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Study of Effects of Electron Irradiation on the Nano-Particles in Al-Zn Alloy by Small Angle Neutron Scattering

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Abstract: The effects of 2 MeV electron irradiation on the nano particles in a room temperature aged Al-Zn alloy have been studied using small angle neutron scattering (SANS). A series of electron irradiation was performed on each sample and SANS measurements were made on the PLUTO small angle neutron scattering instrument (U.K) after each irradiation. In general for low doses the results show an initial decrease in the magnitude of the scattering, but associated with an increase in the size of the nano particles. This is followed on prolonged irradiation by an increase in the magnitude of the scattering with a continued increase of nano particle sizes. It is believed that at low doses some nano particles swell but others dissolve, the matrix is then supersaturated and with the enhanced rate of diffusion. As a result of irradiation, the remaining nano particles grow rapidly. As the super saturation reduces a coarsening mechanism takes over, via a radiation enhanced diffusion mechanism.

Key words: Small angle Neutron scattering · G-P Zones · Nano- particles · Coarsening · Scattering length density

INTRODUCTION

Aluminum alloys have found widespread uses in the aero-space industry. The requirements for aerospace engineering materials are for a low mass and high strength coupled with an ability to operate at high temperatures. The strength of the alloys is generally improved by the development of a second phase dispersed through out the host matrix, often in the form of a precipitate. Al-Li alloys achieve precipitation strengthening by thermal aging after a solution heat treatment. These alloys are used in cryogenic applications for example liquid oxygen and hydrogen fuel tanks for aerospace vehicles. Nickel–based super alloys are used in those components subjected to the highest temperatures (e.g. turbine blades). These alloys are strengthened by the precipitation of a gamma prime state. Rolls Royce in the U.K and Pratt and Whitney in the USA have extended the operational range of these alloys by producing single crystal turbine blades. During precipitation from a supersaturated solid solution of an alloy, precipitation of metastable phases prior to the equilibrium phase is often observed.

In some alloys, especially aluminum alloys, solute clusters on the matrix lattice form in the initial stage of precipitation or aging. Such clusters of solute atoms are called GP zones after the names of their discoverers, Guinier and Preston. GP zones were found first in Al-Cu alloy and then in most of the age harden able Al alloys and various other alloy systems such as Fe-Cu, Cu-Fe, Fe-Au, Fe-Mo, Cu-Ti and Cu-Be. 'One common feature of GP Zones is that they are coherent with the matrix and very effectively strengthen the alloy [1]'. Ramlau and Loffler [2] have reported the presence of GP Zones coherent with the matrix in Al-3 at% Zn alloy studied by means of a high resolution transmission electron microscopy.

Kostroz [3] has reported more or less spherical Zn-rich precipitates in Al-Zn alloy after quenching from elevated temperature and aging at relatively low

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temperature. Gerold [4] has interpreted X-ray data indicating that scattering peak is due to the presence of spherical Zn rich particles and has shown that this is because of the interference between these nano-sized particles. Guiner [5] suggested that the effects arise from an inner Zn-rich zone surrounded concentrically by an outer Zn depleted region.. The scattering is influenced by factors such as the size distribution of the nano-particles, their concentration and their coherence with the matrix. These factors contribute to diffuse scattering, especially in the low Q region and by using neutrons we can study thick samples. Aluminum as the base metal is a good choice for a neutron scattering study due to its low absorption and incoherent cross section

Small angle neutron scattering techniques constitute a powerful tool for non-destructive testing of materials. Neutron has a high penetration depth into matter and this allows the study of volume effects and bulky components. Compared to the commonly used X-ray technique, neutrons have an additional advantage of distinguishing among different metals and are sensitive to light elements. Another unique advantage of neutrons relies on the fact that the neutron is scattered differently by various isotopes of an element. Magnetic materials can be studied by neutron scattering, since the neutron has a magnetic moment; the intensity of Bragg peaks in a neutron scattering spectrum is proportional to the square of the magnetic moment per unit volume.

Small angle neutron scattering is different than Bragg or diffuse scattering, in that it makes use of small scattering vectors that are low in Q. The scattering vector Q is defined as the difference between the wave vectors of the incident and scattered neutrons. The magnitude of the scattered vector Q is given by $Q = 4\pi \sin \theta/\lambda$ *where* λ is the neutron wavelength and 2θ is the angle of scattering.

