

## Key Experimental Parameters for Internal-Band Formation: Relationship Between Stress and Oxidation Kinetics in Silver–Magnesium Alloys

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*Microstructural features of dilute (1.3 to 5 at.%) Ag–Mg internally oxidized alloys were studied at temperatures from 400 to 750°C. The experimental conditions needed for oxide-band formation were determined. A model is proposed based on kinetics and stress-relaxation considerations that explains band formation from the first stages. The kinetics are driven by oxygen diffusion and the formation of hyperstoichiometric MgO clusters leading to a dilatation of the crystal. If the Mg content is high enough (>3 at.%), the stress state induced by the clusters form a diffusion barrier that is responsible for the formation of internal oxide bands.*

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**KEY WORDS:** silver alloys; internal oxidation; oxide bands; magnesium oxide; oxidation kinetics; internal stress.

### INTRODUCTION

Superficial oxide growth on metals was investigated in the early 1930s by Wagner.<sup>1</sup> The composition of oxides formed on alloys is dependent on the less-noble element, although this oxidation may be internal if the oxygen solubility is high enough. In 1959, Wagner proposed a second model to

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describe internal oxidation, neglecting external-oxide formation.<sup>2</sup> The oxidation occurs down to a certain depth, called  $\xi$ , which depends directly on oxygen and solute diffusion.

The basic parameters taken into account to express the kinetics of the oxidation reaction are: oxygen solubility ( $C_o$ ) and the diffusion coefficient ( $D_o$ ) in silver, and the solute concentration ( $C_B$ ) and its diffusion coefficient in silver ( $D_B$ ). The ratio between oxygen and solute atoms at the oxidation front is denoted by  $[(D_B/D_o) \ll (C_o/C_B) \ll 1]$ . We can distinguish two cases: first, neglecting solute diffusion  $[(D_B/D_o) \ll (C_o/C_B) \ll 1]$ , the oxidation-front distance from the surface is given by:

$$\xi = \left( \frac{2C_o D_o t}{\nu C_B} \right)^{1/2} \quad (1)$$

leading to the expression of the velocity of the oxidation front:

$$\frac{d\xi}{dt} = \left( \frac{C_o D_o}{2\nu C_B t} \right)^{1/2} \quad (2)$$

and in the second case, taking solute diffusion into account,  $[(C_o/C_B) \ll (D_B/D_o) \ll 1]$ , the distance  $\xi$  is given by:

$$\xi = \frac{C_o D_o}{\nu C_B} \left( \frac{\pi t}{D_B} \right)^{1/2} \quad (3)$$

and the velocity  $d\xi/dt$  is then expressed by:

$$\frac{d\xi}{dt} = \frac{C_o D_o}{2\nu C_B} \left( \frac{\pi}{D_B t} \right)^{1/2} \quad (4)$$

In silver–magnesium solid solutions,  $d\xi/dt$  can be calculated. Regardless of experimental conditions (temperature, oxygen pressure, solute concentration), the oxidation front moves at a faster rate if the solute diffusion is taken into account (Eq. 4).

Band formation during internal oxidation has been studied by many authors.<sup>3–8</sup> However, there are some deficiencies in the explanation, and further research is needed in order to establish a satisfactory model.

Although, some authors indicated that a critical oxidation-front velocity is needed to obtain internal bands,<sup>7</sup> periodic bands have been observed generally during the oxidation of relatively concentrated alloys (up to 2.5 at.% Mg) at high temperatures. In addition, silver nodules are formed on the surface of the alloys and a band-free zone exists close to the surface.<sup>3,5,6</sup>

At lower temperatures (400–500°C), we have previously reported bands of MgO and interband regions depleted in Mg.<sup>9,10</sup>

From the above results, some interpretations have been formulated. Meijering<sup>8</sup> proposed a mechanism based on stress, generated by the precipitating oxides. Douglass<sup>3,5</sup> supports this interpretation and suggests that internal stresses are responsible for higher activation energies, leading to both the slowdown of the kinetics and silver extrusion at the surface. Further information is needed at this time to improve the model of band formation.

In our preliminary results,<sup>9</sup> we focused our study on the Mg concentration profile within the matrix and on a systematic variation of parameters, such as, temperature and the initial microstructural state. From these results, a model has been proposed that takes into account Mg motion from the core to the surface, the generation of stresses and their relaxation, and the presence of a periodic diffusion barrier for oxygen.

This last model needs to be improved by implementing the relationship between oxygen diffusion and the band density. In this way, some key parameters such as temperature, Mg concentration, and grain size would be considered.

The objective of this study was to propose a model that takes into account atomic mobility (Mg, O, Ag) and the stress state leading to a diffusion barrier. This model is supported by experimental results that were not available in our initial interpretation.

## EXPERIMENTAL PROCEDURES

Silver–magnesium alloys (1.3–5 at.%) were prepared by melting silver (99.999%) and magnesium (99.95%), in a graphite crucible, under high-purity argon atmosphere in an induction furnace. The alloy compositions were determined by atomic-emission spectrometry (ICP-AES); a check on homogeneity was performed on different portions of the ingot.

