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**High-Temperature Internal Oxidation of
Ag/1.2 at. % Mg and Ag/0.25 at. % Mg-0.25 at. % Ni***

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HIGH-TEMPERATURE INTERNAL OXIDATION OF Ag/1.2 AT.% Mg AND Ag/0.25 AT.% Mg-0.25 AT.% Ni*

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High-temperature oxygen diffusion and internal oxidation in Ag, Ag/1.2 at.% Mg (Ag-Mg), and Ag/0.25 at.% Mg-0.25 at.% Ni (Ag-Mg-Ni) have been studied, mostly in air and 8% O₂, at 450–835°C. The focus of the studies was on thermogravimetric analysis, microhardness tests, and optical and electron microscopy observations of grain growth and its inhibition by oxidation. The internal oxidation of both alloys exhibited nearly identical activation energies (0.81 eV for Ag-Mg and 0.83 eV for Ag-Mg-Ni) and rate constants. The maximum O content of both alloys was superstoichiometric (e.g., O/Mg > 1.0) and the maximum O/Mg ratios were higher at lower temperatures than at higher temperatures (e.g., 1.25 at 500°C and 1.05 at 800°C). Diffusion of O in pure Ag was ≈60 times faster at 825°C and ≈400 times faster at 500°C than internal oxidation of either of the Ag alloys. Grain growth of both alloys and of the Ag was quantified between 450–800°C and related to internal oxidation.

INTRODUCTION

Precipitation-hardened Ag alloys are being developed for use as sheaths for high-temperature superconductor composite wires.^{1,2} Increased strength over that of pure Ag is needed for reliable strain tolerance and performance in high magnetic fields. Precipitation hardening of these Ag alloys is accomplished by internally oxidizing solute species such as Mg. Deformation studies of Ag/1.2 at.% Mg (Ag-Mg) in Ar and O at room temperature and 900°C have shown that when MgO forms in the alloy, hardness increases and ductility decreases substantially.³ Other studies related to internal oxidation of Ag/0.4–4 at.% Mg alloys have focused on mechanical properties, kinetic data, oxidation mechanisms, and microstructural development. Work has been carried out primarily at low temperatures (≈25–300°C) or high temperatures (to ≈900°C).^{4–7} The principal technological goal of the current study was to increase the strength of Ag-Mg and Ag/0.25 at.% Mg-0.25 at.% Ni (Ag-Mg-Ni) while maintaining oxygen transport kinetics similar to that of pure Ag.^{8,9}

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EXPERIMENTAL METHODS

Square coupons (≤ 0.5 g and 0.5 mm thick) of 99.9% Ag, Ag-Mg, and Ag-Mg-Ni were prepared from cold-rolled sheets. Thermogravimetric analysis (TGA) was performed in flowing 8% O₂ at 450–835°C.¹⁰ Cross-sectional Knoop hardness profiles were obtained for heat-treated coupons. The microstructures of polished surfaces were examined by optical microscopy and scanning electron microscopy (SEM).

RESULTS AND DISCUSSION

The kinetics of mass gain for the alloys was parabolic (Fig. 1). The parabolic rate constant was determined and plotted as a function of temperature to determine the activation energy for internal oxidation (Fig. 2). The activation energies were 0.81 eV for the Ag-Mg and 0.83 eV for the Ag-Mg-Ni. These values can be compared with values for the diffusion of oxygen in Ag (Fig. 3).¹⁰ At 825°C, oxygen diffusion in Ag was ≈ 60 times faster than the rate of internal oxidation of the alloys. This difference in rate widened at 500°C to nearly 400 times faster. It is possible that the relatively slow transport of oxygen through the alloy sheaths may affect the quality of Bi-based superconductors in hardened Ag sheaths.¹¹

For oxidation of the Ag alloys, the maximum ratio of O to solute (Mg or Ni) indicated that superstoichiometry was attained (i.e., O/solute > 1.0). The maximum values for Ag-Mg were ≈ 1.25 at 500°C and 1.05 at 800°C. Above $\approx 400^\circ\text{C}$, the solubility of O in Ag increases with temperature.^{8,9} However, in the Ag-Mg and Ag-Mg-Ni alloys, more O was soluble at lower temperatures.

