

# Mechanical properties of internally oxidized silver alloys

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## Abstract

An increase in strength and a decrease in strain have been observed in Ag–0.4at.%Mg and Ag–0.2at.%Cu alloys during internal oxidation at 420 °C under 1 atm oxygen. This phenomenon, more pronounced in Ag–Mg alloy, is explained by a difference in coalescence degree: small precipitates are found in Ag–Mg (diameter about 1.5 nm) and voluminous precipitates in Ag–Cu (diameter about  $10^3$  nm).

A correlation between mechanical properties and gravimetric studies shows that the most important modifications of these properties occur when a maximal oxygen quantity is stored in irregular and non-compact clusters. This amount is higher than the quantity required for stoichiometric oxide, MgO. Moreover, these clusters evolve towards a more compact structure by a release of oxygen and a small evolution of mechanical properties.

In Ag–Mg alloys the grain boundary segregation of magnesium induces a small grain size (about 15  $\mu$ m); when oxygen penetrates this matrix, the size increases to about 40  $\mu$ m, allowing an increase in plastic deformation.

During internal oxidation of Ag–Mg alloys a high concentration of dislocations is observed, contributing to the strengthening of the material.

## 1. Introduction

The effects of internal oxidation on mechanical properties have been studied in the past by various authors [1–5]. More precisely, studies of polycrystalline Ag–Al and Ag–Si alloys [4] at different temperatures gave the relation between the degree of oxide dispersion and the tensile properties of the material. Experiments carried out on Ag–Al alloys [6] at high temperature established the relation between the strengthening mechanism and the oxide particle size (about 5 nm) and distribution.

The present investigation deals with the variation in tensile properties of Ag–Mg and Ag–Cu alloys during internal oxidation. Previous results concerning the nature of clusters in Ag–Mg and Ag–Cu alloys have been used [7–11]. In dilute Ag–Mg alloys oxidized at low temperature (280–550 °C), small clusters about 1–1.5 nm in size have been observed [9–11]. A study of Ag–0.34at.%Cu shows a precipitate size of about  $10^3$  nm [7].

The aim of this paper is to connect the mechanical properties with the size particle formed. Tensile and gravimetric measurements will allow us to correlate the evolution of strengthening and plastic deformation with the oxygen quantity stored in the matrix. The influence

of dislocation density and grain size will also be discussed.

## 2. Experimental procedure

The starting materials were an Ag–0.2at.%Cu alloy and two Ag–Mg alloys (0.4 and 0.6 at.%Mg). Strips were obtained from these three alloys by a technique described elsewhere [8, 9]. Flat tensile specimens with 20 mm  $\times$  5 mm gauge dimensions were then prepared. In order to eliminate any defect or distortion created during cutting, the specimens were annealed, before testing, under a vacuum atmosphere of about  $10^{-5}$  Torr for 10 h. All specimens were pulled at room temperature in an Adamel tensile-testing machine with a constant elongation speed of 1 mm min<sup>-1</sup>. The ends of the specimens were strongly held between grips so that no slipping was detected, even at loads up to five times the maximum load used in this investigation.

## 3. Experimental results: variation in tensile properties

The stress can be defined by the ratio (load)/(initial cross-section) in the specimen and the strain by the

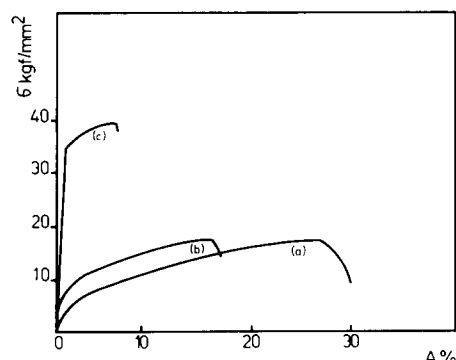
ratio (change in length)/(original length) × 100. The curves are slightly different from the true stress–strain curves because of the complexity of the deformation with increasing strain. This simplification has a small effect on the quantitative and comparative features of the curves.

### 3.1. Stress–strain relation

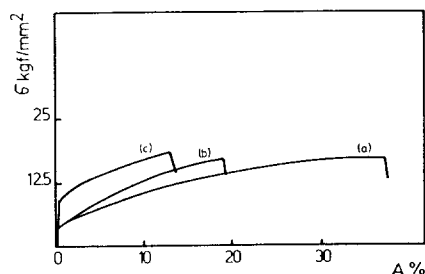
Stress–strain curves for pure silver, Ag–Mg and Ag–Cu alloys before and after internal oxidation are plotted in Figs. 1(a) and 1(b). In both cases pure silver presents a maximum elongation which increases with the thickness of the sample. Unoxidized alloys show a similar behaviour, but oxidized Ag–Mg strips present higher tensile and yield strength values and smaller elongation than Ag–Cu alloys.