If we consider neutron scattering in the static approximation and consider nuclear scattering only, we can write the coherent scattering cross section per atom [3] as follows.

$$\frac{d\sigma}{d\Omega} = 1/N \sum_R b_R \exp(iQ.R) \tag{1}$$

where N is the number of scattering nuclei exposed to the beam and b_R is the coherent scattering length of the chemical species occupying a site with the position vector. If we consider two phase model and assume N_p particles with a homogeneous scattering length density $\rho_p = b_{p/V_{ab}}$ where b is the scattering length averaged over the particle volume and V_{ap} is the atomic volume of the particle and let the particles be embedded in a matrix of homogeneous scattering length density ρ_m / V_{ap} then we can write

$$\frac{d\sigma}{d\Omega} = \mathrm{I(Q)} = 1/\mathrm{N}\,(\rho_p - \rho_m)^2 \left| \int_{vp} (iQ.r) d^3 r \right|^2 \tag{1}$$

where the integral extends over a volume V_p occupied by all the particles. In the most general case this integral will allow one to obtain the spatial and orientational correlations between particles and the effects due to size distribution. With the single particle form factor

$$\mathrm{F_p(Q)} = 1/\mathrm{V_p} \int_{Vp} \exp(iQ.r) \overset{3}{d} r \tag{2}$$

We can write for N_p identical particles

$$I(Q) = V_p^2 N_p (\rho_p - \rho_m)^2 [F_p(Q)]^2 \tag{3}$$

where $(\rho_p - \rho_m)2$ is known as the contrast factor, N is the number of scattering nuclei exposed to the beam and $|F_p(Q)|^2$ is the square of the structure factor which is the function to describe the geometrical shape of each scattering particle. If we extrapolate the measured scattering curve to Q = 0, we obtain $\frac{d\sigma}{d\Omega} = N b^2$ (with scattering cross section per atom as usual) for the case $|F_p(0)|^2 = 1$ and $Np = 1$, $\rho_p = Nb/V_p$ and $\rho_m = 0$

For low concentrations of the identical nano-particles Guinier has approximated the form factor as below

$$F_p(Q) = \exp(-R_g^2 Q^2/3) \tag{4}$$

and

$$R_g = 1/Vp \int_{Vp} r^2 \, dv_p \tag{5}$$

Small angle neutron scattering is a very useful and powerful experimental technique in the study of nanostructures, usually found in branched polymers, reinforced rubber,cell membranes in biology, clays, porous systems and alloys in metallurgy where a wide range of topics has been covered including phase separation in binary and ternary systems, density and concentration fluctuations in single-phase systems and studies of various structural defects such as voids, radiation damage dislocations and surfaces and interfaces. 'For the characterization of this kind of nanostructures small angle neutron scattering technique is very useful tool to provide structural information on length scales 1-1000 nm [6].'

Mergia *et al* [7] studied the growth of δ' precipitates in an Al-8.9 at% Li alloy by small angle neutron scattering experiments in the temperature range 363 to 483 K.

Glade *et al.* [8] has measured the size, number density and composition of nano-sized defects responsible for the hardening and embrittlement in irradiated Fe-0.9 wt% Cu and Fe-0.9Cu-1.0 wt% Mn model reactor pressure vessel alloys. Vacancy clusters were observed in the Fe-Cu alloy, but not in the Fe-Cu-Mn alloy. The results suggested a strong effect of Mn upon vacancy diffusion and clustering.

Small angle neutron scattering studies of the thermal decomposition of an Al-Zn solid solution alloy, for example, were performed by Messolorass [9]. Allen *et al.* [10] have discussed the *in-situ* thermal growth and dissolution of meta-stable precipitates in Al-11.8 at% Zn alloy. This research program which used small angle neutron scattering is aimed at understanding the nano-particles behavior as a function of irradiation dose. In order to obtain a simple kind of damage, electrons were chosen for defect production rather than neutrons.

Experimental Details: The samples of Al -11.8 at% Zn were solution treated at 310±3°C for 3 hours in a vertical tubular furnace. Each sample was suspended by a steel wire into the furnace which was subsequently quenched by dropping it into a bath of ice-water. After quenching, the samples were rinsed in water, dried and then left to age at room temperature. The samples were polished on a mechanical polisher using a sequence of 5 and 1µm diamond paste on separate soft pads to remove a very light oxide layer which was developed on the surface of the sample due to the heat treatment prior to the irradiations. The electron irradiations were carried out with 2MeV electrons at a flux of 10^{14} electrons/cm^2. sec for different durations in the Vande Graaf generator of the University of Reading, U.K. It is worth mentioning that great care was taken to calibrate the dose accurately. The Small angle neutron scattering measurements for the un-irradiated and irradiated samples were carried out on the PLUTO small angle scattering spectrometer, Harwell U.K [11]. Fig 1. shows the schematic of a SANS experiment.

