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THE ROLE OF ENVIRONMENTAL CONDITIONS IN IN-SITU EXPERIMENTS
IN THE HIGH VOLTAGE ELECTRON MICROSCOPE

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ABSTRACT

Thin foil specimens may undergo changes in microstructure during examination in a high voltage electron microscope as a result of specimen interaction with the electron beam and/or its surrounding gaseous environment. When these effects are recognized, and in-situ experiments are performed under well-controlled conditions, useful information can be derived from the observed changes in structure. This is illustrated with three examples; electron beam-induced surface oxidation of Fe-Al alloys, the detection of oxidation-induced surface stresses by dislocation network formation, and the investigation of the structure of glassy phase ceramics through electron beam-induced ionization effects.

RESUME

Une lame mince peut, au cours d'observations en microscopie électronique à haute tension, interagir avec le faisceau d'électrons et/ou avec l'atmosphère environnante. Lorsqu'on sait détecter ces effets en connaissance de cause, on peut mener à bien des expériences in-situ dans des conditions bien contrôlées et obtenir des renseignements utiles concernant les modifications de structure. Ceci est illustré à l'aide de trois exemples; l'oxydation superficielle d'alliages Fe-Al induite par le faisceau d'électrons, la mise en évidence de contraintes liées à la présence d'un film d'oxyde en surface provoquant l'apparition de réseaux de dislocations, et l'étude de la structure des phases amorphes

à l'intérieur de céramiques grâce aux effets d'ionisation dus au faisceau d'électrons.

INTRODUCTION

During the study of foils in an electron microscope, the observed microstructure can be altered due to (1) interaction of the electron beam with the specimen, (2) interaction of the specimen with the microscope environment, or (3), a combination of both. When the origin of the structural change is not recognized, misinterpretation of the results may occur, and misleading conclusion drawn. Conversely, when the conditions of the in-situ experiment in the microscope are closely controlled, the effects can be used to advantage. In the present contribution these positive aspects are emphasized, and several examples of specimen electron beam environment interactions are given which yielded valuable structural information.

BEAM ENHANCED OXIDATION OF Fe-20% Al

The dynamic nature of the environment a specimen is exposed to in an electron microscope is often overlooked even though residual gas analysis of the microscope vacuum has shown that simple operations, such as replacing plates or film, can drastically increase the partial pressure of reactive gases. A classic example of spurious changes in specimen structure originating in this way has been described by Dahmen. During a study of short range ordering in Fe-20% Al it was noticed that after extended viewing of specimens at 125KV a high density of small domains grew in the region exposed to the electron beam, Fig 1. These domains, which could easily be confused with the short range ordering under investigation, were in fact identified as an fcc spinel phase with a

lattice parameter of $\sim 8.1 \text{ \AA}$ growing in epitaxy with the matrix. When the intensity of the electron beam was deliberately increased the oxide particle growth could be readily followed through changes in the diffraction pattern. Sequences of 110 patterns, recorded at ambient temperature, and at -195° C in a cooling stage, are given in Fig 2.

In addition to the matrix and superlattice spots, reflections originating from the oxide particles (indicated by the lines) may be seen to develop with increasing exposure to the electron beam. The temperature insensitivity of the growth rate indicates an athermal process or one with a very small activation energy. These effects have been satisfactorily explained by an oxidation mechanism whereby absorbed H_2O molecules are cracked by the electron beam and react with surface atoms to form oxide islands (Margominsky et al, Ranke and Jacobi).

THE STUDY OF OXIDATION-INDUCED STRESSES BY NETWORK FORMATION IN ELECTRON-IRRADIATED Al-Mg ALLOYS

When a pure FCC metal foil is electron-irradiated in an HVEM at an appropriate temperature, interstitial loops nucleate in the center of the foil, grow, and eventually form a dislocation network. Loop-free zones are found at each surface because the surfaces are good sinks for point defects. During a study of the effect of surface condition on the formation of radiation damage in Al-11% Mg (Westmacott) it became apparent that the presence of oxide films on the foil surfaces completely altered the distribution of the damage in the foil. In this foil specimens deliberately oxidized for 2-1/2 months at room temperature prior to irradiation, preferential formation of interstitial loops at the metal-oxide interface was observed, see Fig 3(a). After post-irradiation annealing the dislocation loops interacted to form irregular

dislocation networks, (Fig 3(b)). The nature of the network was found to vary with the foil orientation; in foils with an {013} surface orientation hexagonal networks were formed, whereas in {001} foils the networks consisted of a square array of dislocations lying approximately along $\langle 110 \rangle$ directions. A contrast analysis of a {001} network is given in Fig 4. In 200 reflections both sets of dislocation are in good contrast; however, when 220 or $2\bar{2}0$ reflections are excited the dislocation sets lying parallel to $\bar{g}$ exhibit residual contrast while the set lying normal to $\bar{g}$ show $\bar{g} \cdot \bar{b} = 2$ contrast. This behavior is consistent with the **dislocations** having Burgers vectors normal to the diffraction vector, i.e. the array consists of pure edge dislocations with Burgers vector lying in the plane of the foil.