Most studies were performed on polycrystalline alloys, prepared as cast ingots in the shape of 10-mm diameter bars. Some single crystals were prepared by the Bridgman method as 6-mm diameter bars. Both polycrystal and single-crystal bars were rolled to a thickness of 3 mm and then cut into 10 × 10 mm squares. Polycrystalline samples were subjected to different annealing treatments, under high-purity argon, in order to obtain different grain sizes. All samples were oxidized under a pressure of  $2 \times 10^4$  Pa.

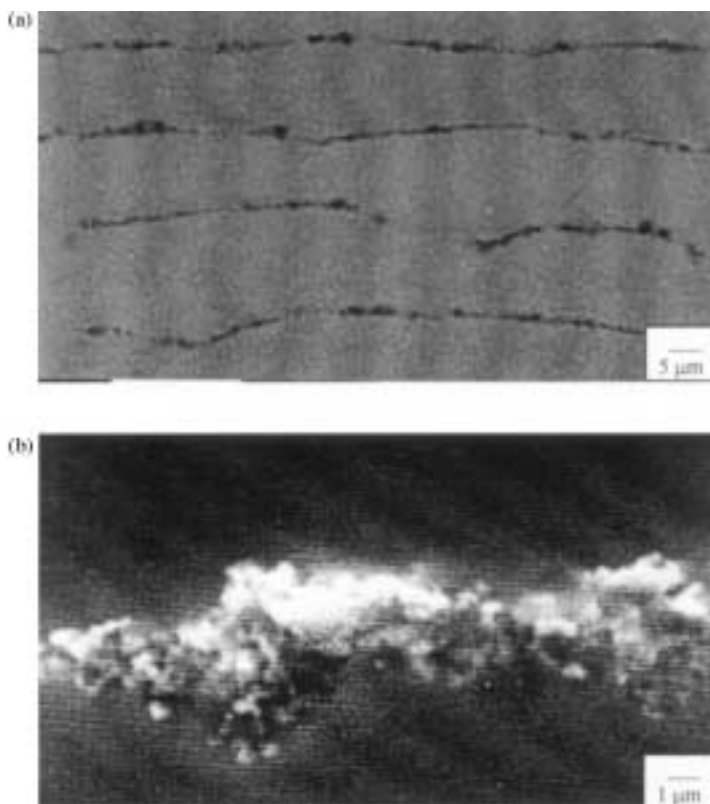
Standard metallographic preparation was used for optical microscopy. The oxidation front was revealed by etching in a solution containing 2% sulfuric acid and 2% chromic acid.

## RESULTS

Oxidation was performed on both monocrystalline and polycrystalline samples. In the case of polycrystalline alloys, recrystallization gave various grain sizes ranging from 5 to 500  $\mu\text{m}$ . All grains, regardless of size, contained annealing twins, as is well known in silver alloys.

In order to obtain band formation, it is necessary to use conditions far from those defined by Wagner, where the ratio  $C_oD_o/C_B D_B$  ranges from  $10^2$  to  $10^3$  (Fig. 1a). The bands, about 1- $\mu\text{m}$  thick, are very irregular in shape (Fig. 1b). From electron-diffraction results it was found that the bands consisted of incoherent MgO precipitates.<sup>9</sup>

Of the parameters affecting internal oxidation—magnesium concentration, oxidation temperature, microstructural state, oxidation pressure



**Fig. 1.** SEM images of internal-oxide bands in Ag-3.6Mg oxidized at 750°C for 1 month. (a) Band distribution and periodicity; (b) band morphology.

and sample thickness—the first three are the most important for band formation. Special attention was focused on the influence of the oxidation kinetics on band formation.

### Influence of Solute Concentration

Identical grain-size samples (100–150  $\mu\text{m}$ ) with different concentrations were oxidized under the same thermal conditions.

The theoretical distance of the oxidization front to the surface for Ag–1.32 at.% Mg oxidized at 550°C for 46 hr is 0.38  $\mu\text{m}$ . The experimental value is 0.30  $\mu\text{m}$ . An optical micrograph shows some twinned grains and an important intergranular precipitation. The grain size near the surface is smaller ( $\approx 20 \mu\text{m}$ ) than the initial one (Fig. 2). A periodic structure of precipitation was not observed. Nevertheless, the formation of a band is suspected from coarse lines parallel to the oxidation front.

On the other hand, a more concentrated alloy (Ag–3.54 at.% Mg), oxidized at 600°C for 17 hr, shows intergranular precipitation with the formation of bands distinctly marked at the oxidation front (Fig. 3). The grain size does not change during oxidation. This provides evidence of the influence of magnesium concentration on the formation of bands.