Oxygen superstoichiometry can be attributed to clustering of O within the Ag lattice (Fig. 4). Clustering involves the combination of solute and O within the solvent matrix. The solute occupies a Ag lattice site. The O atoms then fill adjacent interstitial sites. For a cluster that contains one solute atom (Fig. 4), up to six O atoms can surround the solute. Thus, a solute atom such as Mg, which normally combines stoichiometrically with O, can capture more O atoms than its valence allows. Clusters can also contain several solute atoms. The O/solute ratios of these clusters are lower because the inner O atoms are shared among more than one solute atom. At a critical size, these larger clusters become distinct oxide precipitates within the solvent.

At high temperatures, the metal atoms can diffuse rapidly and clusters can become large. At lower temperatures, diffusion is slower and clusters are likely to remain smaller. As stated previously, smaller clusters retain more O atoms per solute atom, and thus this explanation is consistent with the experimental results. Transmission electron microscopy will be required to confirm this speculation.

Figure 5 shows the TGA results for internal oxidation of Ag-Mg and Ag-Mg-Ni heat treated at 700 and 800°C in 8% O₂. (An atmosphere of $\approx 8\%$ O₂ has been shown to be optimal for heat treating (Bi,Pb)₂Sr₂Ca₂Cu₃O_x superconductors.¹²) At both temperatures, the Ag-Mg-Ni exhibited a higher maximum saturation of O than the Ag-Mg, even though its concentration of solute atoms was less than half that of the Ag-Mg. A lower solute concentration implies smaller average solute clusters and the possibility for additional capture of O. The TGA data also show a gradual reduction or release of O after the maximum saturation point is reached. This effect can be attributed to the formation over time of distinct MgO precipitates. The O/Mg ratio decreases with cluster coarsening and MgO formation, leading to the expulsion of excess oxygen.

The clustering process is promoted by two mechanical effects. Large elastic distortions are induced by differences in lattice parameters between Ag and MgO and NiO. In addition, Ag has a higher linear coefficient of thermal expansion ($\alpha_{\text{Ag}} \approx 19 \times 10^{-6}/^\circ\text{C}$) than that of MgO ($\alpha_{\text{MgO}} \approx 12 \times 10^{-6}/^\circ\text{C}$) or NiO ($\alpha_{\text{NiO}} \approx 19 \times 10^{-6}/^\circ\text{C}$). For example, when Ag-Mg cools from 825 to 25°C, ($\Delta T = 800^\circ\text{C}$), the Ag/MgO interfaces will be stressed. The strain (Δe) that is produced can be approximated by,

$$\Delta e = (\alpha_{\text{Ag}} - \alpha_{\text{MgO}}) \Delta T = 5.6 \times 10^{-3}.$$

This large tensile strain at the interface can be relieved by either plastic deformation or cracking. It is unlikely to be fully relieved, and thus lattice distortion may contribute to O trapping near the solutes.

Formation of large clusters at high temperatures depends on solute diffusion. The Mg or Ni atoms will diffuse toward the surface because it is the source of O. As a result, the central region can become depleted of solute (Fig. 6). Depletion of Mg in the central region of the Ag-Mg was confirmed by SEM and by Knoop hardness measurements that were equal to those of pure Ag. When measured at room temperature, the cross-sectional microhardnesses of the alloys oxidized at 825°C always indicated that the greatest hardness was at the surface.

The kinetics studies showed that O diffusion was significantly faster in Ag than in the alloys. The effect of this faster O diffusion on microstructural development was notable. The grain-growth response for both alloys was studied at temperatures between 450 and 800°C. When the alloys were heat treated at 600°C and above, rapid grain growth occurred in the sample interiors. Near the surface, a region of smaller grains was observed. This surface region was found at all treatment temperatures and increased in depth as temperature decreased, with the 450°C sample being composed entirely of small grains (Fig. 7). We ascribe these small-grain regions to pinning of the grain boundaries by oxide precipitates and clusters. The large-grained interior regions formed before the O diffusion front reached them. At the higher temperatures, the rate of grain growth was faster than that of O diffusion. Hence, the result was interior regions of large grains. At the lower temperatures, the opposite situation occurred. At 450°C, oxygen penetrated the entire thickness before the grains could grow significantly.

