PRECIPITATE PHASESComparative evolution of thermal colloids developed in MgO crystals implanted with alkali metal ions

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Comparative evolution of thermal colloids developed in MgO crystals implanted with alkali metal ions

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Résumé. — Nous avons étudié par M.E.T., le paramètre, la structure, la nature et l'orientation des précipités obtenus par recuits thermiques de monocristaux de MgO implantés avec des ions alcalins (Li^+, Na^+, K^+). A partir du calcul de la limite de cohérence et de considérations sur l'énergie interfaciale, nous proposons une explication de certaines différences observées dans l'évolution de ces précipités.

Abstract. — We have studied by T.E.M., the lattice parameter, the structure, the nature and the orientation of precipitates obtained by thermal annealings of MgO single crystals implanted with alkali ions (Li^+, Na^+, K^+). From the calculation of the critical size for coherency, and from considerations on interfacial energy we purpose explaining some differences observed in the evolution of these precipitates.

1. Introduction.

— Magnesium oxide single crystals have been implanted with 60 to 470 keV alkali metal ions (Li^+, Na^+, K^+) up to about 10^{17} ions $\times$ cm^{-2} doses in order to obtain a mean projected range R_p and a standard deviation in projected range of about 3 000 Å and 800 Å respectively.

The implanted area is much damaged [1]. The concentration of implanted atoms is very high ($\simeq$ 20 %) and their precipitation can occur when the temperature is sufficient to allow the diffusion. On account of disorder caused by knocks of implanted particles in the lattice, other precipitations can happen (magnesium, metal's oxides or mixed oxides...). For instance, Li_2O precipitates have been observed in Li-doped MgO [2].

An absorption band attributed to the presence of alkali metal precipitates embedded in the MgO matrix appears at an annealing temperature of about 573 K (Li, Na) and 723 K (K) [3, 4]. When the crystals are annealed at higher temperatures the evolution of these bands shows that the size of these precipitates increases.

2. Study by T.E.M. of alkali metal precipitates.

— Annealed samples have been observed, in the implanted area, by T.E.M. [1, 5, 6]. The lattice parameter, the structure and the nature of precipitates have been determined by electronic diffraction, and for the small Li precipitates, with moiré pattern. We have only identified precipitates of implanted atoms. Their structure and lattice parameter are approximately those of bulk alkali metal, except for the small Li precipitates.

2.1 By simultaneous diffraction on the precipitates and the matrix and, in some cases, by use of matrix Kikuchi lines, we have determined their orientation relationship with respect to the matrix.

2.1.1 *Li case.* — For a 973 K thermal annealing, all the precipitates have an unusual f.c.c. structure ($a = 4.4$ Å) and they are in simple orientation with the matrix [5, 6] : (001) Li$/\!/$(001) MgO and [100] Li$/\!/$[100] MgO. For a 1 073 K annealing most of them have still the same structure and orientation but for a 1 173 K thermal annealing most of them have the usual b.c.c. structure and their orientation is : (011) Li$/\!/$(111) MgO and [11$\bar{1}$] Li$/\!/$[0$\bar{1}$1] MgO.

2.1.2 *Na case.* — In this case, the lattice parameter of Na ($a = 4.29$ Å) is very close to the MgO matrix one ($a = 4.213$ Å) and for most of the precipitates, the epitaxy is simple : (001) Na$/\!/$(001) MgO and [100] Na$/\!/$[100] MgO [5]. Nevertheless, some of them, more large in general, have a different orientation.

2.1.3 *K case.* — Then the orientation relationship is not simple : for instance, (001) K approximately $/\!/$(0$\bar{1}$3) MgO and [010] K approximately $/\!/$[593] MgO for a large precipitate (2 500 Å) [1].

2.2 The size of the precipitates varies with the annealing temperature. For the Li precipitates, and for those of Na in simple relation with respect to the matrix, the biggest sizes are about 200 to 300 Å (1 073 K annealing) and 500 to 600 Å (1 173 K annealing). Their size distribution is very narrow. For the K precipitates the size distribution is large enough, the size ranging from 20 to 3 000 Å (1 073 K annealing).