### 3.2. Evolution during internal oxidation

Numerous specimens of Ag–0.4at.%Mg and Ag–0.2at.%Cu alloys were pulled at room temperature after different oxidation times. The tensile test for each specimen is represented by a curve similar to curve (c) in Figs. 1(a) and 1(b). From such curves, the yield



(a)



(b)

Fig. 1. (a) Stress–strain curves for specimens ( $e = 6.14 \times 10^{-3}$  cm) of (a) pure silver, (b) Ag–0.6at.%Mg unoxidized and (c) Ag–0.6at.%Mg oxidized at 420 °C under 1 atm oxygen. (b) Stress–strain curves for specimens ( $e = 8.67 \times 10^{-3}$  cm) of (a) pure silver, (b) Ag–0.2at.%Cu unoxidized and (c) Ag–0.2at.%Cu oxidized at 300 °C under 1 atm oxygen.

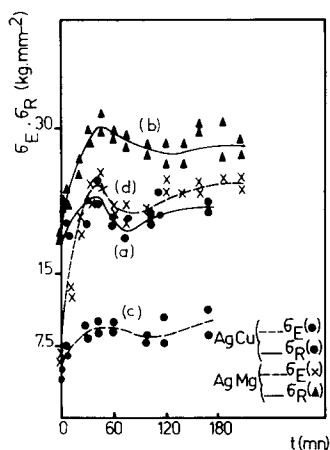


Fig. 2. Variation in (a, c) yield strength and (b, d) tensile strength as a function of oxidation time ( $p_{O_2} = 1$  atm) for (a, b) Ag–0.4at.%Mg ( $T = 420$  °C,  $e = 6.03 \times 10^{-3}$  cm) and (c, d) Ag–0.2at.%Cu ( $T = 300$  °C,  $e = 8.67 \times 10^{-3}$  cm).

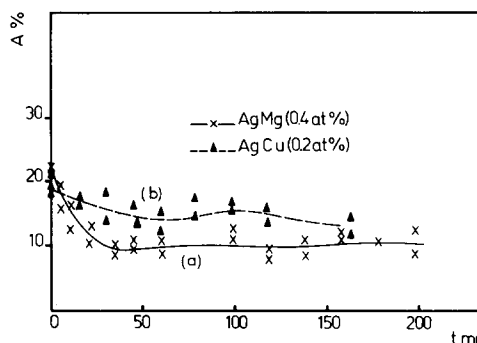


Fig. 3. Variation in approximate elongation as a function of oxidation time ( $p_{O_2} = 1$  atm) for (a) Ag–0.4at.%Mg ( $T = 420$  °C,  $e = 6.03 \times 10^{-3}$  cm) and (b) Ag–0.2at.%Cu ( $T = 300$  °C,  $e = 8.67 \times 10^{-3}$  cm).

strength, tensile strength and approximate strain are evaluated and plotted as a function of oxidation time (Figs. 2 and 3). From the curves in Fig. 2 we observe that the yield strength ( $\sigma_E$ ) and the tensile strength ( $\sigma_R$ ) are more important in Ag–Mg alloys than in Ag–Cu alloys. In all cases the shape of the curves shows an increase to a maximal value followed by a decrease (to a minimal value). At the end of the curve a low increase is again observed. The values of the approximate strain  $A\%$  plotted in Fig. 3 indicate that the most important decrease in elongation is observed for the Ag–0.4at.%Mg alloy.

From these results it appears that: (1) strengthening is more important in Ag–Mg alloys; (2) plastic deformation is more extensive in Ag–Cu alloys.

### 3.3. Correlation with oxygen fixation

Figures 4 and 5 report the values of  $\sigma_R$ ,  $\sigma_E$ ,  $A\%$  and the ratio of the number of oxygen atoms to magnesium

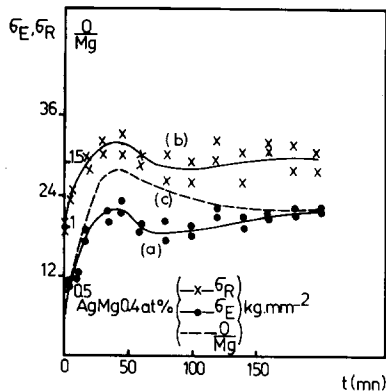


Fig. 4. Variation in (a) yield strength, (b) tensile strength and (c) O/Mg ratio as a function of oxidation time ( $T = 420^\circ C$ ,  $p_{O_2} = 1 \text{ atm}$ ) for Ag-0.4at.%Mg alloy ( $e = 6.03 \times 10^{-3} \text{ cm}$ ).