The results have been interpreted in terms of an oxidation-induced stress model. Oxidation of Al-Mg alloys is known to result in the formation of Mg O surface films (De Brouche) consequently, since the Pilling-Bedworth ratio for Mg O and Al-Mg is greater than unity, tensile stresses develop in the matrix and compressive stresses in the oxide. It is apparent that during electron-irradiation in the HVEM, interstitial loops have nucleated and grown in the metal at the oxide-metal interface in response to the tensile stresses. Furthermore, the Burgers vector of the loops in each set is the same and is such as to provide maximum stress relief in the foil surface, i.e., of the six possible **Burgers vector** perfect prismatic interstitial loops can have, the two selected are the ones lying in the plane of the foil.

The formation of such interfacial networks can be used to monitor stress build up during oxidation, and in-situ HVEM oxidation experiments

in an environmental cell (in progress) are exploiting this example of beneficial electron beam-specimen-environment interactions.

IONIZATION DAMAGE IN GLASSY PHASE CERAMICS

Certain ceramic materials are consolidated from powders by adding sintering aids such as Mg O or CaO. Such materials are found to contain pockets of glassy phase interspersed between the crystalline grains. During a study of the nature of these glassy phases it was observed that the structure changed during exposure in the electron microscope beam. After only short exposures at low accelerating voltages under normal viewing conditions bubble defects nucleated and grew. This effect was first reported by Drew and Lewis, and has been the subject of a recent more extensive study by Laval and Westmacott. A typical sequence illustrating the changes observed in the glassy phase of Si_3N_4 is given in Fig 5. which also shows that the crystalline grains surrounding the glass are unaffected by the beam. Similar changes in structure were found in glassy regions in Mn Zn ferrite and Zn O. From HVEM studies of the voltage and electron flux dependence of the bubble growth rate it was concluded that the effects were due to an ionization damage process peculiar to the glass structure.

A model, consistent with the work of Lineweaver on the oxygen outgassing of glass under an electron beam, was proposed. According to this model the normal covalent bonding in the SiO_2 glass structure, Fig 6a, is modified by the Mg O or Ca O additions, which are concentrated in the glass phase, and regions of ionic bonding are created, Fig 6b. During exposure to electrons in the microscope electron transfer processes in these regions create free metal and liberate free oxygen.

Because the solubility of oxygen in glass is low, supersaturation of the gas occurs rapidly and precipitation of gas bubbles leads to the structure observed in the electron microscope.

It is also shown how the formation of gas bubbles is dependent on the composition of the glass. When polyvalent impurities are present in sufficient concentrations in the glass changes in the oxidation state can occur and free oxygen liberation is inhibited.

CONCLUSIONS

The structural changes that can occur in thin foil specimens during exposure to the electron beam and/or microscope environment in a high voltage electron microscope can be exploited to further understanding of material properties.

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FIGURE CAPTIONS

- Fig. 1. Dark field image of surface oxide islands on Fe-20% Al after 60 Min. exposure in the electron beam.
- Fig. 2. Progressive changes in the (110) diffraction pattern after beam exposures of 2, 10 and 30 min. respectively at 20° C and - 195° C. Note the growing intensity of the (111) oxide zone (denoted by the lines).
- Fig. 3. (a) The formation of near-surface interstitial dislocation loops in Al-11% Mg foils preoxidized prior to electron-irradiation in the HVEM at 180° C. (b) Same area showing dislocation network formation after subsequent annealing at ~230° C.
- Fig. 4. Series of micrographs illustrating the contrast behavior exhibited by (001) foil networks. In (a) $\bar{g} = 020$ and both sets of dislocations are in contrast. (b) with $\bar{g} = \bar{2}20$ the dislocations parallel to $\bar{g}$ exhibit residual contrast, while those perpendicular to $\bar{g}$ show $\bar{g} \cdot \bar{b} = 2$ contrast. (c) the reverse behavior from (b) is seen with $\bar{g} = \bar{2}\bar{2}0$.
- Fig. 5. Sequence of micrographs showing the nucleation and growth of gas bubbles in the glassy phase of Si_3N_4 during exposure to the electron beam.
- Fig. 6. Schematic representation of
- a) silicon oxynitride structure and
 - b) Modification produced by addition of CaO or MgO : Si-O⁻ dangling bonds are created.

XBB 778 7450

Fig. 1

XBB 777 6583

Fig. 2

Fig. 3 (a)

Fig. 3 (b)

XBB 771 578

Fig. 4 (a)

XBB 780 13277

XBB 780 13276

Fig. 4.(b)

XBB 780 13278

Fig. 4 (c)

XBB 791 500

Fig. 5

Fig. 6 (a)

(b)

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Fig. 6 (b)

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