Oxidation of Powder Metallurgical Ag-Cr Alloys In 1 Atm O_2 At 700-800°C

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ABSTRACT

The oxidation of three Ag-Cr alloys with a nominal content of 17, 35 and 69 wt% Cr prepared by powder metallurgy has been studied in 1 atm of pure O_2 at 700 and 800°C. As a consequence of their two-phase nature, these alloys form composite scales containing complex mixtures of chromia, a double Ag-Cr oxide and silver metal. The alloys more dilute in chromium undergo a complex internal oxidation of chromium associated with the formation of a layer of silver metal on top of the scale. The large chromium particles in the region of internal oxidation are not completely oxidized due to the slow rate of chromia growth. A continuous layer of chromia forms only on the alloy containing 69 wt% Cr, but it is surmounted by an external layer of the double oxide. The internal oxidation of chromium is suppressed in this alloy, which corrodes significantly more slowly than those more dilute in chromium.

Key words: silver, chromium, oxidation, two-phase alloys

INTRODUCTION

The binary Ag-Cr system has a monotectic equilibrium. The two metals have very low mutual solubility and do not form any intermediate phase /1/. Thus, below their melting points Ag-Cr alloys are composed of mixtures of the two nearly pure metals in practically all their composition range. On the other hand, chromium oxide is very stable and quite protective, while silver is a noble metal under 1 atm O_2. Therefore, silver-chromium alloys are a simple case of binary two-phase alloys, which can be used to check the correctness of some general considerations and theoretical treatments concerning the high-temperature oxidation behavior of this class of materials /2-4/. In fact, this can be very different from that of solid-solution alloys, mainly as a result of the restriction of the diffusion of the metal components in the alloy, which becomes totally impossible in the presence of two phases, since they are in equilibrium whatever is the difference in their composition /2-4/.

The alloys used in this study have been prepared by means of powder metallurgy, which can provide a much more uniform distribution of the two phases than by conventional methods, and thus can reduce the effect of local deviations from the average alloy composition on their oxidation behavior. In addition, this method also allows one to control to some extent the size of the particles of the two phases. This paper examines the results of the oxidation in pure oxygen at 700-800°C of three two-phase Ag-Cr alloys with widely different composition: the results obtained are interpreted by taking into account the effects of the limited solubility of the two components.

EXPERIMENTAL

Three alloys with a nominal chromium content of 17, 35 and 69 wt% (actual average compositions equal

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to 17, 35.5 and 69 wt% Cr, respectively) have been prepared by powder metallurgy methods. Conventional casting methods were not possible because above the melting point these alloys form two insoluble liquid phases which after cooling produce a material in which the two phases are completely separated from each other.

The particle sizes of the starting silver and chromium powders were 70-100μm with at least 99.9% purity. The powders were mixed in a planetary ball mill for about 3 hr. The powder and balls were sealed in an Ar-filled stainless steel vials during milling with a ball-powder weight ratio of 10:1. Consolidation of powders was performed by hot pressing under vacuum in a furnace at 950°C for Ag-69Cr and Ag-35Cr and at 930°C for Ag-17Cr under a pressure of 39 MPa. The soaking time was 30-40 minutes. The actual density of the consolidated samples was measured using the suspension method in water and was then used to calculate the sample porosity by comparison with the theoretical value. The data concerning the three alloys are shown in Table I.

The alloy microstructures are shown in Figs. 1a-1c. In agreement with the phase diagram of the Ag-Cr system /1/ they all contain a mixture of the solid solutions of chromium in silver (α phase, light) and of silver in chromium (β phase, dark), which are practically identical to the two pure metals as a result of the very low mutual solubility of Ag and Cr. The only difference between the three alloys concerns the volume fraction of the two phases. For all the alloys the phase forms the matrix which contains a dispersion of the particles of the β phase, even though for Ag-69Cr also the β phase has some degree of interconnection. The size of the β phase particles ranges between a few μm up to about 100 μm.

Samples of about 2 cm^2 surface area were ground down to 800 grit emery paper. Kinetic measurements

Table I

Data of the three powder metallurgy Ag-Cr alloys

Alloy	Actual composition, wt %Cr	Theoretical density, g/cm^3	Actual density, g/cm^3	Porosity (%)	Sintering temp., °C
PM Ag-69Cr	69.0	7.98	7.73	3.1	950
PM Ag-35Cr	35.5	9.03	8.74	3.2	950
PM Ag-17Cr	17.1	9.74	9.57	1.7	930