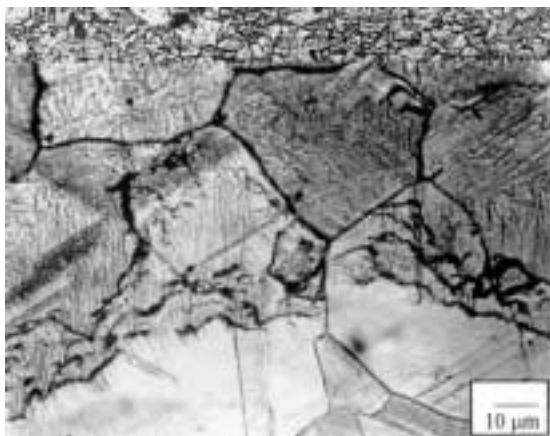
### Influence of Temperature

#### *Polycrystalline–Alloy Oxidation*

After recrystallization annealing at 800°C, an optical micrograph of a sample 4.06 at.% Mg shows a grain size ranging from 300 to 500  $\mu\text{m}$ . The oxidation of this alloy at temperatures from 400 to 720°C is illustrated in



**Fig. 2.** Optical micrograph of Ag–1.32 Mg oxidized at 550°C for 46 hr, showing precipitation in grain boundaries at the oxidation front.



**Fig. 3.** Optical micrograph of Ag-3.54 Mg oxidized at 600°C for 17 hr showing internal-oxide bands.

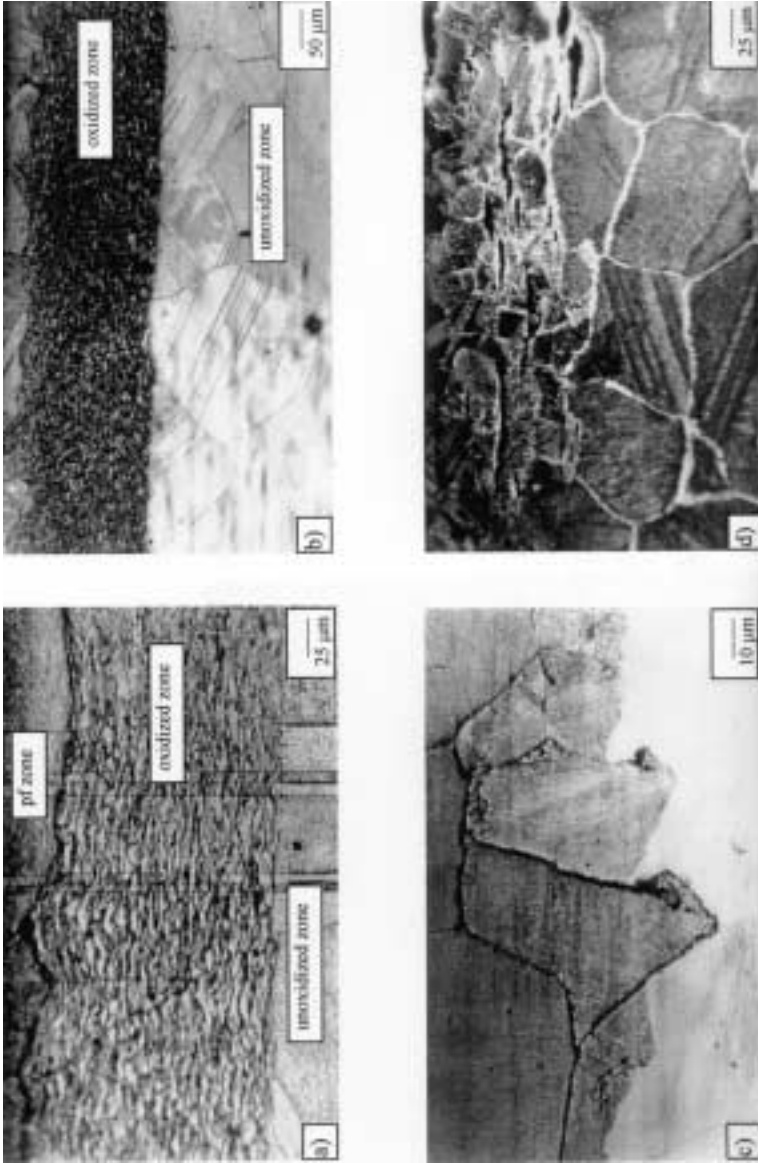
Fig. 4. For high-temperature oxidation (720°C), for 5 hr, a high density of bands is observed; the thickness of these bands is about 1  $\mu\text{m}$  (Fig. 4a), and they appear at a distance of 40  $\mu\text{m}$  to a depth of 200  $\mu\text{m}$ .

The EDS analysis in the band zone shows that the magnesium concentration is about 22 at.% Mg. Of course, this is not exclusively the magnesium content of the band, but it gives a relative quantity. In fact, the magnesium content is much higher inside the band itself, compared to the interband zones (thickness of 2 to 3  $\mu\text{m}$  with 3.5 at.% Mg).

