

A model of liquid metals and its relation to the solidification process

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Abstract

X-ray analysis shows that a liquid is build up of clusters of atoms with a certain number of nearest neighbours. The X-ray analysis shows that 8–11 nearest neighbours surround each atom. Each cluster has a crystal-like structure. Between the clusters there are some free atoms and free electrons. The enthalpy of fusion is according to Richard's rule around the gas constant times the temperature of melting and the heat capacity in the liquid state is normally constant and for some metals lower than that in the solid state. For metals with low melting points it will decrease further with increasing temperature. This behaviour of the metals can be explained by the use of statistical mechanics and by assuming that the clusters, observed by X-ray analysis are rotating around a centre of its mass. The cluster model is applied to explain the diffusion rate in liquid metals. The effect of the experimental set upon measurements of diffusion constants is discussed as well as its effect on crystal growth.

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1. Introduction

The structure of liquid metals has been analysed and discussed during the past decade, and a number of excellent surveys are given in the literature [1–3]. It is evident that the structure of the liquid will influence the solidification process. Among other parameters, the liquid structure will influence the diffusion processes in, and the viscosity of the liquid. A number of well-developed theories are presented in the literature, which describes the process. However some experimental observations have been reported where the existing theories do not explain the experimental results.

It is for instance observed that gravitational forces influence the solidification process. During early low gravity experiments, it was observed that the dendrite arm spacing was much larger following solidification under microgravity conditions than experimental conditions on earth [4]. In addition, it has been observed that both gravitational forces and the sample size influence the diffusion rate.

These observations and discrepancies indicate that a new theoretical model is needed to more accurately describe the liquid structure. In this paper, we will describe the structure of the melt in a different way than previously. The paper starts with a

discussion of X-ray analysis results. Later we will discuss the latent heat during melting and solidification, together with the heat capacity of the liquid. The liquid diffusion rate and its relationship to crystal growth will finally be discussed.

2. X-ray analysis of a liquid

The most common way to describe the structure of a liquid metal emanates from X-ray diffraction patterns. The technique used to obtain the X-ray diffraction pattern for a liquid is similar to the Debye–Sherrer technique used for polycrystalline solids. Fig. 1(a) shows the intensity of the reflected beam, for potassium at two different temperatures, as function $\sin \Theta/\lambda$, where Θ is half the diffraction angle and λ is the wavelength of the X-rays [5]. The X-ray pattern does not contain any distinct lines as for a solid. The figure shows instead a main peak and a series of subsiding peaks to the right.

To interpret an X-ray diffraction diagram, such as the one in Fig. 1(a), it is necessary to transform the diffraction intensity measurements into an atomic distribution diagram, first suggested by Debye [6] and later improved by Warren and Gingrich [7]. Fig. 1(b) shows such a diagram for potassium at two different temperatures. The x -axis is the distance from a particular atom and the y -axis shows the number of atoms at the distance r . $\rho(r)$ is the number density of atoms at a distance r . The number of atoms in a spherical shell is $4\pi r^2 \rho(r)$. The area under