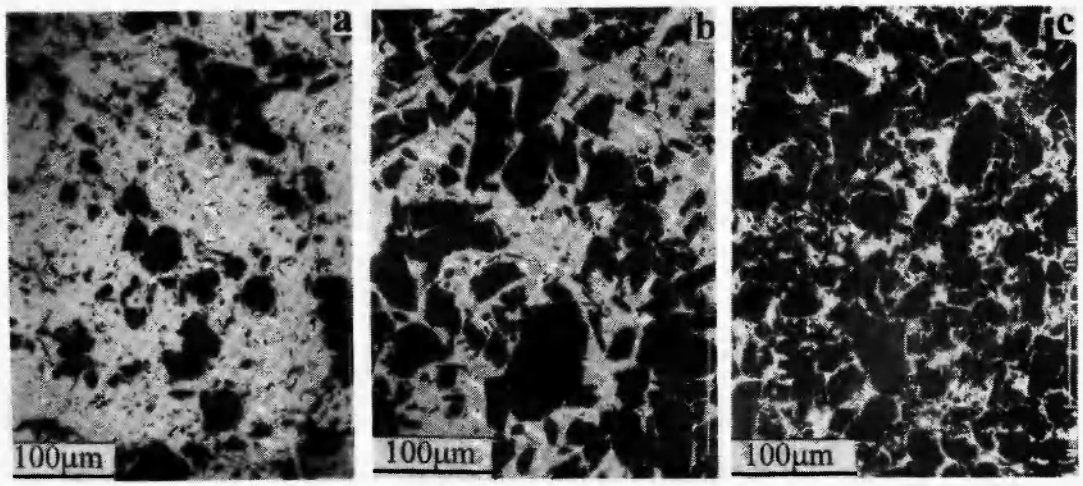

Fig. 1: Microstructures (SEM/BEI) of Ag-17Cr (Fig. 1a), Ag-35Cr (Fig. 1b) and Ag-69Cr (Fig. 1c) containing mixtures of the Ag-rich phase (light) and the Cr-rich phase (gray).

have been carried out in pure oxygen using a Cahn microbalance Mod. 2000. Corroded samples have been examined by means of X-ray diffraction (XRD), scanning electron microscopy in the backscattered-electron mode (SEM/BEI) and energy-dispersive X-ray microanalysis (EDX) to establish the nature and composition of the various phases and their spatial distribution.

RESULTS

Oxidation kinetics

The kinetics curves for the oxidation of the three alloys are shown in Figs. 2a-2b. The oxidation of Ag-17Cr and Ag-35Cr follows the parabolic rate law to a good approximation, while the oxidation rates of Ag-17Cr are higher than those of Ag-35Cr at the same temperature. For each alloy the oxidation rate at 800°C is slightly larger than at 700°C. The oxidation rate of Ag-69Cr is much lower than that of the other two alloys. At both temperatures an approximately parabolic stage is followed by a much slower linear stage after about 2 hours. Moreover, the oxidation rate of Ag-69Cr is much higher at 700°C than at 800°C, contrary to the behavior of the other two alloys. Approximate values of the parabolic rate constants for the three alloys, calculated when possible, are given in Table II.

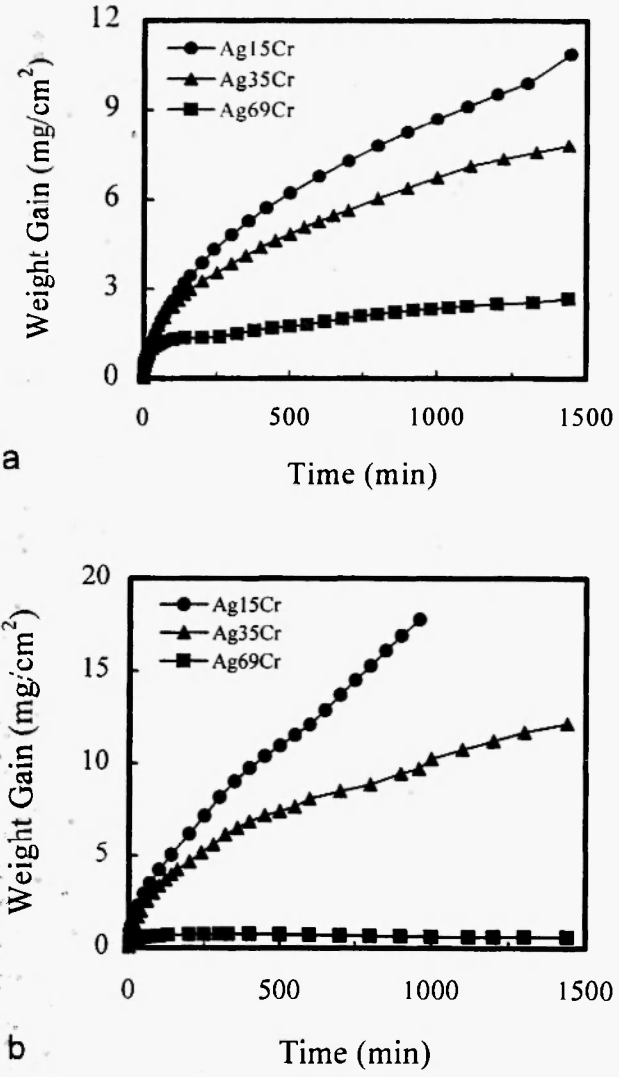

Fig. 2: Kinetics for the oxidation of Ag-17Cr, Ag-35Cr and Ag-69Cr at 700 (Fig. 2a) and 800°C (Fig. 2b).

