al.*⁽⁴⁾, to be able to simulate consistently the both of the second peak characteristic splitting in the pair distribution function $g(r)$ and the high packing density η ($=\pi\sigma^3\rho_0/6$, σ : hard sphere diameter, ρ_0 : average number density) $=0.65$ of amorphous metals. The potentials used in the simulation, however, are not real ones and the relaxed structure is insensitive to the choice of the model potentials. Ichikawa⁽⁵⁾

* The 1683th reprint of the Research Institute for Iron, Steel and Other Metals.

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(3) T. Egami and T. Ichikawa, Mater. Sci. Eng., **32** (1978), 293.

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has pointed out that the second peak characteristic splitting appears in the $g(r)$ when the extent of the tetrahedral perfection in the amorphous structure is not far from the regular tetrahedron.

In this study, we propose a new procedure to relax the DRPHS assembly by putting a constitution atom in the geometrical center of the polyhedron constructed by its surrounding atoms and to pursue the variation in the atomic arrangement of the DRPHS assembly throughout the structure relaxation process. The geometrical relaxation procedure does not need any kind of model potentials and therefore provides a quite simple way for application to the multi-components, particularly metal-metalloid amorphous alloys⁽⁶⁾ in which the reasonable model potentials can not be found yet.

II. Geometrical structure relaxation

The DRPHS assembly consisting of 1213 equal-diameter spheres ($\sigma=2.5$ Å for iron atom) was prepared in a computer by Ichikawa's⁽⁵⁾ algorithm with the tetrahedral perfection parameter $K=2.0$ that yielded the maximum packing density $\eta=0.645$ among Ichikawa's model assemblies. The density of the assembly is likely to correspond to that of real amorphous iron⁽⁷⁾. However, there is no second peak splitting in the $g(r)$ of the assembly, which is rather close to that of Percus-Yevick hard sphere structure⁽⁸⁾ with $\eta=0.65$ (Fig. 2a). This means, as pointed out previously by Suzuki *et al.*⁽⁹⁾, that Ichikawa's as-formed model structure with $K=2.0$ simulates a highly disordered state frozen instantaneously from the liquid state.

First we choose arbitrarily a sphere in the DRPHS assembly. This sphere is then moved to occupy the geometrical center of the polyhedron constructed from its surrounding spheres as shown in Figure 1. The displacement $\Delta\vec{r}_i$ of the i -th sphere from the initial position to the geometrical center in the polyhedron is given by

$$\Delta\vec{r}_i = \frac{1}{m} \left\{ \sum_{j=1}^m (|\vec{r}_j - \vec{r}_i| - \sigma)(\vec{r}_j - \vec{r}_i) / |\vec{r}_j - \vec{r}_i| \right\}, \quad (1)$$

where \vec{r}_i is the position of the i -th sphere, and \vec{r}_j and m are the position and number of the neighboring spheres around the i -th sphere. Hence the polyhedron is defined by the neighboring spheres contained within a spherical region of 1.3σ in radius from the i -th sphere at the origin.

The geometrical relaxation has been actually performed on 422 spheres located in the inner section of the 1213 spheres whole assembly under the condition

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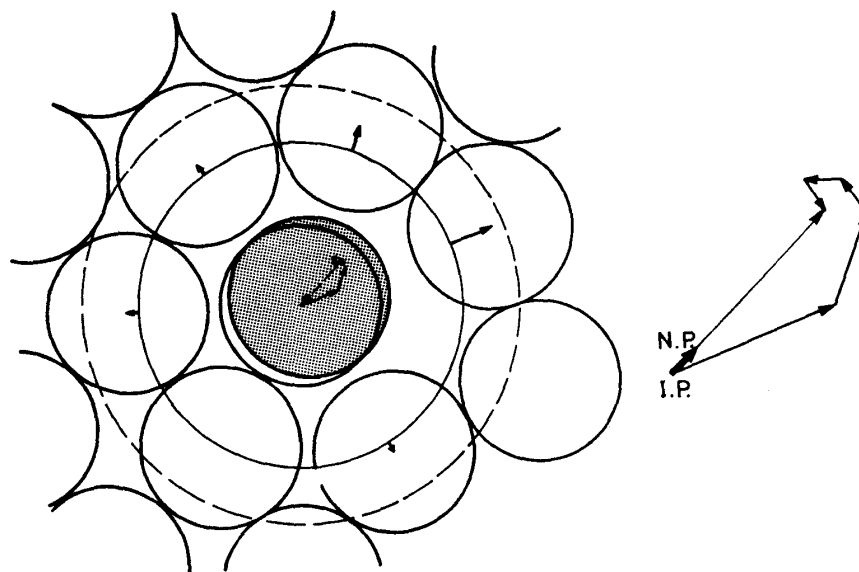