In the band-free zone, located close to the surface, the following observations can be made:

1. Initially, the Mg concentration is homogeneous throughout the sample. During oxidation, Mg atoms are supposed to diffuse from the core toward the surface. However, measurements have shown that the magnesium concentration increases gradually from the surface (2.4 at.%) to the first band. Such an observation can be explained by the outward diffusion of silver.
2. The oxygen concentration decreases from the surface toward the first band. This reduction is significant (ratio = 2). It is suggested that this oxygen excess is responsible for a dilatation of the matrix cell and, therefore, of the creation of numerous defects.

To obtain a similar oxidized zone (to that observed at 720°C) at a lower temperature, Ag-4.06 at.% Mg was oxidized at 600°C for 24 hr. This



**Fig. 4.** Optical micrograph of Ag-4.06 Mg oxidized at (a) 720°C for 5 hr; (b) 600°C for 24 hr; (c) 500°C for 70 hr (note the absence of internal-oxide bands); (d) 500°C after 166 hr of oxidation (note the appearance of bands).

is illustrated in Fig. 4b. As in the previous case, one observes: (1) a band-free region of  $40\ \mu\text{m}$  width; (2) a zone,  $200\ \mu\text{m}$  thick, having a very high band density.

This alloy, oxidized at  $500^\circ\text{C}$  for 70 hr, would theoretically lead to an oxidized zone of 0.32-mm thick. However, Fig. 4c shows that no bands formed during this oxidation. Most precipitates of MgO are located in boundaries of divided grains that have a size of about 100 to  $150\ \mu\text{m}$ . The same behavior was seen at  $400^\circ\text{C}$ .

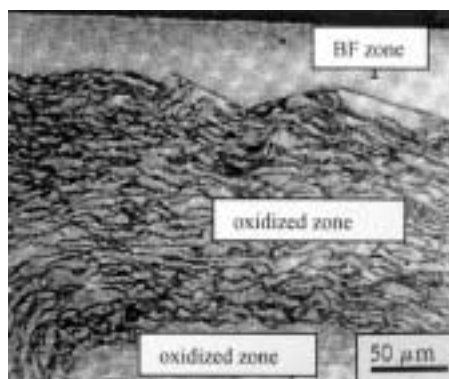
### *Monocrystalline–Alloy Oxidation*

The oxidation of a monocrystalline alloy (Mg–2.89 at.%), at  $750^\circ\text{C}$  (Fig. 5) gives a high-density, periodic band sequence. This morphology is analogous to that observed during the oxidation of polycrystal material under the same conditions.

However, at low temperatures ( $500^\circ\text{C}$ ), Fig. 6 shows straighter internal-oxide bands; the interband zone can be as wide as  $200\ \mu\text{m}$ . It is remarkable that a high density of dislocations is generated far from the surface. In this monocrystalline case, close to the surface, one observes (Fig. 7) a 5– $10\ \mu\text{m}$  recrystallized zone.

### **Influence of Oxidation Time**

Initially, Ag–4.06 at.% Mg, having a grain size of 300 to  $500\ \mu\text{m}$ , was oxidized at  $500^\circ\text{C}$ . After oxidation for 70 hr, intergranular precipitation was very clear, accompanied by recrystallization with smaller grains ( $100\text{--}150\ \mu\text{m}$ ); bands did not form (Fig. 4c).



**Fig. 5.** Optical micrograph of Ag–2.89 Mg monocrystalline, oxidized at  $750^\circ\text{C}$  for 12 days.



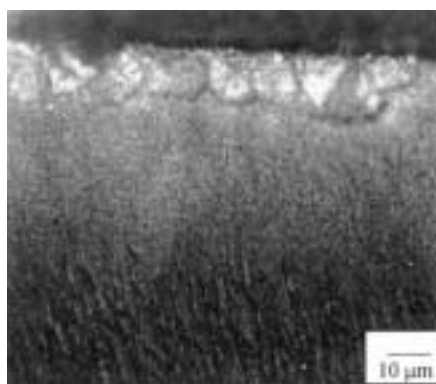


**Fig. 6.** Optical micrograph of monocrystalline Ag-2.89 Mg, oxidized at 500°C for 20 days, showing a spaced and straight-band morphology.

When the same alloy was oxidized for a longer time (166 hr), portions of bands are visible; precipitates still decorate the grain boundaries. On the other hand, at the band location, recrystallization takes place with smaller grains (30 μm) (Fig. 4d). Such behavior is time dependent, as reported by Douglass<sup>3</sup> for the internal oxidation of Ag-3 at.% Mg alloys at 600°C.

#### *Grain Size and Precipitation*

*Intergranular Precipitation and Band Formation.* Figure 4c and d show the large number of precipitates of magnesium oxide in grain boundaries.



**Fig. 7.** Optical micrograph of a recrystallized zone, close to the surface, after oxidation of monocrystalline Ag-2.89 Mg at 500°C for 20 days.

