LOCAL ATOMIC STRUCTURE OF AMORPHOUS METALS

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Abstract.— The local parameters are introduced to describe the local atomic structure of amorphous metals. They define the structural defects which facilitate the explanation of various properties, including the volume change by annealing.

1. Introduction

The atomic structure of amorphous metals has been discussed traditionally in terms of the radial distribution function (RDF) and the polyhedron analysis (1-3). In particular the RDF is most frequently used to describe the structure, since it is the only structural quantity which can be directly determined by experiment. However, the RDF fails to describe the variation in the local structure, since it is a quantity averaged over the entire volume of the sample. For instance, as shown in Fig. 1, the same total RDF first peak can result either when the probability is identical for each atom, and the local variation represents purely the statistical fluctuation (case (a), uncorrelated structure), or when the peak is narrower and the peak position is different for each atom, so that the local environment has a collective fluctuation (case (b), correlated structure). It is often uncritically assumed that the case (a) is valid for amorphous structure, but actually the case (b) is more realistic.

The variation in the local structure, the fact that the atomic environment of each atom is different, is in a sense the most fundamental structural characteristic of amorphous solids, since most of the physical properties are determined to a large extent by the short range local structure, and to a much less extent by the long range order. The macroscopic physical properties we observe are most often

the average of the locally varying quantities. In spite of the importance of the local structural variations in understanding the properties of amorphous solids, we have not until recently possessed effective means to describe such a local structure. However, several local parameters have been introduced in ref.(4,5) and in this paper we discuss their physical meaning, describe the structural defects defined by these parameters, and consider the role of defects in elucidating various physical properties, focusing in particular on the interpretation of the macroscopic free volume in terms of these defects.

Fig.1 The first peak of RDF, for (a) uncorrelated structure and (b) correlated structure.

2. Definition of the local parameters

The first local parameter introduced by Egami, Maeda and Vitek (4) is the atomic level stress tensor (6) which can be evaluated by considering the change of the energy of the system due to application of a uniform strain upon this system and thus does not require any ideal reference structure. If the interaction between the atoms is described by a central force pair potential ϕ , the $\alpha\beta$ component of the stress tensor at the position of atom i is

$$\sigma_i^{\alpha\beta} = \frac{1}{2\Omega_i} \sum_j \frac{\partial \phi}{\partial r} \left| \frac{r_{ij}^\alpha}{r_{ij}} \frac{r_{ij}^\beta}{r_{ij}} \right| \quad (1)$$

where $\vec{r}_{ij}$ is the vector between i -th and j -th atom; $r_{ij}^{\alpha,\beta}$ are the α and β components of this vector and r_{ij} its magnitude. Ω_i is the local atomic volume which may be defined as

$$\Omega_i = \frac{4\pi}{3} \bar{a}_i^3 \quad (2)$$

where $\bar{a}_i$ is the effective atomic radius

$$\bar{a}_i = \frac{\sum_j r_{ij} w(r_{ij})}{2 \sum_j w(r_{ij})} \quad (j: \text{all interacting neighbors}) \quad (3)$$

$$w(r_{ij}) = r_{ij}^{-2}$$

The weighting factor r_{ij}^{-2} was introduced because it is proportional to the solid angle to view an atom at the separation r_{ij} .

Another set of the local parameters are the site symmetry coefficients $\epsilon_n^{\ell,m}(i)$ at the position of an atom i defined by expanding the total energy E with respect to the displacement Δr_i of the atom i into the following series:

$$E = E_0 + \sum_n \sum_{\ell=0}^{\infty} \sum_{m=-\ell}^{\ell} \epsilon_n^{\ell,m}(i) Y_{\ell}^m(\theta_i, \phi_i) \frac{|\Delta \vec{r}_i|^n}{n!} \quad (4)$$

where θ_i and ϕ_i are the azimuthal angles determining the direction of $\Delta \vec{r}_i$ and Y_{ℓ}^m is the spherical harmonics.

These parameters cannot be, at present, determined directly by an experiment, and can only be calculated for model systems. We could, of course,

consider other local parameters. For example, local atomic volume (3) is one possibility. Furthermore, for each physical property it is possible to define a local parameter, such as the local Debye temperature for lattice vibrations (7), the local effective mass for electronic structure, or the local spin-wave stiffness for a magnetic system. All these local parameters are, however, likely to be strongly correlated to each other. It is then natural to choose one of the local parameters as the principal parameter, and discuss all other parameters in relation to it. We suggest that such a suitable parameter is the stress tensor (eq.1), and particularly the local hydrostatic stress.

$$p_i = \frac{1}{3} \text{Trace}(\sigma_i^{\alpha\beta}) = \frac{1}{6\Omega_i} \sum_j \frac{\partial \phi}{\partial r} \left| r_{ij} \right| \quad (5)$$

An example of the spatial distribution of this parameter is shown in Fig.2(4) for a cross section of a computer model of an amorphous metal constructed by Maeda and Takeuchi (8). A strong correlation between p_i and the atomic volume Ω_i exists, as seen in Fig.3 which shows the plot of p vs Ω for the above model for each atom.