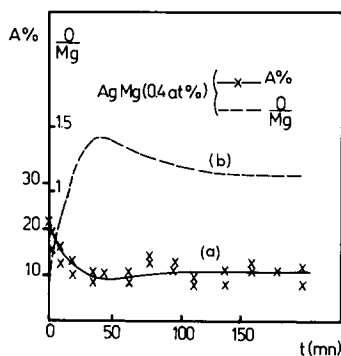


Fig. 5. Variation in (a) approximate elongation and (b) O/Mg ratio as a function of oxidation time for Ag-0.4at.%Mg alloy ( $e = 6.03 \times 10^{-3} \text{ cm}$ ).

atoms, O/M for an Ag-0.4at.%Mg alloy. We observe a coincidence in the maximal value of O/M with both the maximal values of  $\sigma_R$  and  $\sigma_E$  (Fig. 4) and the minimal value of  $A\%$  (Fig. 5). A higher oxygen excess (O/M  $\approx 1.45$ ) corresponds to a high strength and a minimal elongation of the material. During aging under an oxygen atmosphere a release of oxygen is observed and is associated with a diminution in strength and a slight increase in elongation.

## 4. Interpretation

### 4.1. Influence of oxygen quantity stored

When oxygen penetrates the matrix, the first particles formed are elementary species  $MgO^*$ ,  $Mg_2O^*$ , etc. [7–9, 12]. These species do not involve an oxygen excess because it would cause too large distortions of the silver matrix. From these elementary species, most of them being substoichiometric, a coalescence process occurs by oxygen excess fixation to produce irregular clusters

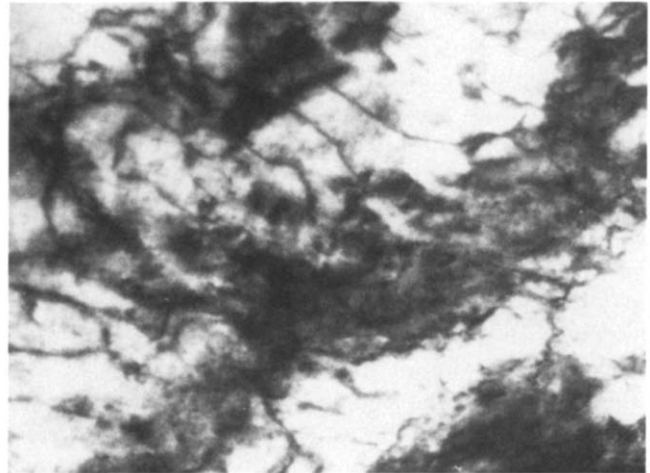


Fig. 6. TEM observation of an Ag-0.5at.%Mg alloy oxidized at  $530^\circ C$ .

[7, 12] which distort the surrounding matrix and allow the accommodation of up to three times the oxygen content for stoichiometric MgO [9]. If  $N$  is the number of magnesium atoms associated with oxygen in a precipitate, a linear relation between O/Mg and  $1/N^{1/3}$  can be assumed. O/Mg is equal to 1 (stoichiometric oxide) and 6 when  $1/N^{1/3}$  takes the values 0 and 1 respectively.

The irregular clusters are not stable and evolve towards a more compact structure [7–9, 12] by releasing part of the oxygen excess. The irregular clusters seem to be responsible for the maximal  $\sigma_R$  and  $\sigma_E$  values and the minimal  $A\%$  value observed. The important oxygen excess induces a high concentration of dislocations [7] (as shown in Fig. 6), which can also explain the observed properties.

The release of oxygen allows the rearrangement of the cluster to a more compact and less voluminous structure. This leads to a diminution in linear and point defect concentrations, as indicated by the slight evolution of the mechanical properties (decrease in strength and increase in elongation).