3. Discussion on the coherency of precipitates. —

According to our observations Li precipitates may exhibit a f.c.c. structure with a lattice parameter (4.4 Å) close to the matrix one or a b.c.c. structure. We have experimentally ascertained a phase transformation from f.c.c. to b.c.c. structure for precipitates of about 250 to 300 Å [6] : the f.c.c. structure imposed by the matrix becomes unstable when the precipitate loses the coherency to lower the strain energy. To try to explain this evolution, it seems to be interesting to calculate this limit of coherency for Li precipitates and for the other ones (Na and K).

3.1 CALCULATION OF THE CRITICAL SIZE OF PRECIPITATES.

— Let P be a metallic precipitate (Li, Na, K) in a matrix M (MgO). If the precipitate is perfectly coherent (one molecule of precipitate takes the place of one molecule of matrix) the interfacial energy is zero and the strain energy per molecule of precipitate is given by [7] :

$$\Delta g_s = 2 \, \mu_M \, C(v_p - v_M)^2/3 \, v_p$$

with :

$$C = 3 \, K_p/(3 \, K_p + 4 \, \mu_M)$$

v_M and v_p are the specific volumes of molecules in the matrix and in the precipitate. K_p is the P bulk modulus and μ_M the M shear modulus.

Then the strain energy of a spherical precipitate (radius R) may be written :

$$\Delta G_s = \Delta g_s \frac{4}{3} \pi R^3 \frac{1}{v_p} = \frac{8}{9} \pi \mu_M \, C \left(\frac{v_p - v_M}{v_p} \right)^2 R^3 .$$

For an incoherent precipitate the strain energy is nearly zero, on the other hand, there is an interfacial energy (type high angle grain boundary). For a simplified calculation of the critical size, the transformation of a coherent phase to an incoherent one will occur when the strain energy is greater than the interfacial energy in order to minimize the total energy of precipitate.

Table I.

	Lattice parameter a (Å)	ΔH_{sub} (kcal/mole)	$\Delta H_{(110)}$ ergs.cm^{-2}	$\Delta H_{(100)}$ ergs.cm^{-2}	E_s ergs.cm^{-2}	γ_p ergs.cm^{-2}
Li	3.51	39.0	779	1 102	940	313
Na	4.29	25.9	346	490	418	139
K	5.34	19.8	171	242	206	69

3.1.2 Calculation of the critical size of precipitates.

— In the expression giving the critical size,

$$\mu_M = E_M/2(1 + v_M)$$

with E_M = Young's modulus = 2.48×10^{12} dynes.cm^{-2},

Then :

$$\tfrac{8}{9} \pi \mu_M \, CR^3(v_p - v_M)^2/v_p^2 \geqslant 4 \, \pi R^2 \, \gamma_p$$

(γ_p = interfacial energy per unit area of precipitate inside the matrix) and :

$$R \geqslant \frac{9}{2} \gamma_p/\mu_M \, C \left(\frac{v_p - v_M}{v_p} \right)^2 .$$

3.1.1 Estimate of the interfacial energy of precipitates.

— The interfacial energy (type high angle grain boundary) is about one third of surface energy of precipitate. We do not know the surface energy of an alkali metal, but we know that it must be equal to the surface enthalpy enlarged by a contribution due to the surface entropy which is nearly negligible at room temperature. We can calculate this surface enthalpy with a quasichemical method from the enthalpy of sublimation ΔH_{sub} [8]. Let us consider a metallic crystal in which the atoms have a coordination number Z. The number of bonds in one atom gram of crystal is : $Z\mathcal{N}_0/2$ ($\mathcal{N}_0$ = Avogadro number). The energy of a bond ε is equal to the enthalpy of sublimation divided by the total number of bonds : $\varepsilon = 2 \, \Delta H_{sub}/Z\mathcal{N}_0$. The surface enthalpy can be obtained by multiplying this value by the number of bonds broken to form an unit area. For instance, in the case of alkali metals (b.c.c. structure) the coordination number is 8 ; when the crystal is cleaved in the $\langle 100 \rangle$ direction, 4 bonds are broken which creates 2 surfaces.