SUMMARY

High-temperature O diffusion and internal oxidation of Ag, Ag-Mg, and Ag-Mg-Ni was studied at 450–825°C. Oxygen diffusion in Ag was ≈ 60 times faster at 825°C and ≈ 400 times faster at 500°C than internal oxidation. Internal oxidation of both alloys exhibited nearly identical activation energies and kinetic rate constants. For both alloys, internal oxidation rates differed slightly during heating. In the final stage of oxidation, the maximum O content of both alloys was superstoichiometric. The maximum ratios of O to solute at lower temperatures were higher than those at higher temperatures. We invoked a cluster-size effect to explain the results. Smaller clusters, which were more prevalent at lower temperatures exhibited higher ratios. Cluster size was related to the diffusion rates of the solutes within the Ag. Microhardness and grain-growth data from both alloys were consistent with the calculated rate of O diffusion and inferred mobilities of the solutes.

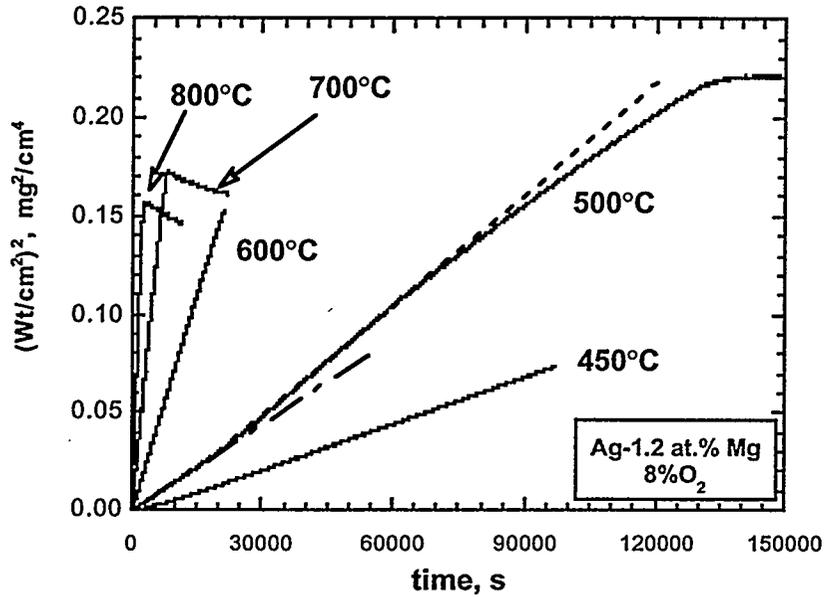
ACKNOWLEDGMENTS

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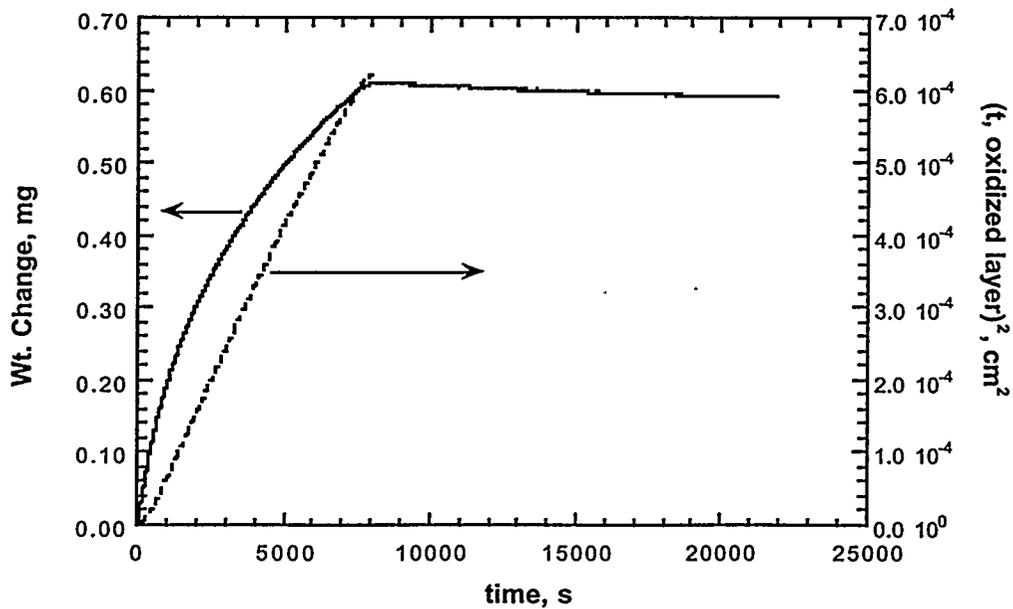
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(a)