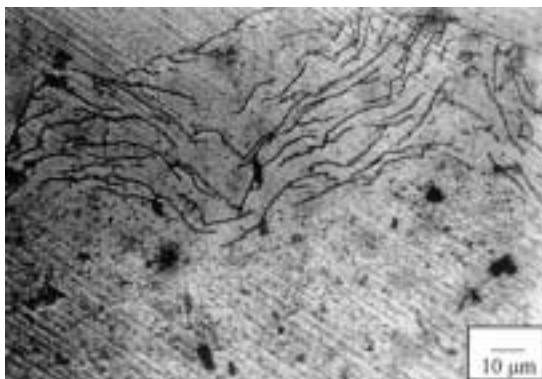


Fig. 8. Optical micrograph of Ag-3.54Mg oxidized at 600°C for 17 hr. Note the thin internal-oxide bands.

A comparison between these two micrographs shows significant amount of oxide in grain boundaries; this process occurs before band formation. These bands are located close to the initial grain boundaries. Although one observes some precipitates in the grain boundaries, the MgO content is higher in the bands, and recrystallization takes place around the bands.

*Grain Size and Band Thickness.* Two samples of the same alloy (3.54 at.% Mg) were annealed, under an argon atmosphere, at two different temperatures (600 and 800°C). For the sample annealed at 600°C, the grains have a size of about 120  $\mu\text{m}$ , whereas the sample annealed at 800°C had a grain size of about 400  $\mu\text{m}$ . Afterward, these two samples were partially oxidized at 600°C.

In the sample having the smaller grains, one observes much intergranular precipitation and the formation of short, thick bands ( $\approx 2 \mu\text{m}$ ) at the oxidation front (Fig. 3). Intergranular precipitation is limited in the coarse-grain sample and this situation is correlated to a high density of fine and regular bands within the grains (Fig. 8).

#### *Oxidation Kinetics*

Microscopic observations after chemical etching are used to locate the oxidation front  $\xi_{\text{exp}}$ . However, this is not sufficiently accurate, because small species identified as clusters are formed that are not detected by OM or SEM observations before the oxide is apparent.

From the results in Table I, it is clear that the oxidation kinetics are accelerated when precipitation takes place in grain boundaries. The slower kinetics were observed during band formation or when the matrix underwent recrystallization. It is necessary to note that the choice of Eq. (1) leads

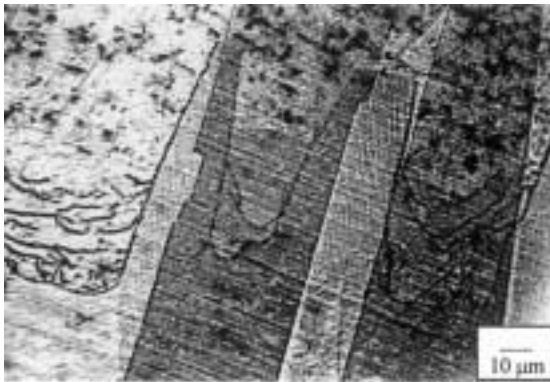
**Table I.** Results Obtained from Partially Oxidized Alloys

$C_{Mg}$ (at.%)	$\varnothing$ . grains ( $\mu\text{m}$ )	$T_{ox}$ ( $^{\circ}\text{C}$ )	$t_{ox}$ (hr)	$\xi_{exp}/\xi_{th}$	Microstructure
3.54	100–150	600	17	1.15	Intergranular precipitation
3.54	300–500	600	8	0.69	Band formation
4.06	300–500	720	5	0.53	Band formation
4.06	300–500	600	24	0.63	Band formation
4.06	300–500	500	70	0.59	Intergranular precipitation; recrystallized grains (100–150 $\mu\text{m}$ ) before bands
5.4	5–10	300	70	5	Intergranular precipitation

Characterized by the initial grain size, temperature, and oxidation time, the ratio between the experimental and theoretical positions of the oxidation front (calculated from Eq. 1), and the material microstructure.

to an overestimation of the  $\xi_{exp}/\xi_{th}$  value compared to Eq. (3), which takes into account magnesium diffusion. Therefore, one can conclude that the kinetics slowdown is due to band formation.

On the other hand, a comparison of two samples of similar chemical composition Ag–Mg 3.54 and 4.06 at.% with similar grain sizes and oxidized at 600 $^{\circ}\text{C}$ , leads to  $\xi_{exp}/\xi_{th}$  values 0.69 and 0.63. Figure 9 shows that Ag–3.54 Mg alloy has an oxidized zone and the start of band formation. In the case of the Ag–4.06 Mg alloy, there are numerous bands (Fig. 4b). There is a considerable difference in oxidation kinetics for these two alloys, which have the same initial microstructural condition. The presence of bands seems to be responsible for the slowing of kinetics.



**Fig. 9.** Optical micrograph of Ag–3.54 Mg oxidized at 600 $^{\circ}\text{C}$  for 8 hr. Note that bands appear in the oxidized zone.