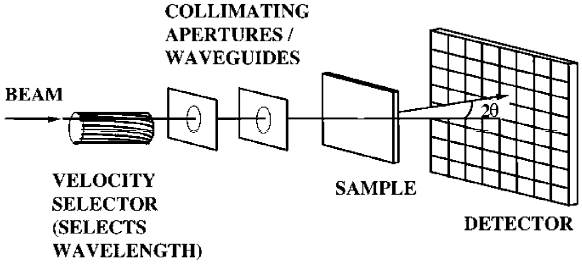

Fig. 1: Experimental schematic of a typical reactor-based SANS instrument.

RESULTS AND DISCUSSION

The small angle neutron scattering results, after correction for background, were calibrated using the known incoherent scattering cross section of a vanadium single crystal.' The SANS results were obtained by using the standard small angle scattering theory by Guinier and Fournet [12] and Beacon [13]. In the Guinier approximation, the radius of gyration ($R_g = (3/5)^{1/2}R$ for spheres) is determined by fitting to the linear portion of a plot of differential scattering cross section (ln $\frac{d\sigma}{d\Omega}$ barns /str/atom) versus Q^2. On the basis of the random model of distribution of nano-particles and in conjunction with the Guinier approximation, a detailed analysis for the estimation of the mean separation (D) between the precipitates, the peak position (Qp) of the scattering curve and the number density of the nano-particles, along with other SANS parameters, is discussed in [14] and [15]. The analysis of the results indicate that at low doses, a decrease in the magnitude of the scattering cross section is observed, which is in good agreement with thermal study in this alloy [10]. In sample A only 10 minutes irradiation has resulted a decrease in the magnitude of the peak scattering by 3 times and changes in size, number density and the mean distance of these nano-particles are noted (Table 1). In sample B, as a result of 20 minutes irradiation, the magnitude of the scattering decreased 3 times and the reduction in the number density about 5 times and increase in the mean distance of nano–particles from 119 to 199 A°. The peak scattering vector (Q_p) in the irradiated sample has moved to the lower Q-value, thus indicating an increase in the R_g of

Table 1: The measured SANS parameters of nano–particles in electron irradiated Al-11.8 at% Zn

Sample	Total irradiation Time (Minutes)	Q_{peak} $(A°^{-1})$	Peak cross-section (b/str/atom)	Particle separation D (A°)	Density of Particles $(cm^{-3})x10^{17}$	Radius of gyration (A°)
A	0	0.0343	20.02	102	2.25	38.33
A	10	0.0266	6.64	159	0.59	40.67
B	0	0.0324	22.8	119	1.42	37.18
B	20	0.022	7.49	199	0.3	46.5
B	40	0.02	13.28	217	0.23	48.9
B	60	0.02	17.25	225	0.21	50.98
C	0	0.35	16.9	104	2.12	36
C	340	0.023	26.4	174	0.45	50.3
C	920	0.02	4.6	209	0.26	54.6
S	0	0.0308	25.95	114	1.6	42.88
S	0	0.0308	25.77	114	1.6	42.77
S	0	0.0308	25.38	114	1.6	43.06
S	0	0.0308	26.17	114	1.6	42.33
S	0	0.0308	26.48	114	1.6	43.24

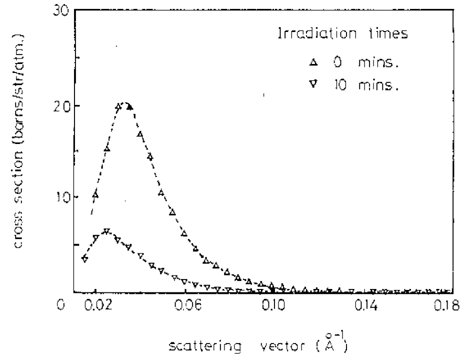

Fig. 2: The small angle neutron scattering results from sample A (aged at room temperature for 280hrs).

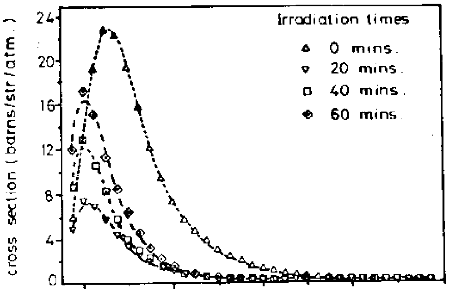

Fig. 3: The Small angle Neutron scattering Results from sample B (aged at room temperature for 300hrs).

the nano-particles from 37 to 46A° which is in accordance to theory. It is interesting to mention that some recovery in the magnitude of the scattering such as 77% and 130% has been noticed in the same sample due to further irradiation by 40 and 60 minutes respectively, although it never attains the original value.