Consequently the surface enthalpy per atom is $4 \, \varepsilon/2$. The density of atoms on this surface is $1/a^2$ (a = lattice parameter) and the surface enthalpy is : $\Delta H_{(100)} = \Delta H_{sub}/2 \, a^2 \, \mathcal{N}_0$. In the same way for a (110) face : $\Delta H_{(110)} = \sqrt{2} \, \Delta H_{sub}/4 \, a^2 \, \mathcal{N}_0$.

In table I, we have recorded the lattice parameter a, the enthalpy of sublimation ΔH_{sub}, the surface enthalpies $\Delta H_{(110)}$ and $\Delta H_{(100)}$ for the (110) and (100) faces, the mean enthalpy or surface energy E_s for Li, Na and K, as well as the interfacial energy γ_p of incoherent precipitates.

v_M = Poisson's ratio = 0.23. So we get the value $\mu_M = 10^{12}$ dynes.cm^{-2}.

In table II, we have recorded the bulk modulus of alkali metals, the values of $\left(\dfrac{v_p - v_M}{v_p} \right)^2$, C and the calculated critical radius.

Table II.

	Bulk modulus K_p (dynes.cm^{-2})	$\left(\dfrac{v_p - v_M}{v_p}\right)^2$	C	R (Å)
Li	0.116×10^{12}	0.014 9 (*)	0.080	118
Na	0.068×10^{12}	0.277	0.048 5	4.7
K	0.032×10^{12}	0.569	0.023 4	2.3

(*) For f.c.c. Li ($a = 4.4$ Å).

3.2 DISCUSSION. — Though the way to calculate the interfacial energy is simplified, the theoretical diameter (236 Å) in the lithium case is roughly equal to the one experimentally obtained (250 to 300 Å). These precipitates are f.c.c. and perfectly coherent at the first step of growth. After loss of coherency they become b.c.c. which is the stable structure for precipitates of this size [9]. Nevertheless, for the obtained orientation relationship, we assume that some planes [(011) Li and (111) MgO for instance] still coincide. Then the precipitates could have a weak strain energy and they could be partially coherent. The Na and K precipitates lose the coherency when they are small because the specific volume of their molecules is much larger than the one of MgO. Taking into account the orientation of most Na precipitates with respect to the matrix and their very close respective lattice parameters, we can assume nevertheless that these precipitates are partially coherent : then most of planes would be in coincidence (all the { 100 } planes but

only one plane out of two for { 110 } because' the structure is different). So the interfacial energy of such precipitates would be nevertheless weak enough (probably much below 139 ergs.cm^{-2}), but certainly a strain energy would be contributing to the energy of precipitate. On the other hand the K precipitates are not in a simple orientation with the matrix and are probably incoherent.

4. Conclusion. — In the total energy of a precipitate, we consider two terms : a strain energy ΔG_s proportional to the volume i.e. to R^3 and an interfacial energy E_i proportional to the area i.e. to R^2. So the ratio $E_i/\Delta G_s$ proportional to $1/R$ is large if R is small, it is the case when the precipitate is nucleated : then the interfacial energy is preponderant. By another way the critical number of atoms to form a nucleus is function of this energy [10]. At the first step of nucleation, the coherent precipitates (Li for instance) have a weak energy, therefore a weak critical number of atoms. They could be nucleated more easily, which would contribute to explain the differences observed in the appearance temperatures of Li, Na and K precipitates.

More, a weak interfacial energy on the one hand could lead to a more homogeneous precipitation in the matrix, and on the other hand could limit the process of coalescence, these influences together leading to a more narrow size distribution. This could explain the narrower size distribution for Li and Na than for K.

DISCUSSION

Question. — T. E. MITCHELL.

I presume that the reason that you never see Mg metal or alkali metal oxides is simply that MgO is more stable than Li_2O, Na_2O or K_2O ?

Reply. — G. CHASSAGNE.

Yes, I agree with this comment, indeed our observations confirm this view.

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