### 4.2. Nature of precipitates

#### 4.2.1. Silver–magnesium alloys

According to transmission electron microscopy (TEM) measurements [10, 11], at  $300^\circ C$  the cluster size is less than 1 nm. On the basis of this observation and the gravimetric measurements on Ag-0.4at.%Mg alloy in the temperature range  $280\text{--}550^\circ C$ , a cluster model in which the O/Mg ratio can take a value up to 3.2 was established [9]. In this cluster model, built on a unit cell of silver (Fig. 7), the number  $N$  of magnesium atoms is equal to 14. The volume  $V$  of the cluster is given by the relation  $Na_0^3/4$  and is equal to about  $0.25 \text{ nm}^3$ . Assum-

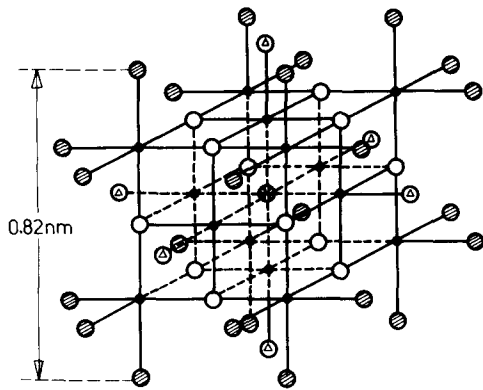


Fig. 7. Model of a compact cluster in dilute Ag-Mg alloys: ●, magnesium atoms; ⊗, ○, stable oxygen atoms; ⊙, ⊚, mobile oxygen atoms.

ing that this volume is a sphere, the diameter of the cluster is then  $d = (6\pi V)^{1/3} \approx 1.5$  nm. According to Kelly and Nicholson [13], the distance between these oxide particles is given by  $A = (\pi d^2 / 6X_{Mg})^{1/2}$ , where  $X_{Mg}$  is the atomic fraction of magnesium.  $A$  is about 17 nm for Ag-Mg alloys.

#### 4.2.2. Silver-copper alloys

Similar results to those obtained for Ag-Mg alloys enable us to propose the same oxidation mechanism in Ag-Cu alloys [12]. Nevertheless, the aging process is faster in Ag-Cu alloys and a rapid growth leads to precipitates resolvable by TEM. Thus the precipitate size can exceed  $10^3$  nm in Ag-0.34at.%Cu oxidized at 300 °C (Fig. 8). From this value the distance between the clusters,  $A$ , in dilute Ag-Cu alloys is evaluated as  $16 \times 10^3$  nm.

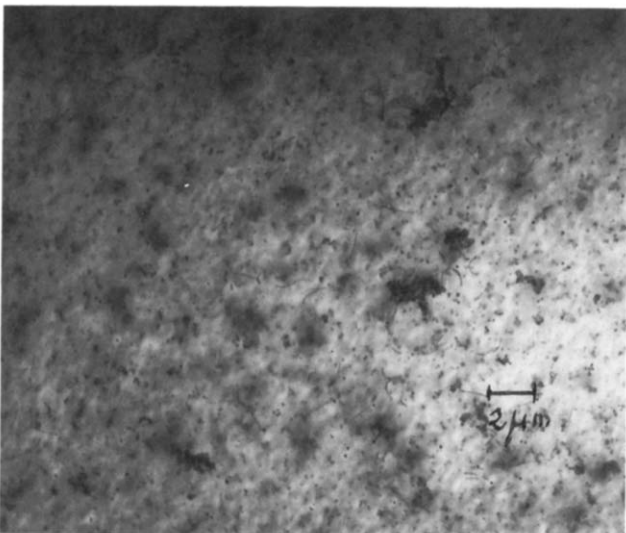


Fig. 8. TEM observation of an Ag-0.34at.%Cu alloy oxidized at 400 °C.

By comparison of these results in the Ag-Mg and Ag-Cu systems we can assume that a high dispersion favours the strength of the material and a conglomeration allows a more important plastic deformation. These properties are influenced by the grain size: grain boundary segregation of magnesium [14], leading to small grains (15 μm), is detrimental for ductility, while the coarsening process during internal oxidation, producing larger grains (40 μm), is favourable for an increase in plastic deformation.

## 5. Conclusions

A correlation between mechanical properties and gravimetric studies has pointed out a difference between the two alloys Ag-Mg and Ag-Cu during internal oxidation. The oxide particles in these two materials are very different: small particles in Ag-Mg (diameter about 1–1.5 nm) and coarser precipitates in Ag-Cu (diameter about  $10^3$  nm). The distance between these clusters is evaluated in the two cases. The results show a dependence of mechanical properties on precipitate concentration and size. A high oxide dispersion in Ag-Mg alloys favours strengthening ( $\sigma_R$  and  $\sigma_E$ ) of the material. A high conglomeration in Ag-Cu alloy allows plastic deformation.

The storage of a large oxygen excess induces a high concentration of dislocations and is favourable for high strengthening in Ag-Mg alloys. The increase in grain size during oxidation can explain the increase in plasticity of the material.

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