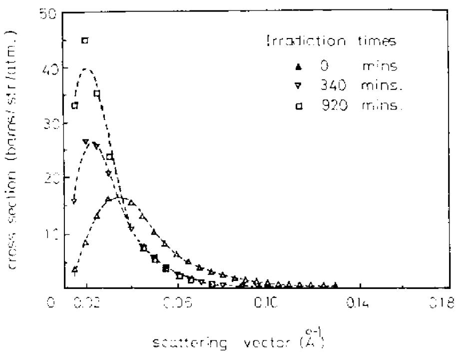

Fig. 4: The Small angle Neutron scattering Results from sample C (aged at room temperature for 283 hrs).

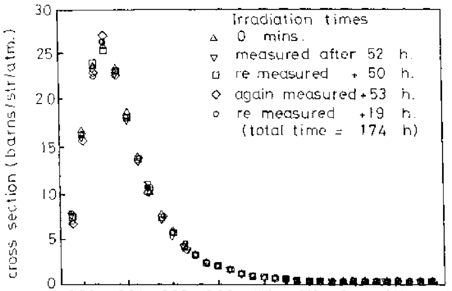

Fig. 5: The Small angle Neutron scattering results from un-irradiated sample S (aged at room temperature for 250 hrs and then measured at different periods of time).

In sample C, an increase in the magnitude of scattering is clearly noticed as a result of 340 and 920 minutes (Fig. 3). In all high dose irradiation measurements, the peak cross section never decreases in comparison to the low dose irradiation. The analysis also indicates an increase in the size and reduction in the number density of the nano-particles, together with movement of the peak position towards lower Q-value. However, these changes in SANS measurements are not seen in the un-irradiated sample “S” measured at 5 different periods of time. The various experimental parameters for samples obtained from the detailed analysis of small angle neutron scattering data are tabulated in Table 1. On the basis of above results regarding low doses, it is believed that some particles may dissolve, but others may enlarge as a result of irradiation.

Liu *et al.* [16] in the analysis of X-ray small angle scattering reported dissolution phenomenon for extremely lose dose neutron irradiation in aluminum alloys. They have reported that G-P zones (20- 60 A°) with a concentration of 10^{17} cm^{-3} were found to shrink by 5-10% on 10^{-5} dpa of neutron at 20K. The dissolution phenomenon is also reported by Cauvin and Martin [17] in electron irradiated Al-Zn during electron microscopy work. It is believed that on prolonged irradiation the matrix becomes supersaturated and with an enhanced rate of diffusion, as a result of irradiation, the remaining nano–particles grow rapidly. As the super saturation reduces, a coarsening mechanism takes over, i.e .small nano- particles redisolve and grows on the larger nano-particles via a radiation enhanced diffusion mechanism. The enhanced diffusion phenomenon has been reported by Sklad and Mitchell [18] in an Al-3.5 at% Cu alloy. Ro and Mitchell [19] reported enhanced diffusion in electron irradiated Ni-Al binary alloys via microscopic studies. Radiation enhanced precipitation has also been reported by Hori *et al*, [20] in Fe-Cu (C) alloy studied via electron microscopy. It was found that the mean size of the precipitate is larger than that in pure Fe. This suggests that the growth process of Cu precipitation enhanced by a small amount of C atoms. Aposotolopoulos *et al.* [21] has reported coarsening phenomenon in Al-8.9at% Li alloy irradiated by neutrons.’

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CONCLUSIONS

The obtained results have demonstrated that the SANS method is a powerful tool in the study of the radiation damage and the determination of the nanostructure is an important step in characterizing the mechanical properties of the structural material. The analysis indicates that an increase in size and reduction in the number density of the nano-particles, together with the peak position movement towards lower Q value is seen. At low doses some nano-particles are dissolved, but others may enlarge as a result of irradiation. On prolonged irradiation the matrix becomes super saturated and the remaining nano-particles grow rapidly. As the super saturation reduces, coarsening mechanisms take over, i.e small nano-particles redisolve and grow on the larger particles via radiation enhanced diffusion mechanism. No such changes in SANS parameters have been seen and SANS is reproducible.

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