Fig. 1. Atomic movement in geometrical relaxation model of DRPHS assembly. Open circle means the position before relaxation and shaded one is that after relaxation.

of constant volume so as to avoid the complications due to the surface effects on the relaxation process. This relaxation procedure is repeated up to 50 iterations.

III. Results

The pair distribution function $g(r)$ was calculated for all atoms lying within 10Å from the center of the assembly. Figure 2 shows the $g(r)$'s of the as-formed assembly and the geometrically relaxed ones with 1, 10 and 50 iterations, respectively. The interference function $S(Q)$ obtained as the Fourier-transform of the $g(r)$ is shown in Figure 3.

Within initial several iterations, very drastic changes have happened in both the $g(r)$ and $S(Q)$. These changes are almost saturated until 50 iterations. Here we can find the characteristic behaviors of the second peak splitting in the $g(r)$ and the second peak shoulder in the $S(Q)$ which are in an essential agreement with the experimental observations for amorphous iron⁽⁷⁾. It is of interest to note that this agreement in the geometrical relaxation model is comparable in degree with that of the energetic relaxation model using various model potentials⁽⁴⁾.

The mean atomic displacement due to the geometrical relaxation with 50 iterations is about 0.2 Å, that is to say, about 9% of the atomic diameter $\sigma=2.5$ Å. Figure 4 shows the cross sections of the assembly without the geometrical relaxation and that with 50 iterations of the relaxation.

IV. Discussion

Here discussions are given to the structure change and kinetics of the geometrical relaxation of the DRPHS assembly. In order to see clearly the structure