(b)

Fig. #1. Representative TGA data: (a) internal oxidation of Ag-Mg heated to various temperatures in 8% O₂; (b) at 700°C in 8% O₂, mass change and square of thickness of oxidized layer; linear fit indicates parabolic kinetics.

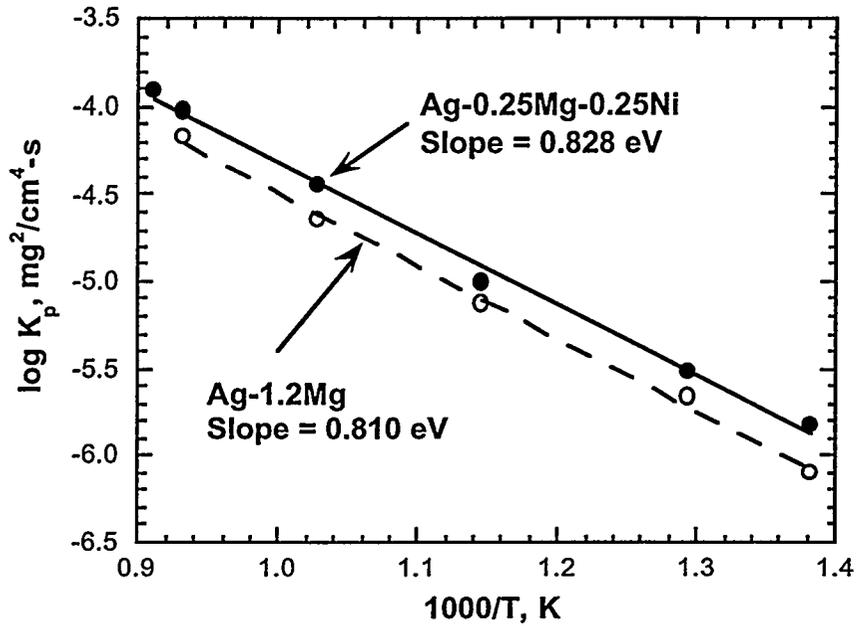


Fig. #2. Arrhenius plot for internal oxidation of the alloys; activation energies shown.

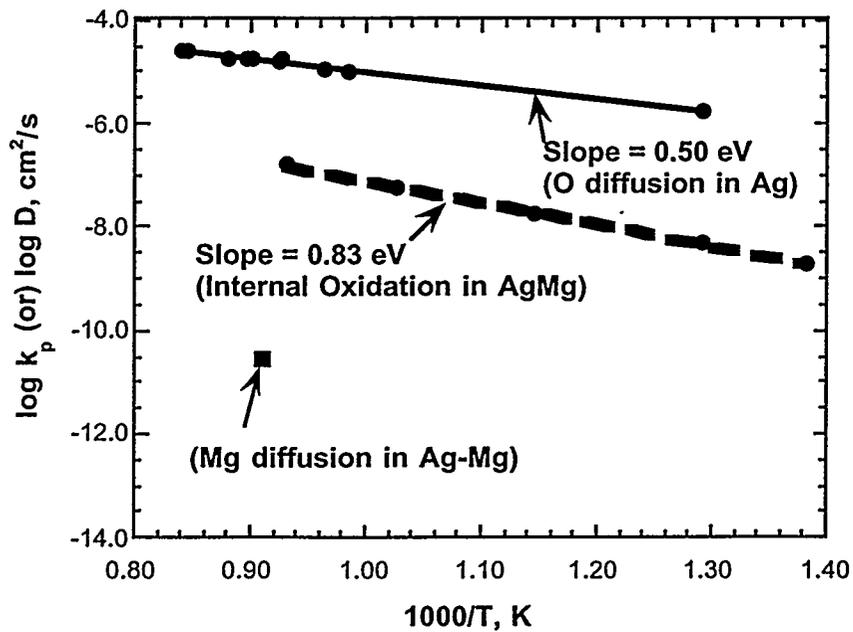


Fig. #3. Internal oxidation and Mg diffusion for Ag-Mg, and oxygen diffusion in Ag.¹⁰