3. Structural defects defined by the local parameters

The values of p_i calculated for the model amorphous structure (5) are rather large, with $\langle p_i^2 \rangle^{1/2}$ being 0.067 eV/Å³ (=10.7 GPa). Furthermore, they exhibit substantial fluctuation from site to site as seen in Fig.2. There are, however, significant spatial correlations, defining regions of 10~20 atoms each with either compressive or tensile hydrostatic stresses. These regions are often found in pairs with areas of high shear stresses between them. Physically these regions represent areas of different density (5). We may identify these regions as structural defects and call them p -type (compressive stress) or

Fig.2 Atomic level pressure of amorphous iron. Arrows toward the right, tension; the left, compression. The length of the arrow corresponds to the magnitude.

Fig.3 Microscopic pressure-volume relationship. The solid line is the least square fit by the quadratic equation shown above.

n-type (tensile stress) local density fluctuations (LDF)(5,9) However, as p_i always shows a continuous distribution there is no unique way of identification of the extent of these regions (a statistical definition is given in ref. 5). In this sense, these regions are not structural defects which can be unambiguously defined geometrically, but have to be regarded as elementary units of the structural irregularity. On the other hand, if they are treated as structural defects, their behaviour strongly parallels the behaviour of the crystalline defects. In particular these two basic defects are somewhat analogous to the interstitial (p-type) and the vacancy

(n-type), but they are more diffuse. The atomic transport can then be understood by their diffusion (p-type and n-type defects contribute in an opposite way to the transport, similarly as electrons and holes in semiconductors). Plastic deformation is most likely to be localized in the shear zone between the pairs of p and n-type defects. Their local motion may provide the physical basis for the two-level tunnelling state (10) and may contribute to the anelasticity, anomalous specific heat, and magnetic after-effect (11). The recombination of the n-p pairs explains the structural relaxation, and indeed the calculated RDF from the relaxed regions minus RDF from the defect regions strongly resembles the change in the RDF observed during the structural relaxation (5). Furthermore, these defects provide important insight into the structural stability and the compositional dependence of the structure (9). Because of the limitation in space, we discuss here only their role in determining the macroscopic free volume.

4. Macroscopic free volume and the structural defects

The free volume theory of liquids is well known (12) and has been applied to amorphous solids(13). Our analysis shows, however, that straightforward application of this theory to amorphous metals can be misleading. The free volume was originally defined as a macroscopic excess volume of the liquid, compared to the extrapolated volume of the solid. This free volume is then assumed to be distributed over the whole system in the form of vacant spaces between the atoms. This picture may be valid for liquid at high temperatures, or amorphous polymers in which the atomic repulsive potential is much stronger than the attractive potential. In amorphous metals, however, the interatomic potential is more harmonic, and the local structural variation results not only in the free volume-like low density regions (n-type

LDF), but also in the compressed high density regions (p-type LDF) which could be viewed as the "anti-free volume". The n-type and the p-type LDF contribute to the total volume in an opposite way and thus although the creation or annihilation of an n-p pair leads to a volume change owing to the anharmonicity of the potential, this volume change is always very small. The macroscopic free volume can be defined as

$$\Delta \Omega^M = \bar{\Omega} - \bar{\Omega}(\bar{p}) \quad (6)$$

where $\bar{\Omega}$ is the average atomic volume and $\bar{\Omega}(\bar{p})$ is the atomic volume for the atoms with the average hydrostatic stress $\bar{p}$. These quantities can be evaluated using the data of Fig.3 and they are summarized in Table I. The total microscopic free volume can be defined as

$$\Delta \Omega^m = \langle (\Omega - \bar{\Omega})^2 \rangle^{1/2} \quad (7)$$

and when evaluated using data of Fig.3, $\Delta \Omega^m / \bar{\Omega} = 0.067$. Thus the macroscopic free volume is much smaller than the total microscopic free volume and these two quantities are not even linearly related.

The experimentally determined volume change during the structural relaxation is about 0.4% (14) while the observed change in the RDF due to annealing is as much as 10 % for the third to fifth peaks (15). These two observations cannot be reconciled in the framework of the free volume theory. They are, however, readily explained in terms of the p-type and n-type defects, since the macroscopic volume change corresponds to $\Delta \Omega^M$ if a substantial portion of the defects are annealed out, while the change in the RDF is more closely related to $\Delta \Omega^m$ which is much larger than $\Delta \Omega^M$. It is, therefore, very much misleading to try to estimate the defect density from the macroscopic volume change.

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Table I

$\bar{\Omega}(\bar{p})$	9.4353 Å ³
$\bar{\Omega}$	9.505 Å ³
$(\bar{\Omega} - \bar{\Omega}(\bar{p})) / \bar{\Omega}$	0.0073

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