Small-angle scattering studies of inhomogeneities in condensed matter

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Abstract. The experimental methods of small-angle scattering of X-rays, neutrons and light have been established as excellent tools for investigating particulate inhomogeneities in condensed matter media in the size range of $10\text{ \AA}$ – $10000\text{ \AA}$. In this paper we bring out the usefulness of small-angle X-ray scattering studies of particulate microstructure in condensed matter. Notwithstanding the extreme extensivity of the field of its applicability, we shall discuss in detail only one field, namely, precipitation of second phase particles in phase separating alloys. Specifically, we shall analyse the example of γ' precipitation in $\text{Ni}_{0.8}\text{Al}_{0.2}$ alloy system in order to demonstrate the efficacy of the small-angle scattering techniques. We shall touch upon the maximum entropy technique, a relatively new and efficient method of SAXS data analysis, used to derive material data with excellent certainty and statistics from these experiments.

Keywords. Small angle scattering; SAS; SAXS; precipitates; Ni–Al alloy; maximum entropy method.

1. Introduction

Often condensed matter consists of inhomogeneities in the form of particles embedded in otherwise homogeneous medium referred to as the matrix. Further, the properties of such materials are mainly determined by the particulate microstructure. Therefore, there has been an enormous interest in systematizing the understanding of the formation and growth of these inhomogeneity particles in different situations. These processes are, of course, dependent on the thermodynamic conditions to which the material is subjected and on the initial condition from where the system evolves. These microstructural developments and their correlation with observed changes in physical properties in different conditions have formed the subject of many studies through different experiments. They provide the necessary inputs into physical modelling of the underlying processes. The SAS experiments and the data analysis and unfolding methods have been employed as powerful tools for investigating the much needed information on the microstructural parameters. As there exist excellent monographs and reviews (Guinier and Faurnet 1955; Beeman *et al* 1957; Brumberger 1965; Vonk 1976; Glatter and Kratky 1982; Feigin and Svergun 1987) on the general subject describing details of the necessary specialized SAS instrumentation, data analysis methods and varied application areas, we give in § 2 only a condensed account of the SAS technique. The method of data analysis based on maximization of the information theoretical entropy as applied to our SAS data is also discussed in § 2. We shall present in § 3 the data on a specific application namely γ' precipitation in $\text{Ni}_{0.8}\text{Al}_{0.2}$ alloy studied by small angle X-ray scattering (SAXS). Section 4 discusses the results obtained from both the electrical resistance measurements and SAXS studies on the γ' precipitate growth process and conclude on the usefulness of SAS experiments.

2. Principles of small-angle scattering

In an event of scattering of a wave, the coherent scattering intensity pattern arises from the interference of the waves scattered by individual scatterers –the electrons in the case of electromagnetic waves like X-rays or light, and the nuclei in the case of neutrons. Although the individual scattering events are isotropic, the necessity for constructive interference strongly limits the directions over which measurable scattered intensities can be recorded to the immediate neighbourhood of the direct beam direction (or Bragg directions, which do not concern us here). As we consider only the elastic scattering, the wave vector suffers only a change in direction by the scattering angle 2θ , which decides the magnitude q of the wave vector transfer $\mathbf{q}$, because $q = 4\pi\sin\theta/\lambda$. In SAS we are usually interested in the range of q such that $10\text{\AA} \leq q^{-1} \leq 1000\text{\AA}$ corresponding to correlation over spatial extents much larger than the interatomic spacing in normal condensed matter media. The scattered intensity $I(q)$ depends on (i) the contrast factor i.e. the square of the difference K between the scattering cross-sections of the matrix and that of the particle, (ii) the form factor $P(q, r)$ and (iii) the structure factor $S(q)$. The intensity is given by

$$I(q) = \rho_p \cdot K^2 \cdot P(q, r) \cdot S(q). \quad (1)$$

For uniform and random spatial distribution of the particles $S(q)$ is a constant of q and the only q dependence of I is due to that of $P(q, r)$. P depends on the shape and size of the scatterer particle; for example, for a spherical particle of radius r [see Beeman *et al* (1957), Brumberger (1965), Glatter and Kratky (1982) and Feigin and Svergun (1987) for other shapes]

$$P(q, r) = \left(\frac{4\pi}{3}\right)^2 \cdot \frac{\{\sin(qr) - qr \cos(qr)\}^2}{q^6}. \quad (2)$$

In case the material contains particles with a size distribution $D(r)$ over a range of sizes $r_{\min} \leq r \leq r_{\max}$, the intensity is given by

$$I(q) = \rho_p \cdot K^2 \cdot \int_{r_{\min}}^{r_{\max}} D(r) \cdot P(q, r) dr. \quad (3)$$

