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INTERNAL OXIDATION OF SILVER-MAGNESIUM AND SILVER-COPPER ALLOYS

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Silver-magnesium alloys containing 0.04, 0.35 and 2.3 at % Mg have been investigated at 803 K. Calorimetric measurements permit explanation of the hardness and electrical resistivity caused by the dispersion of oxide particles during the process of internal oxidation. It appears that in low-concentration alloys there is no thermal effect and that the stability of dispersed oxide particles is probably due to a significant entropy Results are qualitatively the same as for Ag-Cu alloys.

The work described forms part of an investigation into the relationship between the mechanical properties and the thermal effect accompanying the process of internal oxide formation. It was carried out to explain some results already proved in our laboratory [1] by other techniques (resistivity, X-ray, gravimetry).

Experimental procedure

The specimens used in this study were 1 mm and 0.1 mm thick sheets. They were maintained at the temperature of the conduction-calorimeter vessel, under purified nitrogen at a pressure of one atmosphere; when equilibrium had been established, oxygen was introduced (Fig. 1).

Results and interpretation

The following conclusions can be deduced from these experiments (Fig. 2):

1) For low-concentration alloys (0.04 at % Mg) there is no thermal effect; the thermal curves are similar to those which occur in the pure metal.
2) For high-concentration alloys (2.3 at % Mg) the thermal effect is pronounced; we find an enthalpy of 70 Kcal, about half the effect corresponding to the formation of the stoichiometric oxide MgO.

Otherwise, for the Ag — 0.35 at % Mg alloy, the phenomenon is more pronounced for plates (1 mm thick) than for sheets (0.1 mm thick) (cf. Fig. 3).

To explain these results it should be borne in mind that the diffusion measurements [1] carried out in our laboratory have shown that the atoms of oxygen penetrating into the alloy bind with magnesium atoms to produce moving "complexes" in the matrix. Later on, these complexes grow into stable clusters which

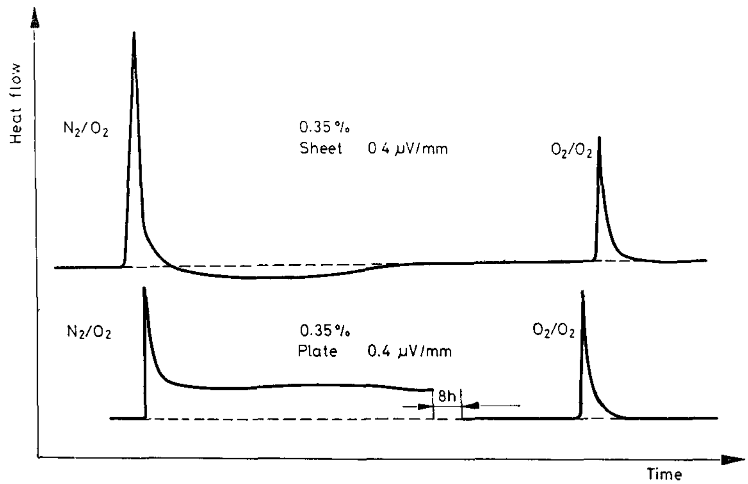

Fig. 1. Apparatus

precede the oxides, in the narrowest meaning of the word. From our results, it may be shown that these complexes are produced with a negligible enthalpy so that a significant entropy must be expected, owing certainly to the dispersion of these very small particles.

For concentrated alloys (2.3 at% Mg) we may expect a distribution in size of the clusters, some of them being closely like the oxide MgO, which explains the enthalpy observed. Thus, we find the distribution in size to be more important for plates than for sheets, which permits an explanation of the difference observed in samples of various thicknesses, as can be seen in Fig. 3.

Conclusion

Expressing enthalpy in terms of magnesium content must lead to a continuous rise of the measured enthalpy. This enthalpy must in any case remain minor in comparison to the enthalpy corresponding to stoichiometric oxide formation.

