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RADIATION EMBRITTLEMENT STUDIES USING ANOMALOUS SMALL-ANGLE X-RAY SCATTERING*

D. E. Alexander and B. J. Kestel
Materials Science Division
S. Seifert
Chemistry Division
9700 S. Cass Avenue
Argonne National Laboratory
Argonne, IL 60439

P. R. Jemian
Materials Research Laboratory
University o Illinois at Urbana-Champaign
UNICAT, Argonne, IL 60439

G. R. Odette, D. Klingensmith and D. Gragg
Dept. of Mechanical and Environmental Engineering.
University of California
Santa Barbara, CA 93106

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To be presented at the Fall Meeting of the Material Research Society: Symposium R-Applications of Synchrotron Radiation Techniques, Boston, MA, November 29 – December 3, 1999.

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DALE E. ALEXANDER[*], B. J. KESTEL[*], S. SEIFERT[**], P. R. JEMIAN[***], G. R. ODETTE[+], D. KLINGENSMITH[+] and D. GRAGG[+]

[*] Materials Science Division and [**] Chemistry Division, Argonne National Laboratory, Argonne, IL, 60439

[***] Materials Research Laboratory, University of Illinois at Urbana-Champaign, UNICAT, Argonne, IL 60439

[+] Department of Mechanical and Environmental Engineering, University of California-Santa Barbara, Santa Barbara, CA, 93106.

ABSTRACT

Anomalous small angle x-ray scattering (ASAXS) was performed on an Fe-0.9 wt.% Cu-1.0 wt.% Mn alloy subjected to annealing or electron irradiation. ASAXS takes advantage of natural variations in the atomic scattering factor which exist at energies very near an element's x-ray absorption edge. By performing systematic SAXS experiments at energies near these absorption edges of the constituent alloy elements it is possible to vary the contrast of scattering centers containing the elements and in doing so quantify scatterer composition. The results of such an analysis for the samples in this work indicate the presence of Cu-rich, $Cu_{85}Mn_{15}$ precipitates in the alloy. By applying the maximum entropy technique to the scattering data, it was possible to extract size distributions of scattering centers for the different treatments. The results demonstrate the ability to detect and characterize small (11 Å radius) scatterers at quite low irradiation damage levels ($5x10^{-4}$ displacements per atom).

INTRODUCTION

Radiation escaping the power producing core of an operating nuclear reactor interacts with the pressure vessel containing the core causing the ferritic steel composing it to embrittle with time. This degradation phenomenon has important implications on the safe and economic operation of commercial plants. Efforts to understand radiation embrittlement on a fundamental, mechanistic level demand the ability to characterize the very fine-scale, nano-sized hardening centers believed formed in the microstructure at quite low radiation damage levels [1]. Small-angle scattering techniques using x-rays or neutrons are beneficial in this regard. By sampling relatively large volumes of material, these techniques provide statistically quantitative size and number density information particularly useful to embrittlement modeling efforts [1].

In the case of x-rays, an additional characterization dimension is available given the energy tunability of synchrotron sources. Anomalous small-angle x-ray scattering (ASAXS) takes advantage of the atomic scattering contrast variation with energy near an element's absorption edge. By performing SAXS at energies very near the absorption edge of one of these elements, the contrast of scatterers can be varied in a systematic fashion allowing information to be gained on those specific scatterers containing the element. As demonstrated in other alloys [2,3], this technique holds promise for characterizing element-specific scattering centers in real pressure vessel (PV) steels.

This paper addresses results of an effort to demonstrate the ASAXS technique in a model alloy of interest to commercial U.S. pressure vessel (PV) studies. The presence of low solubility Cu impurity in real PV steels is known to correlate with increased embrittlement rates under neutron irradiation [1]. One treatment examined in this work was a thermal anneal designed to nucleate and grow Cu precipitates thus providing a good proof-of-principle sample for ASAXS analysis. We also examined material that was electron irradiated at the temperature of interest to commercial PVs (300°C). This irradiation treatment has previously been observed to induce a significant increase in the yield strength in model PV alloys [4]

EXPERIMENT

The ASAXS experiments performed essentially reproduce those reported earlier [5] with substantial improvements described below. As before, a ternary Fe-0.9 wt. % Cu-1.0 wt. % Mn model alloy was studied in annealed (450°C for 24 hours), electron irradiated (10 MeV electrons to $5x10^{-4}$ dpa (displacements per atom) at 300°C) and as-received (i.e. untreated) form. Thin foils were prepared by core drilling 4 mm diameter disks from the alloy sheets and mechanically polishing the material to about 40 μm using 600 grit, 30 μm, 12 μm and 9 μm alumina papers, successively with a final vibratory polish of 0.3 and 0.05 μm alumina.