We can summarize the results as follows:

- A minimal Mg content is needed ( $C_{\text{Mg}} > 2 \text{ at.}\%$ ) in order to obtain periodic oxide bands.
- Regardless of the oxidation temperature, a band-free zone is always observed close to the surface. The oxygen concentration in this zone decreases as a function of depth, whereas the magnesium concentration increases.
- Band formation is correlated with the matrix recrystallization.
- In the case of multiband formation, a kinetics slowdown occurs after intergranular precipitation. However, intergranular precipitation, without band formation, leads to an increase in the kinetics.
- Oxidation in single crystals at low temperature leads to a few bands with high-stress interband regions and recrystallization close to the surface. Band pattern is analogous to polycrystalline samples at high temperatures.

## DISCUSSION

The phenomenon of band formation, observed in relatively concentrated alloys ( $C_{\text{Mg}} > 2 \text{ at.}\%$ ), depends on several variables. Among these, one can consider the stress generated during oxidation and associated defects and the different diffusion regimes of atoms and the mobile elementary species.

### Formation of Oxide Particles

Fast oxygen diffusion in the silver bulk does not allow, on its own, the formation and growth of an external-oxide layer. This diffusion is accelerated, notably at low temperature, by the presence of grain boundaries. In dilute alloys, the magnesium flux can be disregarded compared to the oxygen flux. On the other hand, in concentrated alloys, the displacement of magnesium atoms is not negligible.

The instantaneous reaction between oxygen and magnesium atoms leads to the formation of clusters<sup>11-15</sup> that distort the crystal lattice. These clusters, appearing at low temperature, are difficult to observe by transmission-electron microscopy (TEM),<sup>16</sup> because they are very small and not well crystallized; they consist of magnesium atoms in substitutional silver sites and interstitial oxygen atoms and evolve toward stoichiometry by oxygen release and substitution of silver atoms by magnesium.

These clusters are supposed to be the origin of MgO precipitation. The precipitates coarsen by Oswald ripening, as demonstrated by TEM results.<sup>17</sup>

Their nucleation and growth are favored by the presence of grain boundaries, which contain a significant amount of oxygen. Thus, the precipitates are observed initially close to grain boundaries.

An explanation of the points will be made and let us conclude that the observed dilatation is triggered by the instantaneous reaction between oxygen and magnesium atoms.

One can evaluate the distortion of the matrix during clustering of magnesium and oxygen atoms prior to oxide formation.

Using the silver-radius value and the relation  $v = 8r^3N/\sqrt{2}$ , the molar volume is  $10.17 \text{ cm}^3$ .

Magnesium atoms having a Goldschmitt radius of  $0.16 \text{ nm}$  for 12-fold coordination, inserted in a FCC silver cell, have a molar volume equal to  $13.95 \text{ cm}^3$ . The clustering of magnesium atoms, in the silver lattice, leads to an increase of molar volume of 37% (which gives about 3.35% distortion of the lattice parameter). In such a dilated cell, the radius of octahedral sites that host oxygen atoms is equal to  $0.066 \text{ nm}$ , which is exactly that of the oxygen atomic radius. In this case, no dilatation could be attributed to oxygen atoms.

Given the MgO molar volume of  $11.25 \text{ cm}^3$ , the formation of precipitates leads to a molar-volume increase of 10.5% with regard to silver. Comparing the high-compact clusters of Mg atoms in silver with MgO, a notable difference regarding the degree of matrix distortion is noted. Let us suppose that, in the situation of very compact clusters, the magnesium atomic radius is different from that obtained in solid solution. This result can be explained by the proximity of oxygen atoms and by the relatively strong bonds between magnesium and oxygen during cluster formation.<sup>18</sup> Although it is difficult to know the exact conditions for the transition of the clusters to oxide precipitates, one could consider a maximal compactness of the cluster leading to MgO formation.

### Band Formation

Whatever the experimental conditions, internal-oxidation kinetics depend on oxygen diffusion.

- In polycrystalline alloys, bulk and intergranular-diffusion coefficients are different, particularly at low temperature. In the intergranular case, oxygen atoms accumulated in grain boundaries diffuse into the bulk afterward. If the initial solute concentration is high enough, a great deal of precipitation is observed close to grain boundaries, and magnesium-oxide bands appear roughly parallel to the surface, exhibiting an irregular thickness.

- In monocrystalline alloys, bulk-oxygen diffusion is responsible for more regular internal-oxide bands. They form in a very highly stressed zone parallel to the surface, the zone acting as a diffusion barrier for oxygen. Finally, the stressed zones become unstable, recrystallization occurs, and oxygen can diffuse again through the new grain boundaries. This process continually repeats, developing the periodical bands.

### *Kinetics*

In the case of intergranular precipitation without internal-band formation, faster kinetics are observed (see Table I, ratio  $\xi_{\text{exp}}/\xi_{\text{th}} = 1.15$  for  $C_{\text{Mg}}$  at.% = 3.54 at 600°C).

In monocrystalline samples with spaced straight bands (Fig. 6), the experimental and calculated values for  $\xi$  are similar because the kinetics decrease is scarcely affected by just two bands.