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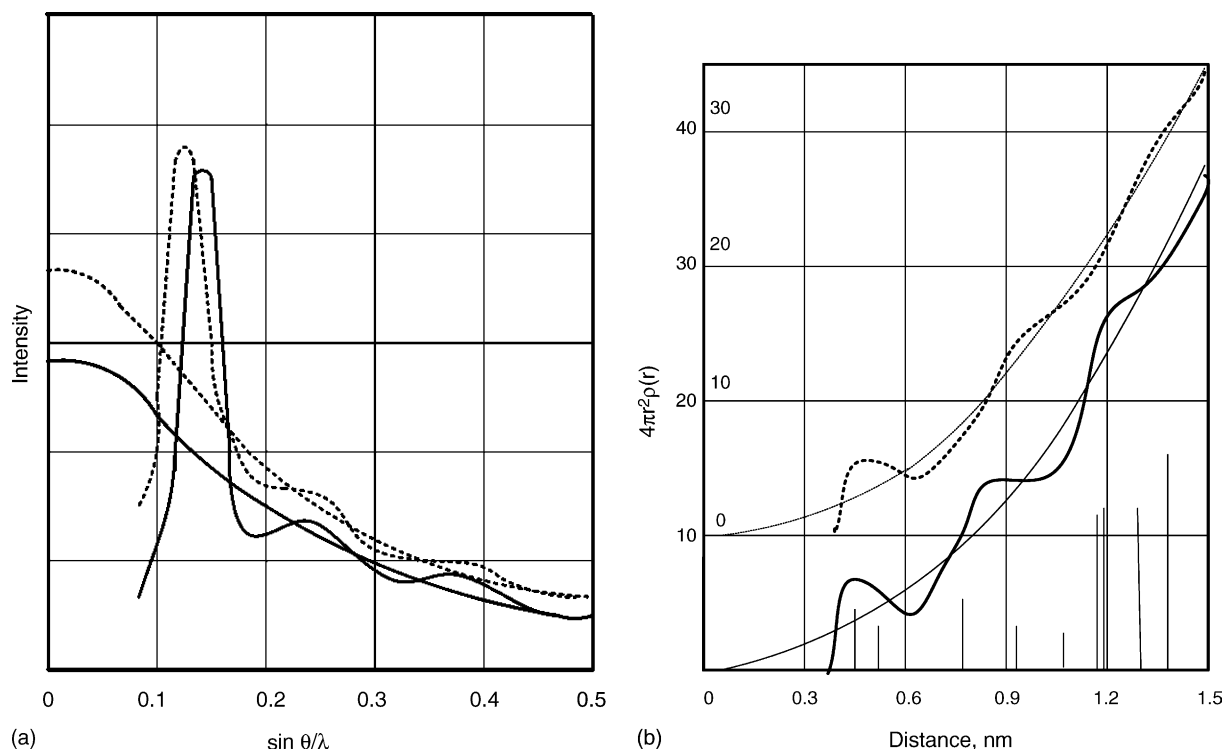


Fig. 1. X-ray diffraction pattern for liquid potassium at 70 and 395 °C [5]: (a) Intensity curve, (b) distribution curve and vertical lines represent the crystal pattern of crystalline phase. Full line, 70 °C; dotted line, 395 °C.

the curves between any two values of r is numerically equal to the number of atoms in the corresponding spherical shell. All metallic liquids show curves similar like the example given in Fig. 1(b). Below we will analyse those curves more carefully.

3. Structure of liquids

The x-ray analysis gives the following information. By integrating the area under the first peak, one generally finds that an atom is surrounded by 8–12 nearest neighbours. This number varies between different metals and has been discussed elsewhere [5,8]. Table 1 shows the number of nearest neighbours for sodium, potassium, copper and aluminium. We will now introduce the concept that a liquid metal consists primarily of clusters similar to the polyhedron described in nano-crystalline materials and that each clusters contain 8–12 atoms. However, in this case the clusters will vary in size with time between a lower limit and an upper limit. The limits can probably be 8 and 12.

By a careful analysis of the X-ray curves presented in Fig. 1, it is found that the area under the second peak from the right is

around eight times larger than the area under the first peak. Based on this, it is reasonable to assume that each cluster is surrounded by eight similar clusters in an outer shell. These clusters can rotate and exchange position with each other. There is also an exchange of atoms between the cluster and they may change their size. The X-ray diffraction patterns of a liquid metal (Fig. 1(a)), show that the cluster size decreases with increasing temperature, Fig. 1(b). Molecular attraction forces bind the atoms inside the clusters and the clusters float in, and are bound together by the free electrons surrounding them.

4. Heat capacity of a liquid

The possibility of describing the physical properties of a liquid in the same way as for a solid has been attempted for many years. In spite of these attempts, no simple and generally accepted model exists today. It is difficult to find a relationship, which correctly describes the liquid heat capacity. It is difficult to understand why the liquid has a lower heat capacity than the solid phase. No good relationship is available to describe the thermal expansion and the viscosity of a melt. We will here present and discuss some models to describe a liquid.

The atomic structure in a melt can be described as consisting of a large number of polyhedron. We assume that during the melting process those polyhedrons start to rotate. Movement of the melt thus occurs by rotation of clusters of atoms. The group is assumed to be equal to one cluster. Each group of atoms rotates around its own centre of mass, and the melt may be thought of as looking like a gearbox. In addition, atoms can be exchanged between the clusters, which will therefore vary in size with time.

Table 1
Entropy of melting and nearest neighbours [8]

Specie	Number of nearest neighbour in liquid	Latent heat divided by melting temperature
Na	9.5	1.70
Ca	9.5	1.70
Cu	11.5	2.29
Al	10.6	2.70
Sn	8.5	3.35

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