Scattering was performed at the undulator beamline of the BESSRC CAT at the Advanced Photon Source at Argonne National Laboratory. A well-collimated 400 μm square beam was incident and the scattering from the sample was detected on a 1536x1536 pixel CCD camera placed at a distance of 985 mm distance from the sample. For the photon energy range of interest (6335-7110 eV) these experimental conditions corresponded to a usable scattering vector, Q, range of about of 0.02 1/Å$\leq$ Q $\leq$0.4 1/Å, where $Q = (4\pi/\lambda)\sin\theta$ for monochromatic x-rays with wavelength, λ, scattered through an angle 2θ with respect to the incident beam. The sample position was held constant and the photon energy was varied unidirectionally with respect to the absorption edge energy collecting data in a series of about 12 energies up to 200 eV below a given element's edge. Subsequent to the sample energy series, background/blank data were also collected at the same energies in the same fashion.

The latest experimental arrangement greatly benefited from the use of the CCD detector and an evacuated sample chamber. Unlike the count rate limitations of gas proportional detectors, the CCD camera allowed full use of the APS source intensity. For these experiments, a scattering data set was collected quite rapidly (in 2 seconds). Five such data sets were acquired in rapid succession for each energy and then combined to provide one summed set. The use of an evacuated sample chamber eliminated air scattering and obviated the subtraction of an instrument background from the sample scattering.

The raw scattering intensity data was processed in the following manner. A mask was first applied to the detector data to remove any bad pixels from the two dimensional image. $I_{raw}(E,Q,t)$ versus Q data (E is the photon energy, t is the time) were then obtained by azimuthally averaging and equal-log Q increment-binning the two-dimensional CCD data. The data were corrected for synchrotron source time decay, transmission variations with energy and a constant background was subtracted to yield $I_{corr}(E,Q)$ according to,

$$I_{corr}(E,Q) = \frac{I_{raw}(E,Q,t)}{T(E)\ I_0(E,t)} - I_{backgd}(E,t), \qquad [1]$$

where T(E) is the foil transmission and $I_0(E,t)$ is the incident beam monitor counts and $I_{backgd}(E,t)$ is a flat background determined from the large Q (>0.28 1/Å) region of the data. The net scattering data, $I_{net}(E,Q)$, that due only to anneal or irradiation treatments, was then determined by subtracting the as-received (as-rec) corrected sample data from either the corrected annealed (ann) or the corrected irradiated (irr) data: $I_{net}(E,Q) = I_{corr,\ ann\ or\ irr,}(E,Q) - I_{corr,\ as\text{-}rec}(E,Q)$.

RESULTS AND DISCUSSION

From scattering theory [6], the net SAXS intensity from a sample containing a single type of spherical scatterers may be described by,

$$I_{net}(E,Q) = \text{Const} \times r_e^2 \left| n_{scat}\, f_{scat}(E) - n_{matrix}\, f_{matrix}(E) \right|^2 \times \int_0^\infty F(r) \frac{4\pi r^3}{3} \left| 3\, \frac{\sin(Qr) - Qr\cos(Qr)}{(Qr)^3} \right|^2 dr \ , \qquad [2]$$