When bands form in polycrystalline alloys, the position of the oxidation front  $\xi_{\text{th}}$ , (last band or precipitates visible in grain boundaries) is always lower than the calculated value given by Wagner's relation (see Table I). Therefore, the oxygen-diffusion values during oxidation are different from those determined in pure silver (taken as reference values), as expected because of stresses associated with reactive diffusion. One can note that, according to the proportion of bands formed in the matrix, the ratio  $\xi_{\text{exp}}/\xi_{\text{th}}$  changes, band formation being responsible for the reduction of this ratio.

Discontinuous oxygen diffusion associated with precipitation phenomena can explain the periodic band formation. The following facts about oxygen diffusion in the alloy can be summarized as follows:

1. Diffusion is accelerated within grain boundaries and in solute-depleted zones.
2. To the contrary, diffusion is slower in the distorted matrix, particularly near the oxidation front where irregular oxide clusters exist (bands precursors). This effect is also observed within the bands enriched in magnesium.
3. Magnesium diffusion takes place close to the oxidation front and depends on the free oxygen coming from the surface, the grain boundaries, and oversaturated clusters. This allows oxidation to be maintained.

Furthermore, a comparison of our experimental results on monocrystalline samples with those of Bosch *et al.*<sup>7</sup> for Ag-3 at.% Mg shows that a minimum oxidation-front velocity  $d\xi/dt$  is not a good criterion for band formation as suggested by Bosch. In fact, for monocrystalline 2.89 Mg at.%, in which two internal bands formed, the calculated  $d\xi/dt$  from Eqs. (1) and

(2) is  $1.33 \times 10^{-9}/\xi$ , this value being lower than that calculated by Bosch (ranging from  $8.2 \times 10^{-8}/\xi$  to  $1.8 \times 10^{-7}/\xi$ ) for oxidation at low oxygen pressure.

### *Distortions in the Alloy*

During oxidation, the material undergoes successive deformation, during which both a matrix dilatation and relaxation occurs. The dilatation is due to magnesium and oxygen atoms in solid solution and species formed from them. The oxygen atoms of atomic radius 0.066 nm diffuse through smaller interstitial sites (0.060 nm) in the silver lattice. The magnesium atomic radius is 0.160 nm (coordination no. 12 in substitutional sites). Because the silver atomic radius is 0.144 nm, magnesium atoms dilate the unit cell. The elementary species, containing a limited number of oxygen and magnesium atoms, dilate the matrix. This dilatation is more important in the case of the more voluminous and irregular clusters containing an excess of oxygen. The cell distortions have been measured.<sup>12</sup> In an alloy (0.5 at.% Mg), oxidized at low temperature (300–400°C), the lattice parameter  $a$  has a value of 0.4095 nm; this measurement, made on a matrix containing very dispersed clusters, shows the strong dilatation of the silver cell ( $a_o = 0.4086$  nm) well. The results obtained for an alloy containing 1 at.% Mg give a value of  $a = 0.4100$  nm. Dilatation will be even higher for higher Mg contents ( $C_{Mg} > 3$  at.%).

Excessive dilatation leads to a relaxation mechanism aided by defects (point and line defects) and grain boundaries. Recrystallization close to the surface in monocrystalline alloys permits relaxation of the distorted matrix (oxygen excess).

Vacancies have a strong interaction with oxygen atoms enabling faster oxygen diffusion prior to Mg–O bond formation. Vacancies promote magnesium atom displacements.

### *Mechanism*

The appearance of oxide bands is characterized by the following steps:

1. An adsorption process takes place associated with the molecular oxygen dissociation. Consequently, a flux of oxygen atoms diffuses through the sample.

2. In the bulk matrix:  $(C_o D_o)_B \gg (C_{Mg} D_{Mg})_B$ . The clusters formed are initially very small and located near the surface. Evolution of clusters to oxide leads to dispersed precipitation. On the other hand, if the alloy initially contains small grains, oxidation at low temperature takes place by oxygen and magnesium diffusion to grain boundaries. The difference between both fluxes of atoms is less important. At an oxidation pressure

of  $2 \times 10^4$  Pa, one can establish that:  $(C_o D_o)j > (C_{Mg} D_{Mg})j$ . The volume precipitates can be formed in grain boundaries deep in the alloy.

3. As the oxidation front moves inward, the oxygen flux decreases, whereas that of magnesium atoms remains almost constant. The magnesium and oxygen content at the oxidation front leads to a concentration of clusters. In the beginning, these irregular clusters distort the matrix, acting as an oxygen-diffusion barrier. These unstable clusters change, releasing a part of their oxygen excess and thus allowing a sufficient oxygen potential to be maintained, which permits displacement of magnesium atoms from the nonoxidized zone.