Scale microstructure and composition

The scale microstructures of the three alloys are shown in Figs. 3-7 respectively. In spite of the two-

Table II

Approximate parabolic rate constants ($g^2cm^{-4}s^{-1}$) for the oxidation of the three Ag-Cr alloys in 1 atm O_2 at 700-800°C

		Ag-15Cr	Ag-35Cr	Ag-70Cr
700°C	(in)	1.34×10^{-9}		8.39×10^{-11}
	(av)	1.36×10^{-9}	7.08×10^{-10} (parob)	1.25×10^{-11}
	(fi)	4.24×10^{-9}		linear
800°C	(in)	3.21×10^{-9}	2.03×10^{-9}	5.80×10^{-11}
	(av)	4.24×10^{-9}	1.75×10^{-9}	1.52×10^{-12}
	(fi)	1.33×10^{-9}	1.55×10^{-9}	linear

(in) = initial values; (av) = average values; (fi) final values.

phase nature of these alloys, the general structure of the scales is rather uniform along planes parallel to the alloy surface, while their composition changes significantly with the distance from the alloy/scale interface. In no case did these alloys form exclusive Cr_2O_3 layers. Although pure silver cannot be oxidized under the present conditions, all alloys also form a double oxide of silver and chromium which according to XRD measurements is $AgCrO_2$. In no case was depletion of chromium in the alloy substrate observed.

Samples of Ag-17Cr oxidized at 700°C (Figs. 3a-3b) show an outermost continuous region of pure silver (light), with an irregular surface both externally and internally. Beneath this layer there is a region composed of a matrix of the double oxide $AgCrO_2$ (medium gray) and containing silver particles of various sizes. The inner region is composed of a mixture of particles of $AgCrO_2$ (medium gray) and Cr_2O_3 (dark) distributed in a silver matrix. In this region, and especially close to the front of internal oxidation, there are also some large particles of pure chromium still intact, surrounded by silver or by a thin chromia layer. This inner layer is more than 200 μm thick, while there is no sharp interface between this region and the bulk alloy. For Ag-17Cr at 800°C (Figs. 4a-4c), the outermost layer of pure silver is thinner than at 700°C and sometimes discontinuous. Beneath this region, there is a layer composed of particles of the double oxide $AgCrO_2$ (medium gray) dispersed in the silver matrix, which is much thicker than the corresponding layer at 700°C. Close to the alloy there is a thin region containing Cr_2O_3 particles dispersed in a silver matrix, tending to form a nearly continuous network, while the interface with the alloy matrix is very irregular. At variance with the behavior at 700°C, the chromium particles in the internal oxidation region are completely oxidized.

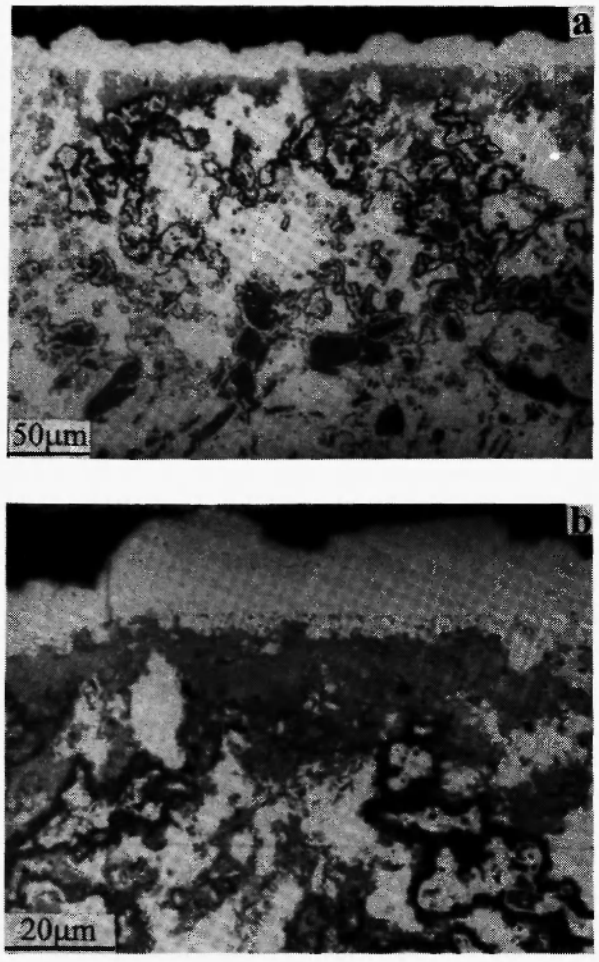

Fig. 3: Cross section (SEM/BEI) of Ag-17Cr oxidized at 700°C for 24 hr in pure oxygen.
Fig. 3a: general view;
Fig. 3b: expanded view of the sample surface region.