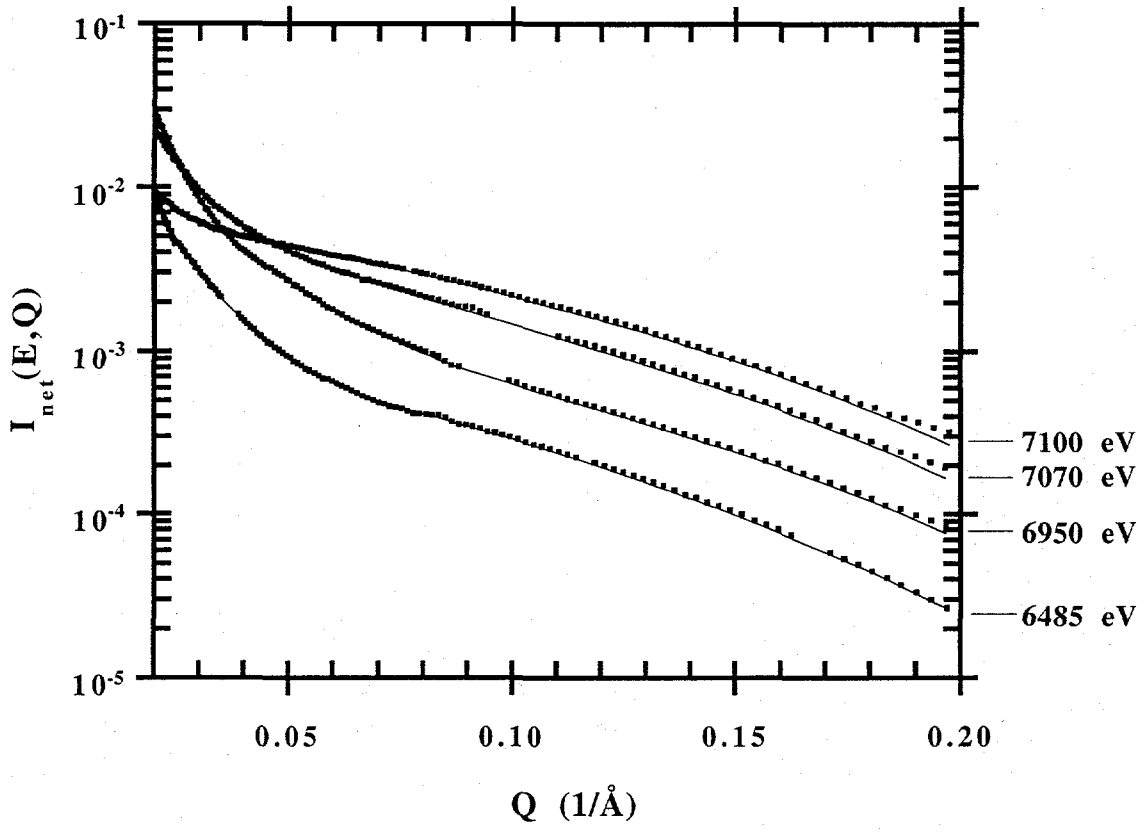

Fig. 1 Measured (symbols) and maximum entropy fits (lines) of net scattered SAXS intensity curves for the annealed ternary alloy taken at various photon energies near the Mn-K and Fe-K absorption edges.

where r_e is the electron radius and $n_{scat,matrix}$ and $f_{scat,matrix}(E)$ are the average atomic number density and atomic scattering factors of the scatterer and matrix, respectively, r is the scatterer radius, and F(r) is the volume fraction size distribution.

The mathematical technique of maximum entropy analysis [7] may be used to extract F(r) from the measured net scattering intensity curves. The analysis was applied to both the irradiated and annealed sample data over the Q range of 0.02 1/Å≤Q≤0.20 1/Å. Fig. 1 shows an energy series of measured net scattering curves with their corresponding maximum entropy fits derived for the annealed sample. The variation of the net, normalized scattering data with photon energy evident in the figure is an indication of the anomalous scattering effect. The energies indicated in Fig. 1 span the Mn-K and Fe-K absorption edges. Although data was also taken at higher energies near the Cu-K edge it proved unusable due to very intense matrix fluorescence of the the dominant Fe component in the alloy. This fluorescence contributed a strong background signal making differentiation of the SAXS difficult.

Size distributions, N(r), for the samples are simply obtained from the volume fraction size distributions by dividing it by the scatterer volume: $N(r)= F(r)/(4\pi r^3/3)$. Fig. 2 shows selected normalized, contrast-weighted size distributions from the annealed and irradiated samples. Since a scattered intensity standard was not used in these experiments, it is not possible to derive quantitative values of scattering center number densities from this analysis. However, from these distributions it is possible to obtain the average radius of scatterers which are found to be 14.7±0.6 Å and 11.4±0.8 Å for the annealed and irradiated samples, respectively. Since the number density in the sample is a constant, variations in the distribution height with energy observed in the figure are again indicative of the contrast variations owing to the anomalous scattering effect

Integrating the volume fraction size distributions gives an experimental measure proportional to the scattering contrast, $\left|\Delta\rho_e^{meas}(E)\right|^2$. The resulting observed energy variations in contrast may be used to quantify the composition of the scatterers through comparison with

calculated values determined from the known variation of atomic scattering factors with photon energy. The annealed sample's treatment was designed to precipitate Cu-Mn. If scatterers consisting solely of Cu_xMn_{1-x} precipitates, where x is the fraction of Cu atoms in the precipitate, and a matrix consisting of pure Fe are assumed, the contrast portion of eqn.[2] may be calculated as,

$$\left|\Delta\rho_e^{CuMn}(E)\right|^2 = r_e^2 \left|x\, n_{Cu}\, f_{Cu}(E) + (1-x)\, n_{Mn}\, f_{Mn}(E) - n_{Fe}\, f_{Fe}(E)\right|^2 \qquad [3]$$