As a result of the process mentioned above, there are two neighboring zones: The first zone is an oxidized zone very rich in magnesium, at the oxidation front, presenting a very strong dilatation. This zone is metastable and evolves toward a microstructural state characterized by small grains as a result of recrystallization. The precipitate alignment and, therefore, band formation are strongly induced by magnesium enrichment within the dilated zone. The recrystallized zone enables oxygen to diffuse through grain boundaries. A few oxygen atoms react with the excess magnesium, but most oxygen continues to diffuse into the bulk. The second zone is a nonoxidized region, depleted in magnesium, and greatly relaxed. As the band forms, the oxygen-diffusion barrier is lowered, and oxygen can diffuse again very quickly in this neighboring region, depleted in magnesium, because of the difference between the respective diffusivities:

$$(C_o D_o)B \gg (C_{Mg} D_{Mg})B$$

The process may occur deep in the sample, if the magnesium concentration is high enough to lead to a significant cluster density, which creates a new diffusion barrier for oxygen.

In addition, the matrix dilation and its relaxation produce a displacement of silver atoms. Their migration, toward the surface of the sample, has the effect of decreasing the overall magnesium concentration in this region.

The mechanism of oxide-band formation (Fig. 10), previously proposed<sup>9</sup> is, therefore, further reinforced by this study.

## CONCLUSIONS

As established from studies on internal oxidation of dilute Ag-Mg alloys at low temperature, MgO-like clusters are formed during the first steps of this process. These clusters are small and distort the lattice, but they do not act as obstacles for oxygen diffusion.



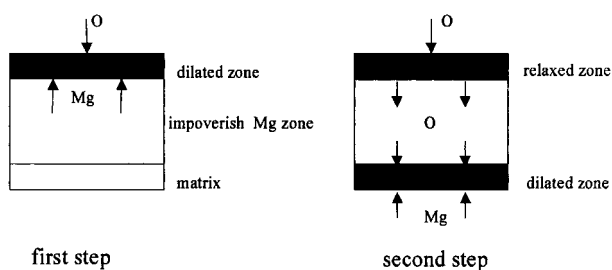


Fig. 10. Band-formation diagram.

The systematic kinetics study of internal oxidation presented here takes into account some key parameters (temperature, magnesium content, grain size), which allow the following conclusions to be made:

1. In concentrated alloys, a higher stress state takes place in magnesium-enriched zones, roughly parallel to the sample surface. The magnesium oxide located in these zones acts as an oxygen-diffusion barrier and evolves into internal bands. The formation of these bands is accompanied by recrystallization, which forms small grains and which allows oxygen to diffuse again and repeat the process.
2. Close to the surface, the oxidized regions are free of bands and are enriched in silver; the silver comes from zones where the bands are located. The diffusion of Ag atoms decreases magnesium concentration. This diffusion can be explained by the volume difference caused by the magnesium-oxide precipitation within the silver matrix. This effect is not surprising; it has already been observed in Ag-Mg and in other Ag-base alloys, such as (Ag-In), in which the molar volume of the oxide is higher than that of MgO.

## REFERENCES

1. C. Wagner, *Z. Phys. Chem.* **B21**, 25 (1933).
2. C. Wagner, *Z. Elektrochem.* **63**, 772 (1959).
3. D. L. Douglass, *J. Met.* p. 74 (1991).
4. S. Guruswamy, S. M. Park, J. P. Hirth, and R. A. Rapp, *Oxid. Met.* **26**, 77 (1986).
5. D. L. Douglass, *Oxid. Met.* **44**, 81 (1995).
6. D. L. Douglass, B. Zhu, and F. Gesmundo, *Oxid. Met.* **38**, 365 (1992).
7. R. A. Bosch, F. V. Level, and G. S. Ansell, *Trans. ASM* **57**, 960 (1964).
8. J. L. Meijering, *Advan. Mater. Res.* **5**, 1 (1971).
9. L. Charrin, A. Combe, J. Cabane, and A. Charaï, *Rev. Metall. Mater.* p. 669 (1998).
10. L. Charrin, A. Bequart-Gallissian, A. Combe, and A. Charaï, *Scripta Mater.* **42**, 701 (2000).
11. L. Charrin, A. Combe, and J. Cabane, *Oxid. Met.* **37**, 65 (1992).
12. L. Charrin, A. Combe, and J. Cabane, *Oxid. Met.* **40**, 483 (1993).

13. L. Charrin, A. Combe, A. Charai, F. Cabane, and J. Cabane, *J. Phys. IV* **4**, 41 (1994).
14. A. Combe and J. Cabane, *Oxid. Met.* **21**, 21 (1983).
15. M. B. Semega, L. Charrin, A. Combe, and J. Aride, *Phil. Mag. A* **66**, 1139 (1992).
16. A. Charai and G. Nihoul, *Phil. Mag. A*, **58**, 571 (1988).
17. A. Charai, C. Boulesteix, A. Combe, and J. Cabane, *Scripta Met.* **17**, 833 (1983).
18. L. Charrin, A. Combe, and G. Moya, *Acta Metall.* **29**, 1593 (1981).