The outer surface of Ag-35Cr after corrosion at 700°C (Figs. 5a-5c) is partly covered by pure silver and partly by chromium oxide. Chromia forms a semi-continuous and very irregular layer, covered only in part by silver metal particles which close to the chromia layer contain some double oxide (medium gray). Beneath the chromia-rich layer there is a region of internal oxidation where the small chromium particles have been completely converted into oxide, while the large particles are still composed of metallic chromium and are covered either directly by chromia or by a silver layer surmounted by chromia. A plain view of the sample surface (Fig. 5c) shows the presence of a semicontinuous external layer of silver metal.

On the contrary, Ag-35Cr oxidized at 800°C (Figs. 6a-6c) shows a continuous outermost silver layer overlying an almost continuous medium gray layer of double oxide, similar to what was observed for Ag-17Cr at 700°C, but thinner and more regular. Beneath the double oxide layer there is a discontinuous and very irregular layer of chromia which tends to follow the surface of the large chromium particles. Finally, in the innermost region of the scale the smaller chromium

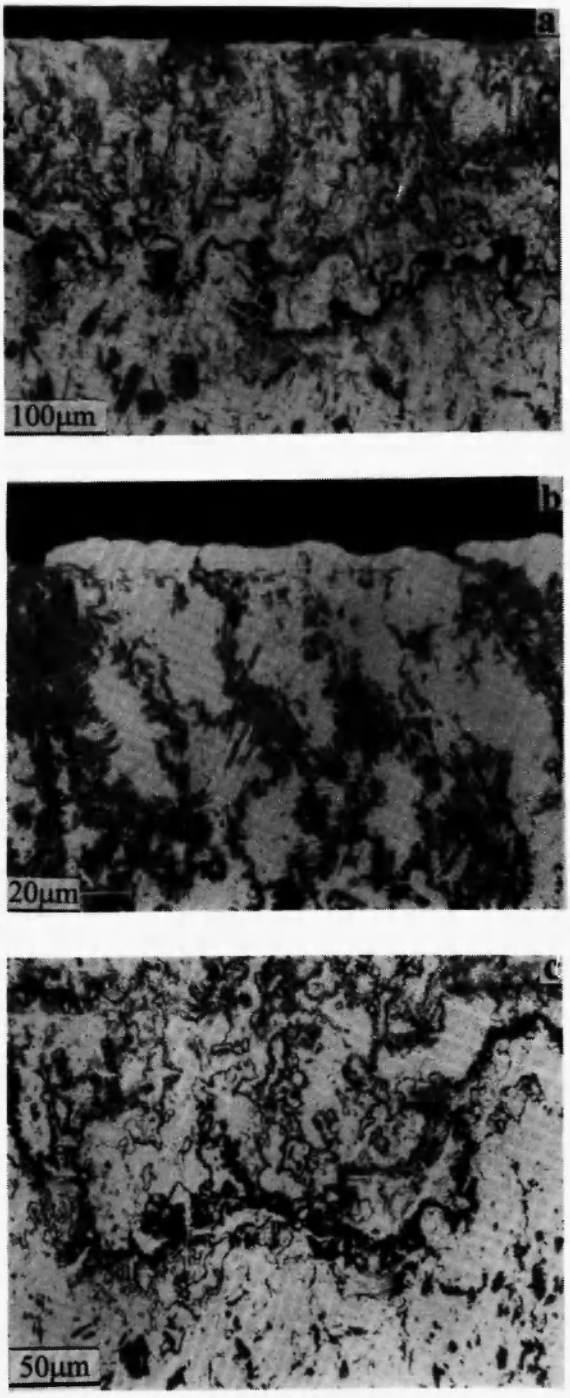

Fig. 4: Cross section (SEM/BEI) of Ag-17Cr oxidized at 800°C for 15 hr in pure oxygen.
Fig. 4a: general view;
Fig. 4b: expanded view of the sample surface region;
Fig. 4c: expanded view of internal oxidation front.