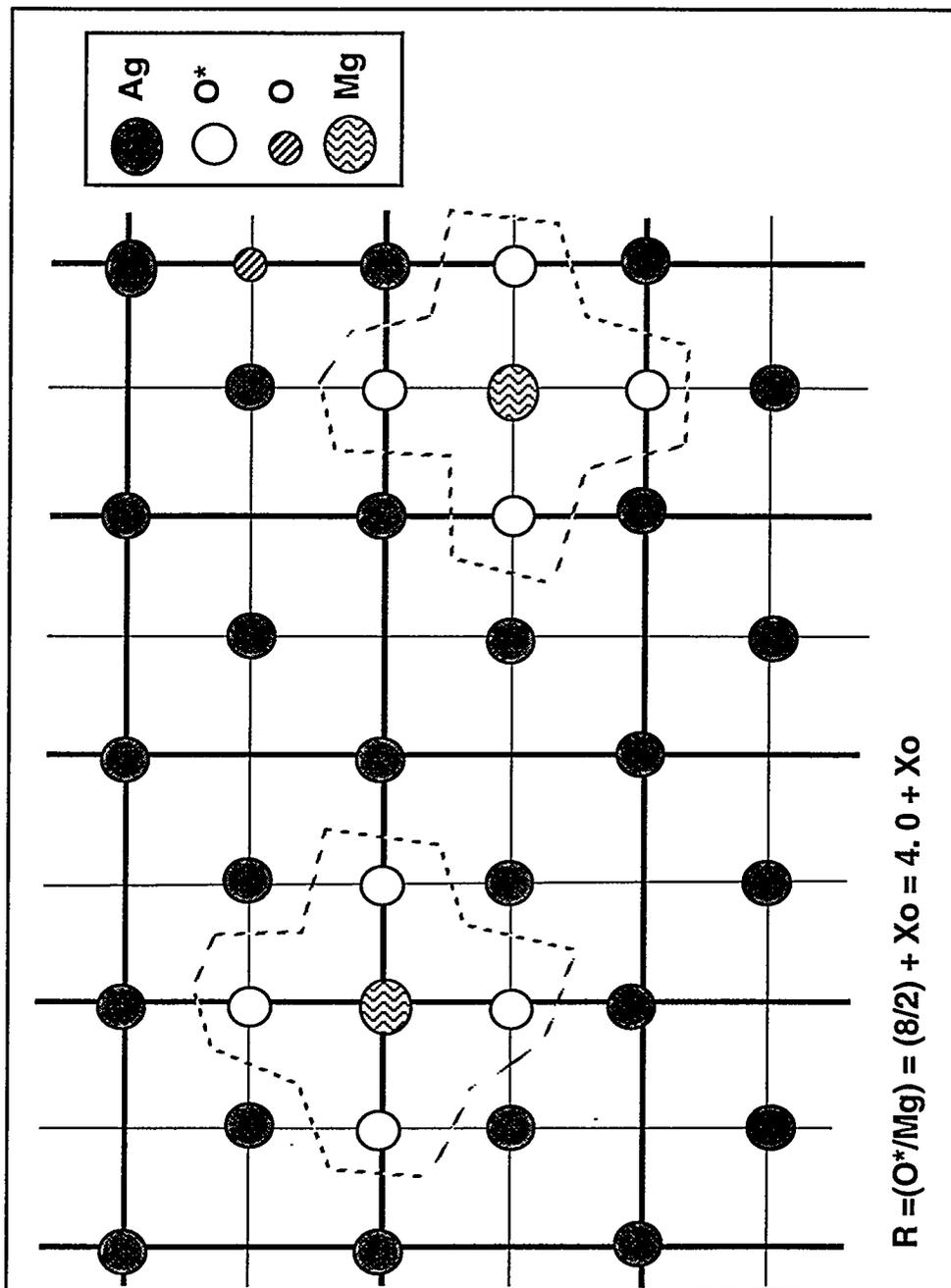


Fig. #4. Schematic two-dimensional representation of two small Mg/O clusters. O* is O atoms associated with clusters. Normal O is regular O in lattice.