References

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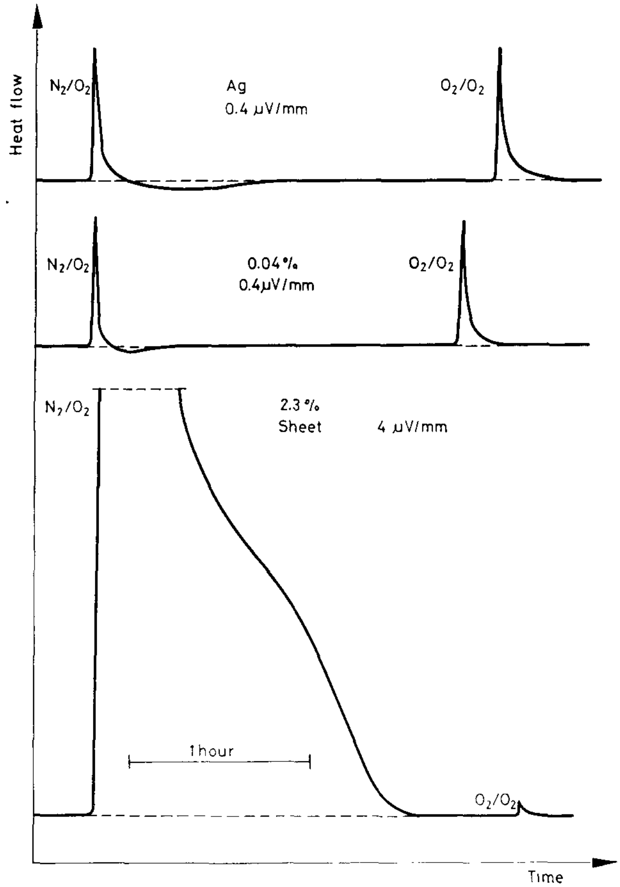

Fig. 2. a) Ag; b) Ag–0.04% Mg; c) Ag–2.3% Mg; N_2/O_2 experiment; O_2/O_2 calibration of the phenomenon corresponding to the introduction of oxygen

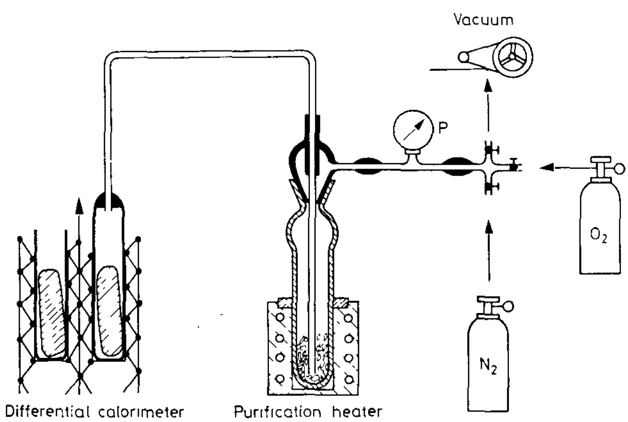

Fig. 3. Influence of the thickness

RÉSUMÉ — Des alliages argent-magnésium contenant 0.04, 0.35 et 2.3 pour cent de magnésium en atomes ont été examinés à 803°K. Les mesures calorimétriques permettent d'expliquer la dureté et la résistivité électrique dues à la dispersion de particules d'oxydes lors de la réaction d'oxydation interne. Il apparaît que dans les alliages à faible concentration il n'y a pas d'effet thermique et que la stabilité des particules d'oxyde dispersées est due, probablement, à une entropie importante.

Les résultats sont qualitativement les mêmes que pour les alliages Ag-Cu.

ZUSAMMENFASSUNG — Silber-Magnesium-Legierungen mit 0.04, 0.35 und 2.3 Gew. % Mg wurden bei 803 K untersucht. Die kalorimetrischen Messungen ermöglichen die durch Dispersion der Oxidteilchen (1, 2, 3, 4) während des inneren Oxidationsvorganges bedingte Härte und elektrischen Widerstand zu erklären. Es scheint, daß es in Legierungen geringer Konzentration keinen thermischen Effekt gibt und daß die Stabilität der dispergierten Oxidteilchen wahrscheinlich einer bedeutenden Entropie zuzuschreiben ist.

Die Ergebnisse sind qualitativ dieselben wie für Ag-Cu-Legierungen.

Резюме — Были исследованы при температуре 803 К серебряно-магниевые сплавы, содержащие 0,04, 0,35 и 2,3 ат.% магния. Калориметрические измерения позволили объяснить твердость и электрическое удельное сопротивление, вызванные дисперсией частиц окислов во время процесса внутреннего окисления. Очевидно, что в низкоконцентрационных сплавах нет термического эффекта и что стабильность диспергированных частиц окислов, повидимому обусловлена важностью энтропии. Качественно результаты те же самые, как и для Ag—Cu сплавов.