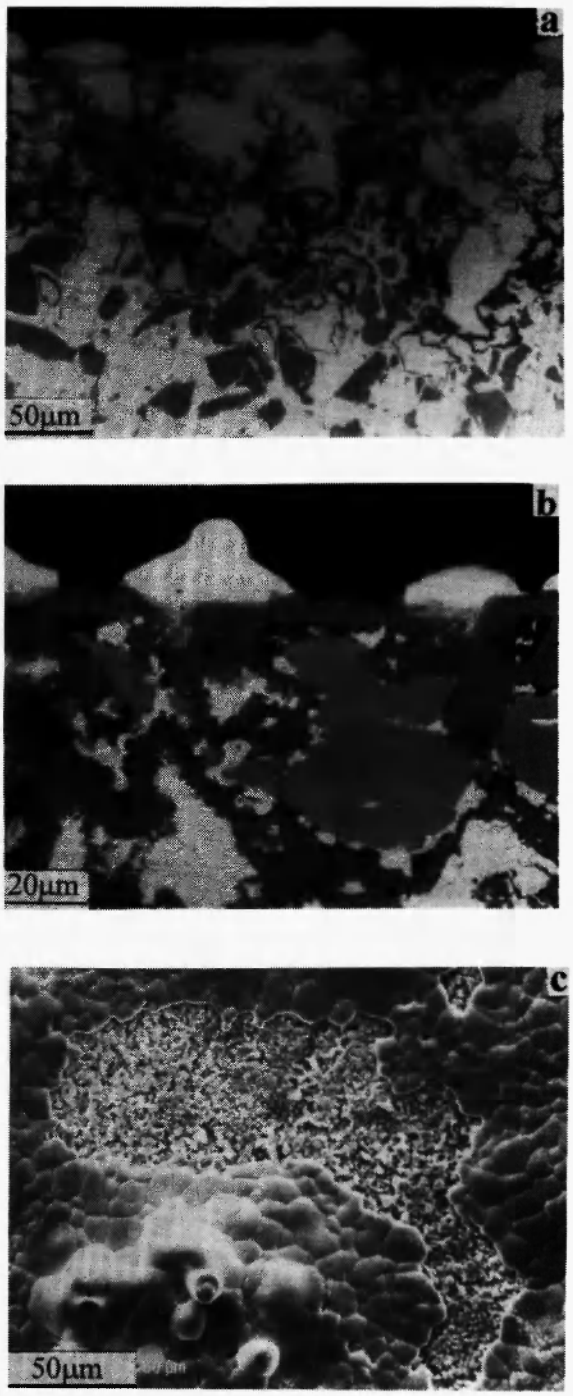

Fig. 5: Scale Structure and surface morphology (SEM/SEI) of Ag-35Cr oxidized at 700°C for 24 hr in pure oxygen.
Fig. 5a: general view of the cross section (SEM/BEI);
Fig. 5b: expanded view of the external region of Fig. 5a (SEM/BEI);
Fig. 5c: top morphology (SEM/SEI).

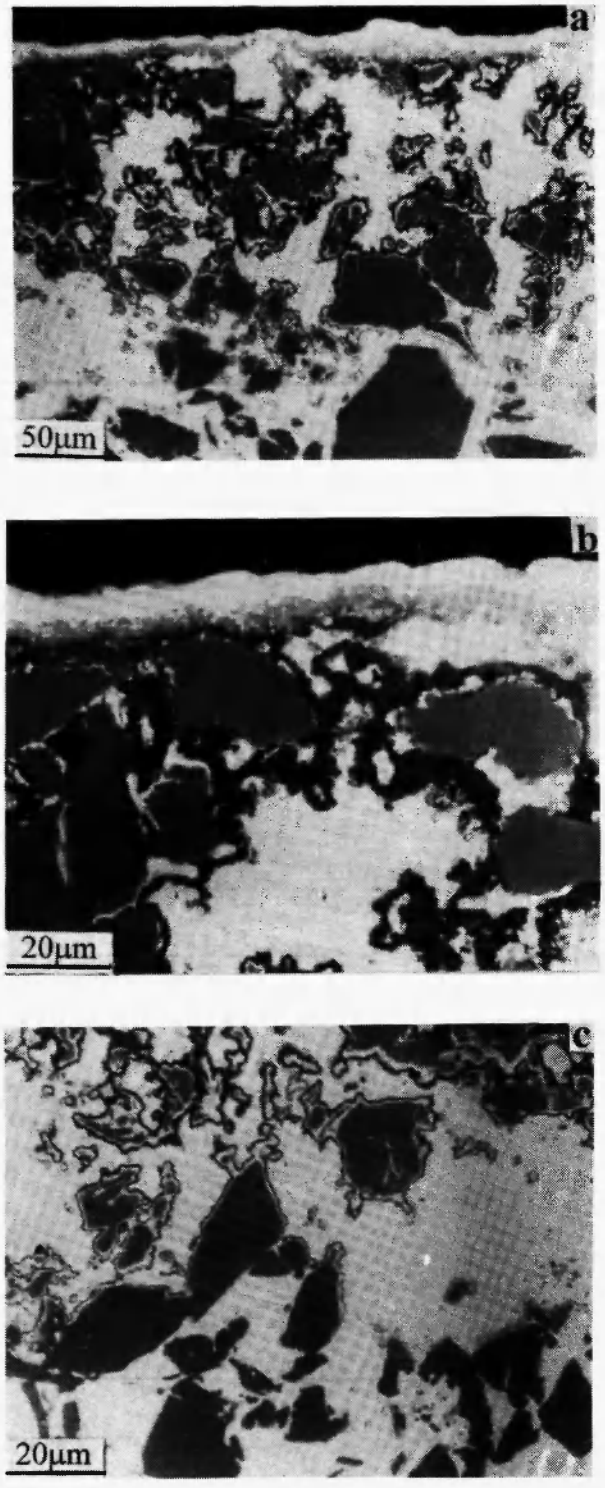

Fig. 6: Cross section (SEM/BEI) of Ag-35Cr oxidized at 800°C for 24 hr in pure oxygen.
Fig. 6a: general view;
Fig. 6b: expanded view of the internal oxidation front.

particles within the silver matrix have been oxidized, while the large particles are still in the metal state, generally surrounded by silver and then by a thin chromia layer. The interface between the inner scale region and the alloy matrix for Ag-35Cr is irregular at both temperatures.