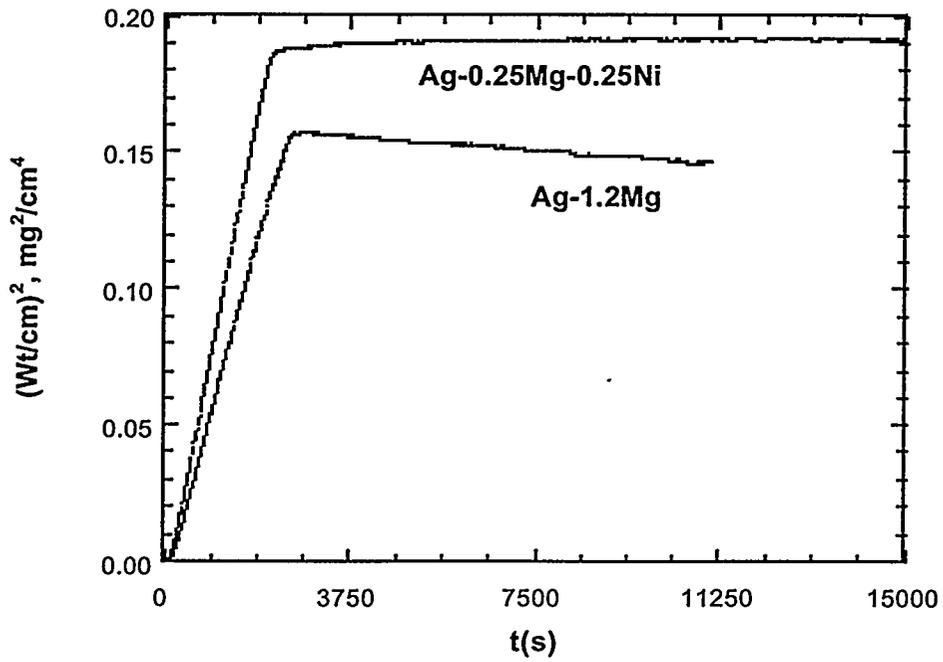
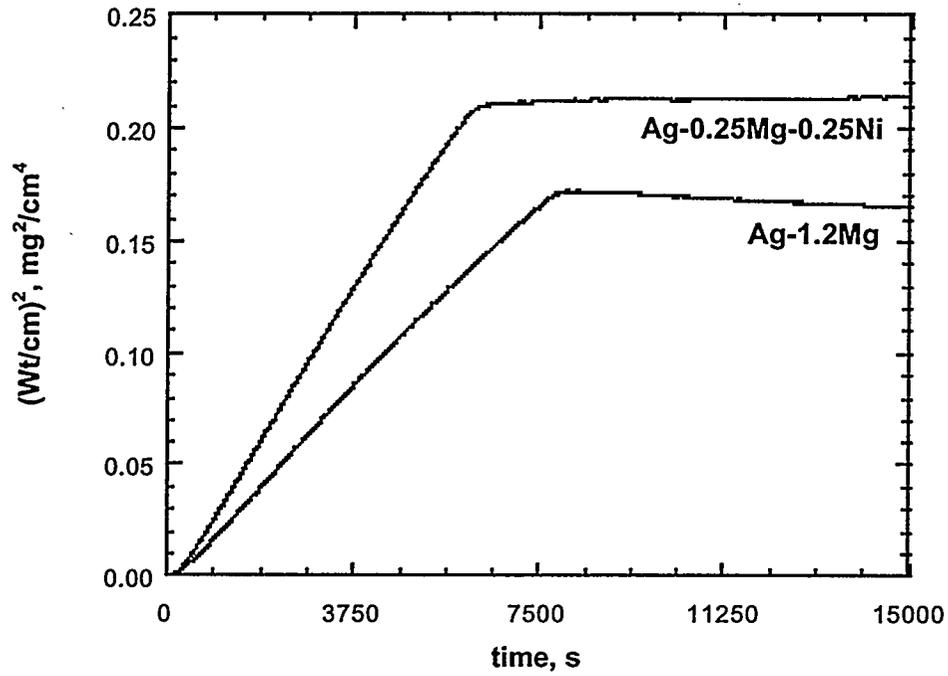


Fig. #5. TGA data for internal oxidation of Ag-Mg and Ag-Mg-Ni heated in 8% O₂ to (a) 700°C and (b) 800°C.