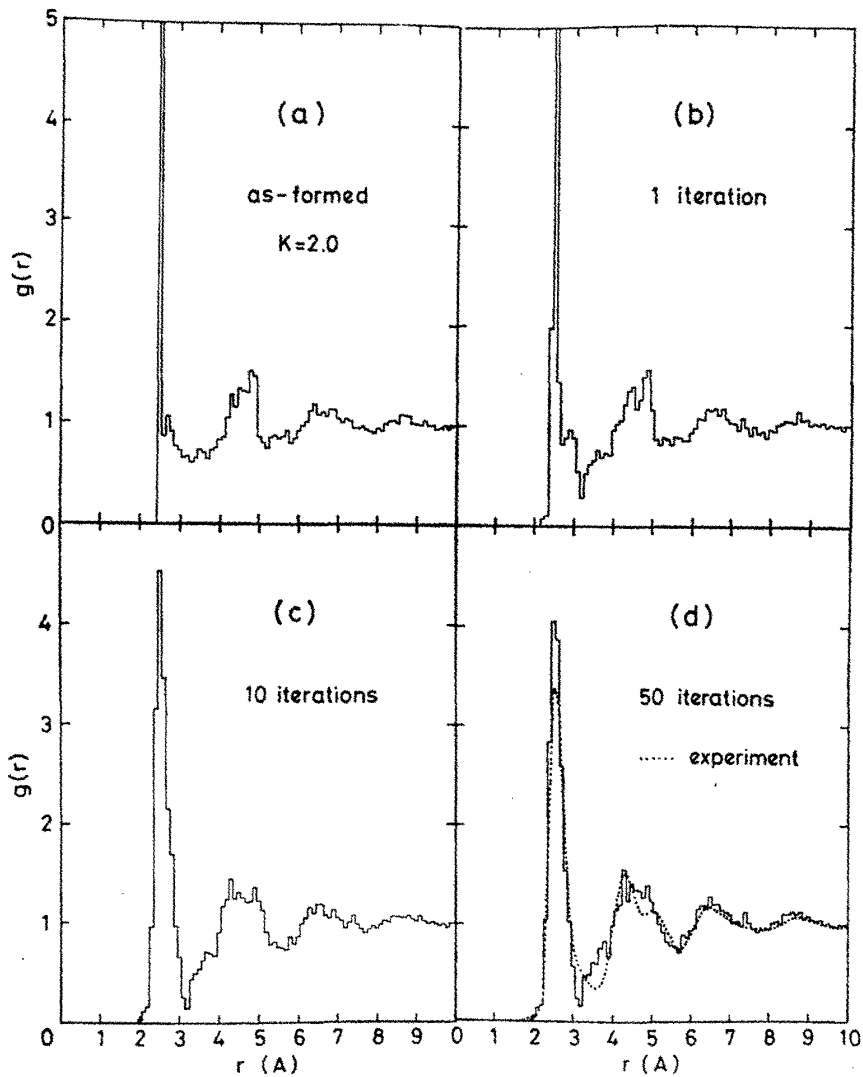


Fig. 2. Pair distribution functions (solid line) of DRPHS assembly during geometrical relaxation process. Dotted line is experimental $g(r)$ of amorphous iron⁽⁷⁾.

change due to the relaxation, we introduce the differential interference function $\Delta S^t(Q)$ defined as follows,

$$\Delta S^t(Q) = S^t(Q) - S^0(Q), \quad (2)$$

where $S^t(Q)$ is the interference function of the assembly relaxed with t iterations and $S^0(Q)$ is that of the as-formed assembly before the relaxation.

In Figure 5 the behaviors of $\Delta S^t(Q)$'s are shown for four representative iteration numbers of $t=1, 4, 10$ and 50 over the whole range of the scattering vector Q including the first and second peaks ($Q=2\sim 7 \text{ \AA}^{-1}$). The heights of the first peak ($Q\sim 3 \text{ \AA}^{-1}$) and the main second peak ($Q\sim 5.2 \text{ \AA}^{-1}$) are increased with the iteration number of the relaxation, while the height of the shoulder ($Q\sim 6 \text{ \AA}^{-1}$) is decreased.

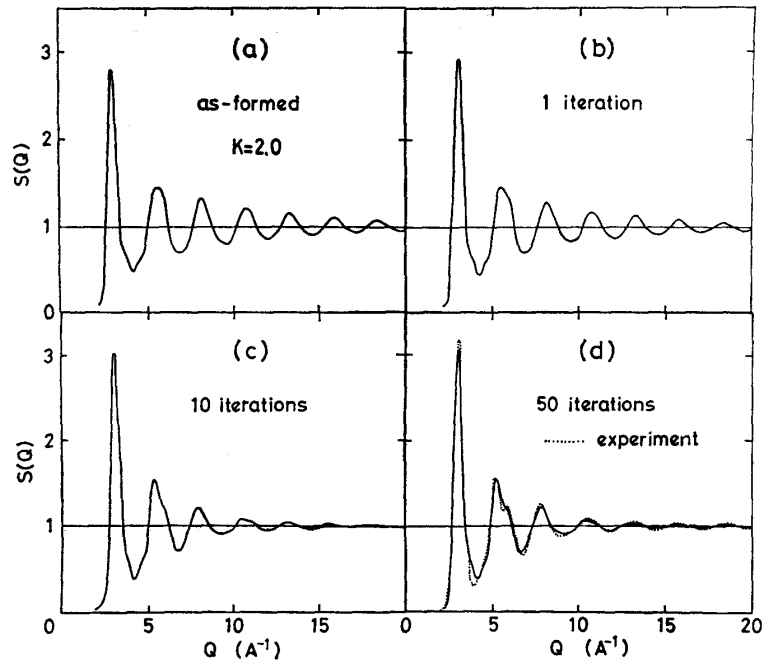


Fig. 3. Interference functions (solid line) of DRPHS assembly during geometrical relaxation process. Dotted line is experimental $S(Q)$ of amorphous iron⁽⁷⁾.