The SAS experiments record the $I(q)$ data at various q points and the material microstructure information, namely $D(r)$, is obtained by unfolding the $I(q)$ data numerically. For this purpose we need to model the $P(q, r)$ for a suitable particle shape using prior information on the system studied. In the literature many different SAS data unfolding methods have been successfully used by different investigators (Guinier and Fournet 1955; Beeman *et al* 1957; Glatter and Kratky 1982; Feigin and Svergun 1987). The methods used by several investigators assume the $D(r)$ function to be in a familiar mathematical form like a Gaussian or log-normal distribution function, and is computationally efficient; but this approach has no physical basis although often justifiable. The method of Glatter (Glatter and Kratky 1982) takes into account in a natural way, the effects of instrument function on the SAS data and is very convenient to compute the interparticle distance distribution function $p(r)$ in addition to $D(r)$. This information enables one to infer on formation of particles as clusters or preferential population in the neighbourhood of existing microstructure like grain boundaries. Svergun (Feigin and Svergun 1987) has developed a method, based on Tikhonov's theory of ill-posed problems, which ensures smoothness of $D(r)$ through proper choice

of regularizer function. It is seen (Vonk 1976; Hansen 1991) that these methods do not ensure positivity of $D(r)$, a condition inviolable by definition. However, relatively recently Potton and coworkers (Mauer *et al* 1985) utilized the mathematical formalism of maximum information theoretical entropy for unfolding $D(r)$ information from $I(q)$ data obtained from SAS experiments. This method formulates an entropy function

$$\mathcal{T} = - \sum_{i=1}^n D(r_i) \cdot \ln D(r_i), \quad (4)$$

where the precipitate size ranges from r_1 to r_n . $\mathcal{T}$ is maximized subject to the physical constraints that the observed intensities (after deconvoluting the experimental slit function from the recorded data) correspond to (3) and that $D(r)$ is normalized to unity as

$$\sum_{i=1}^n D(r_i) = 1. \quad (5)$$

In our work we impose another constraint: $I(q)$ is distributed around the experimental values with a variance consistent with count statistics because the data is collected by counting by a detector. This constrained optimization is accomplished numerically and then the resulting system of equations, which are algebraic equations, are inverted to obtain $D(r_i)$ for $i = 1$ to n . This method overcomes, in a natural way, the earlier difficulty because positivity of $D(r)$ is ensured here. This benefit is, of course, offset by the necessity of handling large-sized matrices; but this need not be considered a hurdle in the present day computational scenario. In our calculations we have used singular value decomposition algorithms for inverting the matrices. We shall present in the next section the results obtained by employing this method to analyse the SAXS data recorded during precipitation of γ' particles in the $\text{Ni}_{0.8}\text{Al}_{0.2}$ solid solution alloy.

3. Precipitate growth in $\text{Ni}_{0.8}\text{Al}_{0.2}$

We present here the experimental investigation, which highlights the power and applicability of SAS method, in deriving particulate microstructure information. For this study a $\text{Ni}_{0.8}\text{Al}_{0.2}$ alloy was prepared by using an electron beam to melt pure materials taken in the specified ratio, rolled to 50 μm thick foils and homogenized by thermal treatment at about 1600 K for 30 min in pure argon atmosphere. Ageing at lower temperatures give rise to precipitation of γ' particles that continue to grow during subsequent thermal ageing. It is of considerable importance and interest to characterize the process of growth of the precipitates, which usually have a size distribution. In this set of experiments, designed to obtain the activation energy for growth, isochronal annealing treatment was given for equal periods of 30 min at each temperature, ranging from 373 K–1373 K, varied in steps of 50 K. Following each anneal, the electrical resistance R of the sample was measured by four-probe method, and SAXS intensity pattern was recorded. We discuss the results below.

3.1 Electrical resistance measurements

The presence of the γ' particles influence, in principle, the electrical transport properties in two ways. Firstly, the electron mobility could be impeded due to volume scattering of

the electrons. However, because the precipitates in this case are both coherent and compositionally similar to the matrix, this effect may not be discernible, especially in the change in R due to increase in particle volume fraction. The second effect is associated with electron scattering from the strain field at the coherent interfaces between the precipitate and the matrix. The variation in R should reflect directly the dynamic change in the nature and extent of interface consequent to the growth in different stages.

In our experiments R was measured at 77 K following each isochronal anneal (figure 1) where one can notice the variation in R to fall into three distinct ranges, namely, $373\text{ K} \leq T \leq 673\text{ K}$, there appears only a mild rise in R ; in the range $723\text{ K} \leq T \leq 923\text{ K}$ there appears a rather steep decrease in R and at higher temperatures up to 1373 K, a steady rise in R is observed. From this data we conjecture that the precipitates do grow continuously in all the three stages, but the interfaces in these conditions differ both in nature and extent. We shall discuss this aspect in § 4 in more detail by connecting these results with those of the small-angle scattering experiments.