The scales formed on Ag-69Cr oxidized at 700°C and 800°C (Figs. 7a-7b) are very similar to each other and contain only two layers: the outermost layer is irregular and is composed of the double Ag-Cr oxide, while the inner is a thin, continuous but quite irregular layer of Cr_2O_3 only about 2 μm thick at 700°C, and even thinner at 800°C. This layer tends to follow mostly the surface of the large chromium particles in the surface region of the alloy. In some places chromia is

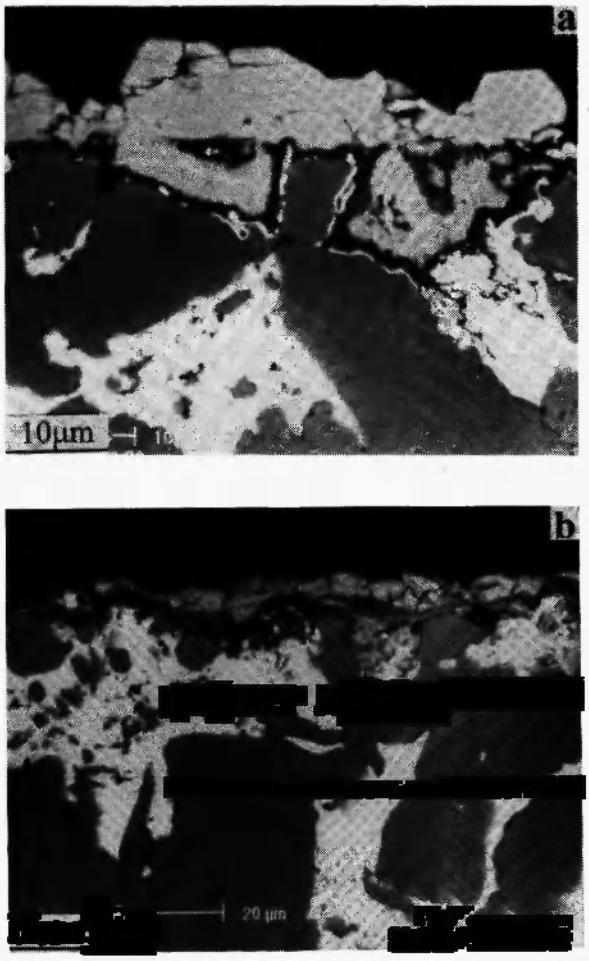

Fig. 7: Cross sections (SEM/BEI) of Ag-69Cr oxidized at 700 (Fig. 7a) and 800°C (Fig. 7b) for 24 hr in pure oxygen.

also present within the layer of double oxide, probably where silver in the alloy contained some chromium particles. The thickness of the scale formed on Ag-69Cr is slightly smaller after corrosion at 800°C than at 700°C.

DISCUSSION

Only chromium forms a stable oxide in the Ag-Cr system, since silver is noble under the present conditions. However, a double Ag-Cr oxide was also observed to form, which in all cases was $AgCrO_2$, as shown both by SEM/EDX and XRD measurements. Moreover, an exclusive external oxidation of chromium was never observed for the present Ag-Cr alloys, even though for Ag-69Cr the internal oxidation of chromium was suppressed.

The scaling behavior of the present alloys can be examined qualitatively using the schematic isothermal phase diagram of the Ag-Cr-O system shown in Fig. 8, where the mutual solubilities of the two metals have been neglected. The oxygen pressures for the Ag/Ag_2O, $Ag/AgCrO_2/Cr_2O_3$ and Cr/Cr_2O_3 equilibria are denoted as P_1, P_2 and P_3, respectively, while P^g is that prevailing in the gas phase, which is lower than P_1 but higher than P_2. For the two alloys more dilute in chromium the oxygen pressure prevailing at the front of internal oxidation (P_3) is sufficient to oxidize chromium, but not silver. Thus, at this location the β phase reacts with oxygen to form Cr_2O_3, while the α phase remains unaffected. The larger chromium particles in the internal region are not oxidized completely, but form a Cr_2O_3 layer only along their surface. A similar behavior, already observed in the oxidation of Cu-Cr alloys /5/, is due to purely kinetic reasons. In fact, the external layer of chromia grown on the surface of the chromium particles protects their core from oxidation in view of the slow rate of growth of chromia. In addition, the degree of oxidation of the chromium particles is related to their size, since large particles need longer times to be oxidized entirely than small particles, as already examined elsewhere /5,6/.