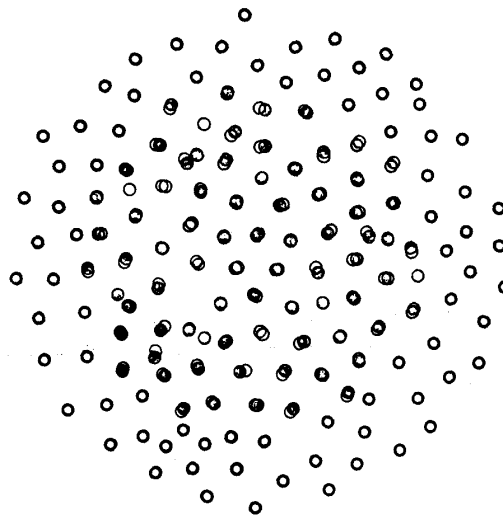


Fig. 4. Cross section of DRPHS assembly. Open circles are location of spheres in as-formed assembly and shaded ones are that in geometrically relaxed assembly with 50 iterations.

Such a change in the atomic scale structure due to the relaxation has been observed by Egami⁽¹⁰⁾ on the experimental X-ray diffraction profile of low-temperature annealed $\text{Fe}_{40}\text{Ni}_{40}\text{P}_{16}\text{B}_4$ amorphous alloy. Based on the defined local coordination model, which is an approach to the amorphous alloy structure from the opposite side of the DRPHS model, Gaskell⁽¹¹⁾ has demonstrated that the

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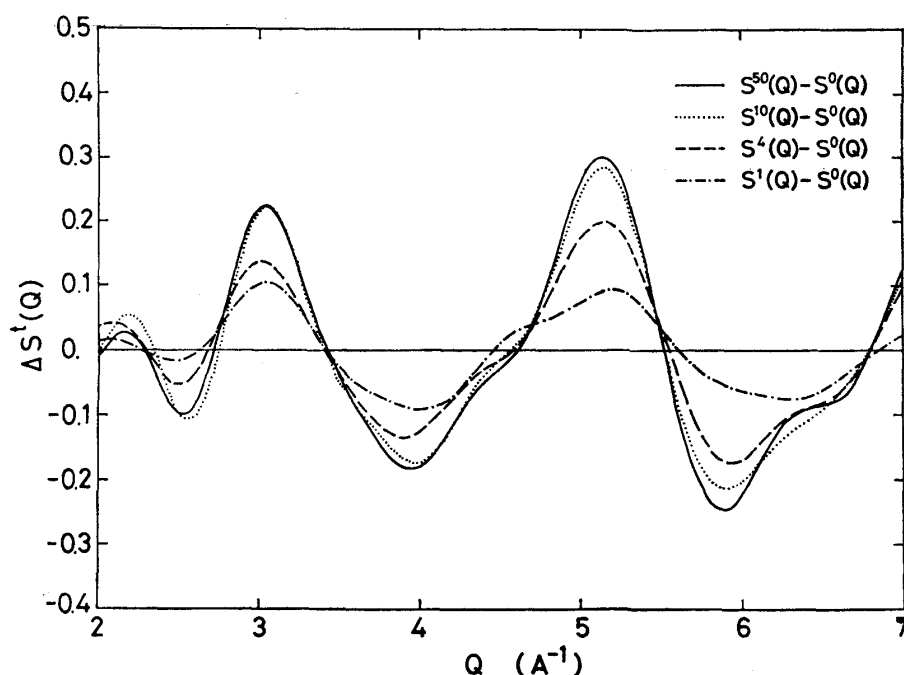


Fig. 5. Differential interference functions over the whole range from the first peak to second one. Superscript number t on $S^t(Q)$ means iteration number in geometrical relaxation.

stabilized, namely relaxed $\text{Pd}_{80}\text{-Si}_{20}$ amorphous alloy consists of the structural units which are more regular than those found in as-quenched alloy.