Fig. 3 compares normalized contrast calculations (eqn.[3]) for different precipitate compositions with normalized, measured contrast values for the annealed sample (closed symbols) and the irradiated sample (open symbols) at energies near the Mn-K edge and the Fe-K edge. The measured data appears to best match x=0.85 indicating Cu-rich, 15 at.% Mn precipitates. This result is consistent with magnetic to nuclear small-angle neutron scattering (SANS) measurements [8] in the identical annealed alloy which indicated Cu-rich precipitates containing about 4 at.% Mn. A Guinier analysis of this SANS data determined a spherical precipitate radius of 17.7Å, also in reasonable agreement with the 14.7Å value observed in this ASAXS work. Furthermore, the similarity between the annealed and irradiated contrast variations observed in Fig.3, particularly in the vicinity of the Fe-K absorption edge, is consistent with the notion that both treatments produce the same type of scatterers (i.e. Cu-rich precipitates). This conclusion was also reached in lower energy electron irradiation experiments of an Fe-1.5 wt.% Cu alloy irradiated at 295°C and examined with high resolution electron microscopy [9].

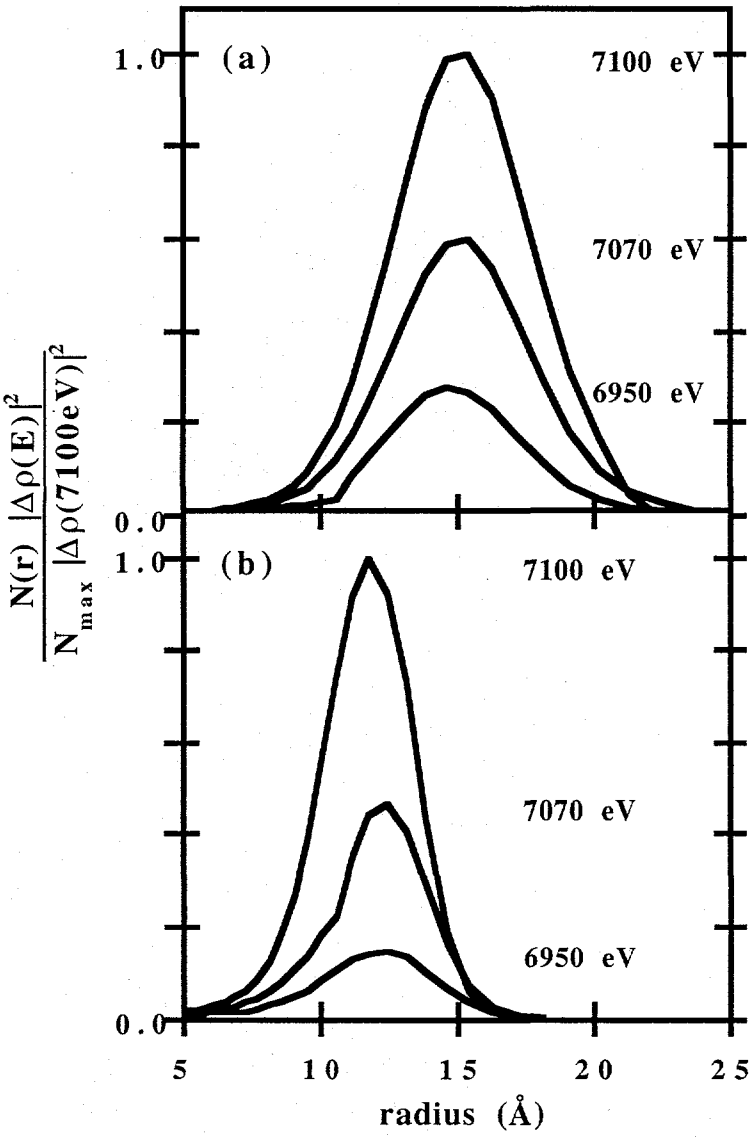

Fig. 2 Contrast-weighted, scatterer size distributions in the ternary alloy normalized to the maximum value at photon energy 7100eV for (a) annealed sample and (b) the irradiated sample.