Proceeding outwards across the internal oxidation region the oxygen pressure increases continuously: when it reaches P_2, the α phase will react with oxygen and chromia to form the double oxide $AgCrO_2$. For the two alloys more dilute in chromium the diffusion path corresponds approximately to a straight vertical line crossing the α + Cr_2O_3 and then the Ag + $AgCrO_2$ regions. The section corresponding to the external layer of silver is completely shifted to the extreme left of the phase diagram.

On the contrary, for Ag-69Cr the double oxide forms

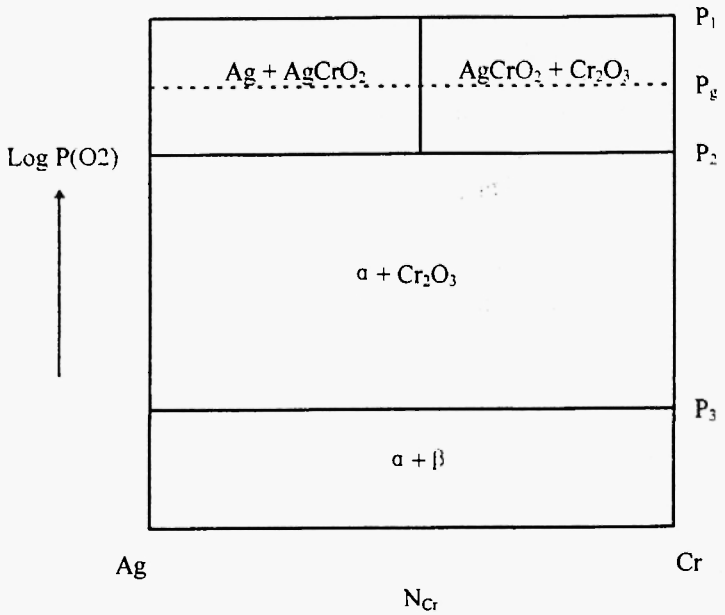

Fig. 8: Schematic isothermal phase diagram for the ternary Ag-Cr-O system.

a continuous layer on top of a continuous layer of chromia, which in turn is in contact with the alloy, while the internal oxidation of chromium is completely absent. In this case, the diffusion path at $P(O_2) = P_3$ shifts to the extreme right (Cr_2O_3) and moves upwards to P_2 without crossing the two-phase $\alpha + Cr_2O_3$ field, after which it shifts to the center of the diagram ($AgCrO_2$) and moves vertically up to $P(O_2) = P^g$.

For solid-solution A-B alloys the critical content required for the transition from the internal to the external oxidation of the most reactive B component, N_B^{0*}, is given by /7,8/:

$$N_B^{0*} = V_{all}\, f_v^*\, F(h)/V_{ox} \qquad (1)$$

where V_{all} and V_{ox} are the molar volumes of the alloy and the oxide (per mole of metal), while f_v^* is the critical value of the volume fraction of internal oxide for the transition, generally set equal to 0.3 /8/. Moreover, F(r) is a so-called auxiliary function given by:

$$F(r) = \pi^{1/2}\, r \exp(r^2)\, \mathrm{erfc}(r)$$

while h is equal to $\gamma\varphi^{1/2}$, where γ is an appropriate kinetics parameter /7,8/ and $\varphi = D_O/D_B$ and D_O, D_B are the diffusion coefficients of O and B in the alloy. Under normal conditions use of Eq.(1) requires a calculation of γ using the classical equations given by Wagner /7,8/ in the absence of external AO scales or by Maak /9/ in the opposite case. However, the negligible diffusion of chromium in silver due to its very low solubility in silver corresponds to very large values of φ and h, yielding $F(h) \cong 1$. Thus, N_{Cr}^{0*} can be calculated simply from Eq.(1): taking $V(CrO_{1.5}) = 14.96$ cm^3/mol and $V_{all} = 9.65$ cm^3/mol as an average of the corresponding values for Ag and Cr around the critical alloy composition, yields $N_{Cr}^{0*} = 0.19$, independently of temperature. Thus, solid-solution alloys with the same values of the relevant parameters as the Ag-Cr system would undergo an internal oxidation of chromium for N_{Cr}^{0} values smaller than about 0.2. On the contrary, in the present Ag-Cr alloys chromium undergoes an internal oxidation up to a mole fraction between 0.47 (Ag-35Cr) and 0.82 (Ag-69Cr). This is mainly due to the limited mutual solubility of the two components and to the consequent presence of two metal phases in the alloy, as already predicted /2-4/ and observed experimentally for some binary systems of this kind /10,11/. In addition, the internal oxidation of chromium does not involve any appreciable outward chromium diffusion (*in situ* internal oxidation), in agreement with general predictions for two-phase alloys /3/.