The average atomic displacement $d(t)$ due to the geometrical relaxation varies as a function of the iteration number t , as shown in Figures 6 and 7. We can find an interesting relation between the $d(t)$ and t in the geometrical relaxation process as follows,

$$\ln d(t) \sim t^{1/2}, \quad (3)$$

If the iteration number is a linear function of the time, the geometrical relaxation of the DRPHS assembly may be described by the Johnson-Mehl-Avrami type kinetic law⁽¹²⁾ with the exponent $n=1/2$. Such a kinetics has been known in the low-temperature recovery of severely deformed bcc metals⁽¹³⁾.

However, Chen⁽¹⁴⁾ has concluded that the kinetics of the low-temperature structure relaxation in melt-quenched amorphous metals obeys approximately a $\ln \tau$ law, where τ is the isothermal annealing time. The $\ln \tau$ law has been also recognized by Egami⁽¹⁰⁾ who has measured the change in the second peak area of the interference function as a function of the annealing time.

Therefore, we calculate the following quantity

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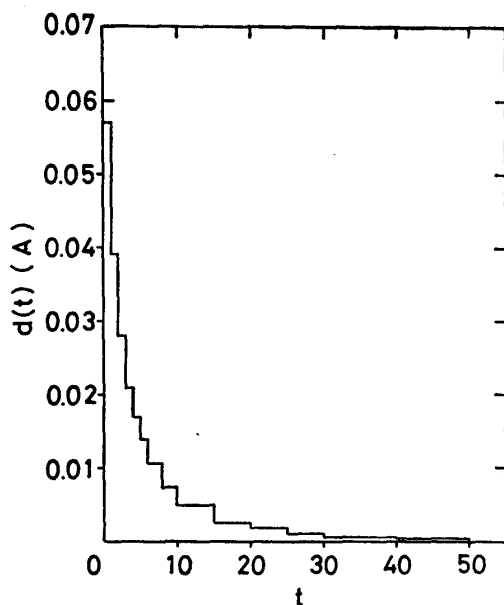


Fig. 6

Fig. 6. Average displacement of spheres (diameter $\sigma=2.5$ A) as a function of iteration number in geometrical relaxation.

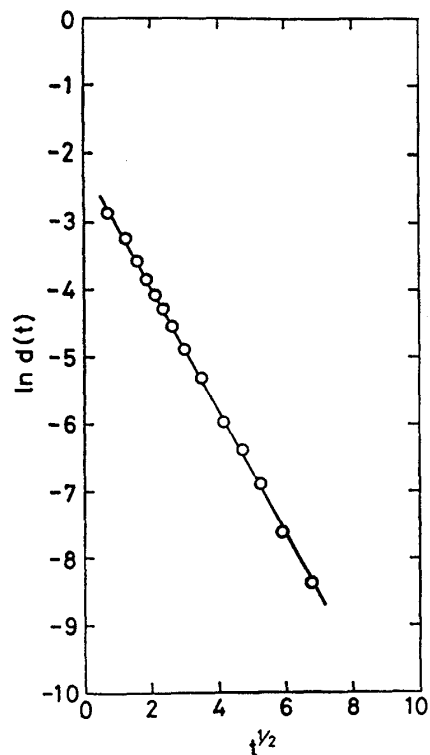


Fig. 7

Fig. 7. $\ln d(t) \sim t^{1/2}$ plot in geometrical relaxation model. $d(t)$ is average displacement of spheres and t is iteration number of relaxation.

$$R(t) = \int_{Q_1}^{Q_2} |\Delta S^t(Q)| dQ, \quad (4)$$

over the both ranges of the first peak ($Q_1=2.2$ and $Q_2=3.4$ A $^{-1}$) and second peak ($Q_1=4.5$ and $Q_2=6.8$ A $^{-1}$) of the interference functions, respectively. The results are plotted as a function of the iteration number t in Figure 8. Figure 9 shows that the $R(t)$'s are a linear function of the $\ln t$ in the initial stage of the geometrical relaxation process, while the deviation from the $R(t) \sim \ln t$ law appears over the range of $t > 10$. Similarly, the validity of the $\ln R(t) \sim t^{1/2}$ law is limited to the range of $t < 25$.