It is important to note that in the third stage, R is monotonic and so we have made a detailed analysis of the data in this stage. We note that during a particular anneal the microstructure grows over and above the extent already developed due to the previous anneal. Therefore the difference $\Delta R_{i+1} = R(T_{i+1}) - R(T_i)$ should be proportional to the microstructure grown during the annealing at T_{i+1} . We calculate ΔR for $973\text{ K} \leq T \leq 1373\text{ K}$ and present the data as an Arrhenius plot in figure 2. This analysis yields the activation energy of 0.0307 eV. This value indicates the growth of the precipitate matrix interface to be an activation process with the above barrier height. This, besides providing useful information on the growth kinetics of γ' precipitate, emphasizes the need for experimentally measuring the size or the size distribution of precipitate after each annealing.

3.2 The SAXS data

As has been mentioned earlier, the particle size information can be obtained from the SAS experiments. After each annealing, we have recorded the SAXS intensity pattern using an Anton Paar make Kratky camera fitted on to a 3kVA X-ray generator. An

Figure 1. Electrical resistance R of $\text{Ni}_{0.8}\text{Al}_{0.2}$ alloy measured after isochronal annealing at temperatures in the range 373 K–1373 K. R is plotted in arbitrary units.

Figure 2. Arrhenius plot of change in resistance due to isochronal annealing. The activation energy $E_a = 0.0307$ eV. $\ln(\Delta R)$ is plotted in arb. units.

Figure 3. SAXS intensity pattern, in arbitrary units, recorded after isochronal annealing treatments.

empty cassette run was recorded for use as the total camera resolution function which was deconvoluted from the actual SAXS intensity patterns. The data after deconvolution are shown in figure 3 where we notice the signature of particle size dispersion. So the size distribution function $D(r)$ has been obtained (see figure 4) for each annealing temperature in the range $373 \text{ K} \leq T \leq 1123 \text{ K}$, using the maximum entropy technique as has been discussed in § 2. Using this $D(r)$ we obtain r_{av}^2 as the second moment of $D(r)$. This data also has been presented as an Arrhenius plot in figure 5, the slope of which gives the activation energy for growth of the interfaces and is found to be 0.0275 eV . This value compares fairly well with the results obtained from the electrical resistance measurements.

Figure 4. The size distribution $D(r)$ of γ' precipitates, in arbitrary units, as it evolves during isochronal annealing treatment.

Figure 5. Arrhenius plot of r_{av}^2 , in arbitrary units, derived from the $D(r)$ which is obtained by unfolding the SAXS data.

4. Discussion and conclusions

The results of the two classes of the experiments, namely, (i) the measurement of the electrical resistance and (ii) the SAXS experiments, presented in §§ 3.1 and 3.2 help us to understand the details of the growth of γ' precipitates in $\text{Ni}_{0.8}\text{Al}_{0.2}$. The electrical resistance in this material arises from the scattering of electrons from the precipitates mainly due to the strain field associated with the particles. The γ' precipitates of the present case being coherent with the matrix, the volume contribution can be neglected as compared to the effect of the interfacial strain field. The lattice constants of the γ phase matrix and γ' particles differ by about 1% and the values range around $3.55 \text{ \AA}$ with close variations in different studies (Phillips 1967; Mauer *et al* 1985; Mohan Rao *et al* 1989). So the particle-matrix interface (PMI) is strained when the particles are smaller than about $355 \text{ \AA}$.

For $373 \text{ K} \leq T \leq 673 \text{ K}$, the total interface area is small and the rise in R is rather slow because the growth takes place at PMI. But in this stage the particle size is limited to

below 350 Å where the coherency strain is large. As the particles grow during subsequent annealing, this strain is relieved by the formation of interfacial dislocations. This is reflected by the drop in R in the second range. As the particles grow further, the density of interfacial dislocations also increases resulting in rise in R for $T > 923$ K. In this stage of growth there are no opposing effects on R , therefore a monotonic increase in R is observed as in figure 2, making it convenient for us to analyse the data in this range and obtain the activation energy for the interfacial growth to be 0.0307 eV as mentioned earlier. Such a low value of the E_a is indicative of interfacial growth process rather than a volume diffusion control mechanism. This explanation depends on the assumption that the γ' particles grow continually through the anneals at all the temperatures. Because this is not clearly seen in the R vs T data, we have verified it by SAXS experiments as has been presented in § 3.2. As may be seen in figure 5, the r_{av}^2 shows a clear Arrhenius behaviour with $E_a = 0.0275$ eV. The consistency of this has been checked by analysing the calculated r_{av} data. Plot of $\ln(r_{av})$ vs $(1/kT)$ shows a slope of 0.014 eV. Thus, we infer that the change in R arises mainly due to electron scattering from the PMI. Further, it is clear that the γ' particles do grow continuously right from the beginning till the last stage of isochronal annealing treatments. Other important growth parameters like the rate constant and diffusion coefficient can be derived from isothermal annealing experiments like those of Chellman and Ardell (1974).

From the analysis of this example we have shown that the SAXS experiments supplement other studies with particle size information. On the other hand, the electrical resistance measurements are highly sensitive to the variation in the strain field and so provide useful information on the growth of coherent precipitates.

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