Ag-17Cr and Ag-35Cr form a continuous layer of pure silver in the outermost region of the scale (only isolated silver nodules for Ag-35Cr at 700°C). The formation of nodules of the pure solvent on the surface of alloys undergoing internal oxidation has already been observed for other systems /12,13/. According to a treatment by Guruswamy *et al.* /12/, the volume change associated with the internal oxidation produces a large compressive stress around the internal oxidation front, which increases the local dislocation density. This stress can be relieved by transport of silver to the surface by dislocation-pipe diffusion, which is the only mechanism accounting for the large amount of silver transported to the surface. For the present alloys, the ratio of the molar volume of Cr_2O_3 (per mole of metal) to that of chromium (2.07) is able to produce the migration of pure silver on the scale surface: the formation of a continuous metal layer (Fig. 5d) is attributed to a coalescence of nodules growing close to each other. In agreement with this, no pure silver layer forms on Ag-69Cr which does not undergo any internal oxidation.

The inability of the present alloys to form exclusive Cr_2O_3 scales is mainly due to the very low solubility of chromium in silver, so that chromium diffuses very slowly compared to oxygen, as shown by the lack of depletion of chromium in the bulk alloy. For alloys containing up to 35 wt% Cr the flux of chromium from the alloy is insufficient to form a continuous chromia scale, so that chromium undergoes an internal oxidation. For Ag-69Cr the internal oxidation of chromium is avoided, but a layer of double oxide forms on top of the chromia layer. Even in this case, the formation of chromia occurs directly on the external surface of the chromium particles, while within the silver particles it occurs only at places initially containing a sufficient concentration of small chromium particles, so that the oxide layer becomes very tortuous.

The gradual decrease of the oxidation rates of these alloys at constant temperature as their chromium content increases is a consequence of the presence of

larger volume fractions of chromium oxide, which is more protective than the double oxide, and is in qualitative agreement with the predictions of Wagner's treatment of the formation of composite scales containing mixtures of the oxides of the two alloy components /14/. For Ag-17Cr and Ag-35Cr the oxidation rates increase as temperature increases, as normally observed. On the contrary, Ag-69Cr corrodes more rapidly at 700 than at 800°C, probably because a continuous layer of Cr_2O_3 forms more easily at 800°C than at 700°C, so that the alloy is protected earlier.

CONCLUSIONS

The oxidation behavior of present alloys is strongly affected by the restriction to chromium diffusion due to the presence of two phases and by the relatively large size of the chromium particles, which result in the formation of complex scales. In fact, after oxidation in pure oxygen for 24 hours at 700-800°C they do not form exclusive Cr_2O_3 scales, even for high chromium contents, but only mixtures of Cr_2O_3 with the double oxide $AgCrO_2$. In particular, Ag-17Cr and Ag-35Cr form a region of internal oxidation of chromium below a layer containing the double oxide or a mixture of the double oxide with Cr_2O_3 dispersed in a matrix of silver metal, while the outermost layer is composed of pure silver metal. Oxidation of chromium in the region of internal attack of these alloys is not complete since large particles often have an unreacted metal core, due to kinetic reasons. Layers of pure silver form on the surface of the same alloys as a result of a stress gradient between the internal oxidation front and the alloy surface resulting from large volume change caused by internal oxidation.

The oxidation of Ag-69Cr produces duplex scales containing an outer layer of double oxide and an inner chromia layer, while the internal oxidation is suppressed. As a result, this alloy oxidizes significantly more slowly than those more dilute in chromium. Finally, in all the three alloys the alloy substrate is not depleted in chromium close to the interface with the corroded region in spite of the preferential consumption of chromium.

ACKNOWLEDGMENTS

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REFERENCES

1. *Binary Alloys Phase Diagrams*, T.B. Massalski, Ed., ASM, USA, 1990.
2. F. Gesmundo, F. Viani, Y. Niu and D.L. Douglass, *Oxid. Met.*, **40**, 373 (1993).
3 F. Gesmundo, Y. Niu and F. Viani, *Oxid. Met.*, **43**, 379 (1995).
4. F. Gesmundo, F. Viani and Y. Niu, *Oxid. Met.*, **47**, 355 (1997).
5. Y. Niu, F. Gesmundo, D.L. Douglass and F. Viani, *Oxid. Met.*, 48, 357 (1997).
6. F. Gesmundo, F. Viani, Y. Niu and D.L. Douglass, *Oxid. Met.* **39**, 197 (1993).
7. C. Wagner, *Z. Elektrochem.*, **63**, 772 (1959).
8. R.A. Rapp, *Corrosion*, **21**, 382 (1965).
9. F. Maak, *Z. Metallkunde*, **52**, 538 (1961).
10. F. Viani, P. Nanni and F. Gesmundo, *Oxid. Met.*, **19**, 53 (1983).
11. Y. Niu, F. Gesmundo, G.Y. Fu and D.L. Douglass, *Oxid. Met.*, **50**, 327 (1998).
12. S. Guruswamy, S. M. Park, J.P. Hirth and R.A. Rapp, *Oxid. Met.* **26**, 77 (1986).
13. D.L. Douglass, *Oxid. Met.* **44**, 81 (1995).
14. C. Wagner, *J. Electrochem. Soc.*, **103**, 627 (1956).