Since the average atomic displacement due to the geometrical relaxation becomes quite small at the large iteration number, the change in the atomic arrangement is restricted to the short range and therefore much reflected in the interference function over the high scattering vector region beyond the first and second peak position. This may imply that the behavior of the $R(t)$ which includes only the region of the first and second peak of the interference function becomes naturally different from the $d(t)$ expressing the whole movement of atoms. The experimental observation of the $\Delta S^t(Q)$ over higher Q region is expected to be

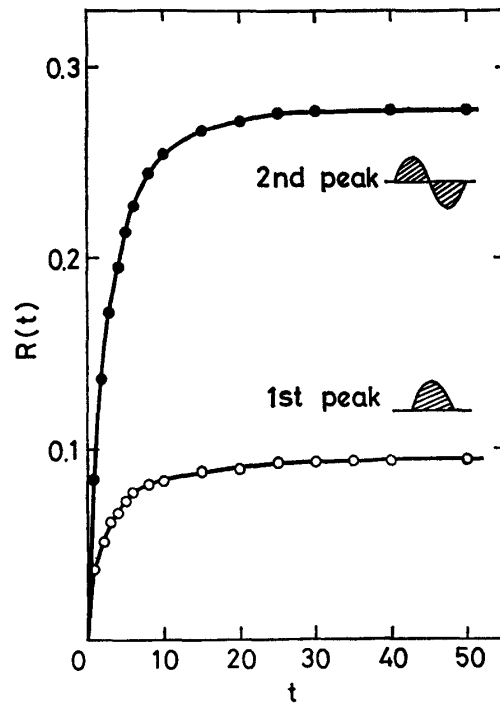


Fig. 8. Relations between area of differential interference function and iteration number of relaxation.

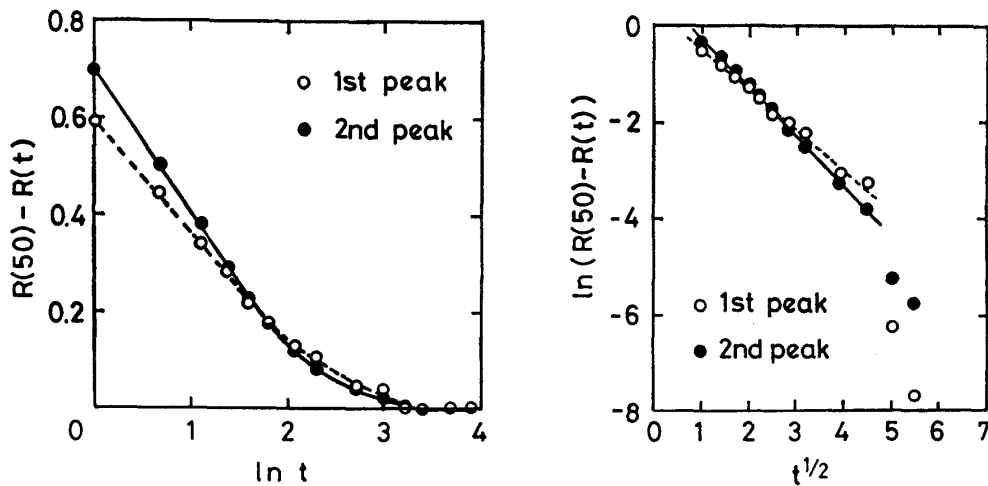


Fig. 9. Johnson-Mehl-Avrami type plot ($\ln(R(50) - R(t)) \sim t^{1/2}$) and logarithmic exhaustion type plot ($R(50) - R(t) \sim \ln t$) for kinetics in geometrical relaxation of DRPHS assembly.

necessary to find the detailed mechanism of the low-temperature structure relaxation in melt-quenched amorphous metals.

Acknowledgements

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