Again, in the absence of an intensity standard, it is not possible quantify values of volume fractions and number densities. It is possible, however, to evaluate relative values for the two treatments of interest after first accounting for an additional normalization. The absolute level of the net scattered intensity, in addition to the various terms listed in eqn.[2], also depends on the total volume of material analyzed which is contained in the *Const* term of the eqn.[2]. For the same incident photon beam probe area, this volume will scale with the sample

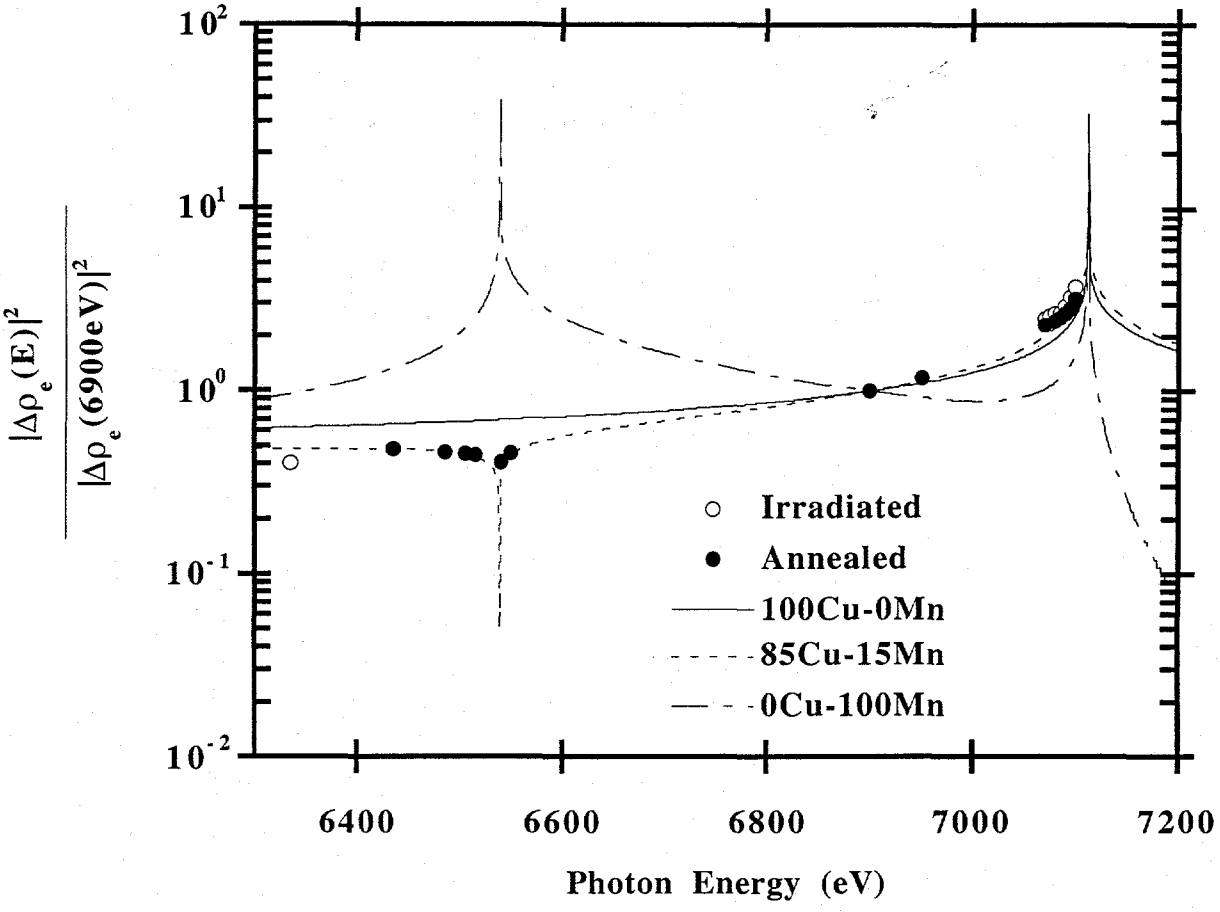

Fig. 3 Measured (symbols) and calculated (lines) contrast ratios as a function of photon energies near the Mn-K and Fe-K absorption edges. Ratios determined relative to the value at 6900eV. Calculated ratios shown for three different atomic percent concentrations of Cu-Mn precipitates.

thickness. Hence, when comparing different samples it is necessary to normalize their net scattered intensity by sample thickness. A simple analysis of measured transmission values indicates that the annealed sample is about 1.7x the thickness of the irradiated sample. Therefore carrying this thickness normalization through the analysis, the annealed sample is found to have about 1.8x greater volume fraction of precipitates than the irradiated sample. Assuming a monomodal size distribution with scatterers of radius, r_{mean}, the number density is related to the integrated volume fraction, F_0, according to, $N_0 = F_0/(4\pi\ r_{mean}{}^3/3)$. Thus the irradiated sample contains about 1.2x more, but smaller, scattering centers than the annealed sample.

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