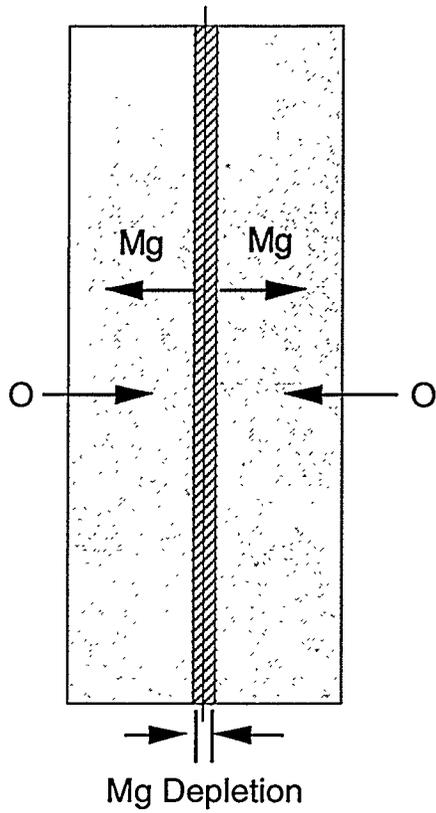


Fig. #6. Schematic cross-sectional view of internal oxidation of Ag-Mg.

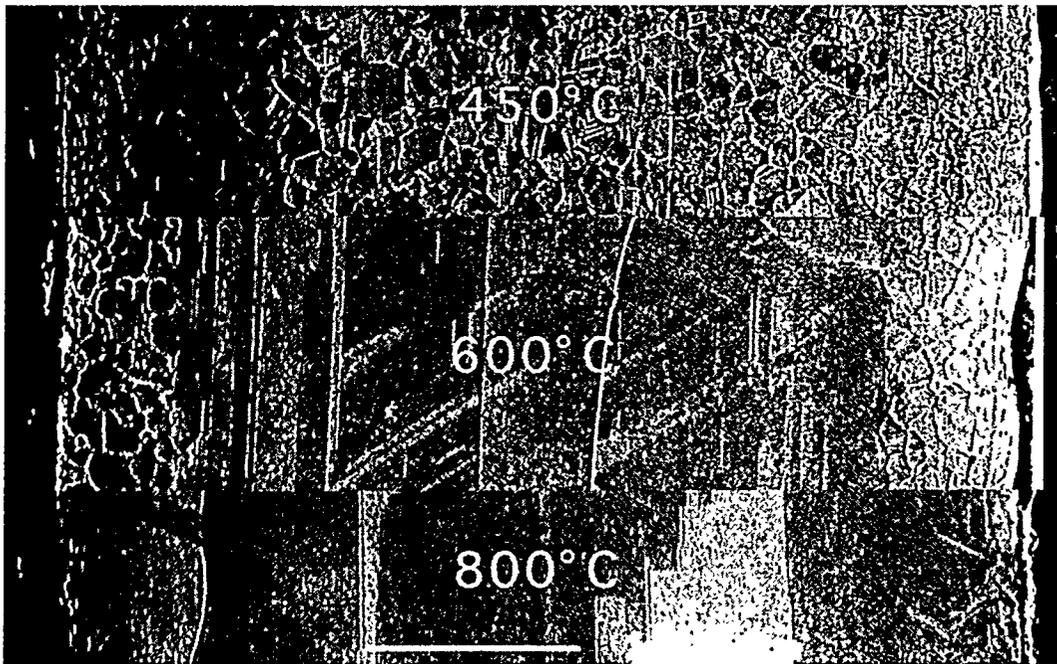


Fig. #7. Cross-sectional microstructure of Ag-Mg heated to the temperatures shown; all microstructures exhibit fine grains near the surface.