Letters

Comments on "A Study of Grain-Boundary Grooving at the Platinum/Alumina Interface", by McLean and Hondros

In this letter an attempt is made to interpret some of the results obtained by McLean and Hondros [1], where the kinetics of groove growth at the intersection of platinum grain boundaries with the platinum/alumina interface was studied. The process occurs without destroying material continuity on the interface so the data obtained in [1] are of interest not only for the particular system studied here, but for solving general questions associated with the problem of structural changes of composite metal/binary compound materials caused by a system tending to a state with the minimum interfacial energy (particle coagulation, spheroidisation both by the mechanism suggested in [2] and due to groove formation at the intersections of metal or compound grain boundaries with the interphase interfaces in fibre-reinforced composites, mass transport between fibres, etc). Only high-temperature results ($T > 1410^\circ$C) are discussed in this note because experimental accuracy at $T < 1410^\circ$C appears to be insufficient for definite conclusions concerning time dependence, activation energy and other significant characteristics of the process to be drawn.

The following are assumed: (1) the rate of a compound ($A_\alpha B_\beta$) diffusion transport is rate-determining in the process, (2) at any temperature this transport is done by the atoms of compound forming elements (A and B) through the metal matrix (M), (3) the process is quasistationary, i.e. relaxation time of A and B concentration fields in the matrix is small as compared with the time of changing of interface form and position, (4) solid solutions A and B in M are ideal.

Use is made of the approach proposed in [3] which allows the problem of mass transport in an element/compound system to be reduced to similar problem in an element/element system. The essence of the approach consists in the following. If the concentration of one of the compound forming elements in the matrix is practically equal in all its points then the concentration of other elements on the metal/compound interface may be determined from Gibbs-Thompson equation

$$K_m = K_0 \exp(2\sigma Vm/RT) \qquad (1)$$

provided these surface equations and, hence, their curvature m in each point are known (σ = specific interphase surface energy, V = compound molar volume, K_m = equilibrium constant of $A_\alpha B_\beta$ compound formation reaction out of matrix solved elements that corresponds to the surface point where its curvature is m, K_0 is the same for the planar surface, R and T have conventional meaning). Ascribing a and b indices to the values associated with A and B, respectively, and denoting concentration by C, (1) may be rewritten as

$$C_{am}{}^{\alpha}\, C_{bm}{}^{\beta} = C_{a0}{}^{\alpha}\, C_{b0}{}^{\beta} \exp(2\sigma Vm/RT)$$

If the conditions are such that co-ordinate dependence of C_a may be neglected then the equation for C_{bm} is

$$C_{bm} = K_0{}^{1/\beta}\, C_a{}^{-\alpha/\beta} \exp(2\sigma Vm/\beta RT)$$

For the case of C_b concentration being practically equal everywhere in the matrix

$$C_{am} = K_0{}^{1/\alpha}\, C_b{}^{-\beta/\alpha} \exp(2\sigma Vm/\alpha RT)$$

This allows a compound to be treated as one element when solving problems of mass transfer, the rate of which is determined by the diffusion process.

It has been suggested in [3] that co-ordinate concentration dependence of one or the other compound forming elements may be neglected if the amount of this element in solution is much greater than that of the other. However, it may easily be shown that it is not valid for a general case. Let $C_a = \phi_a(x, y, z)$ and $C_b = \phi_b(x, y, z)$ be solutions of Laplace equations together with the equation

$$j_a/j_b = \alpha/\beta \qquad (2)$$

which is the condition for quasistationary process connection between the fluxes of A and B in each matrix point and corresponding stoichiometric coefficients. Equation 2 may be rewritten as

$$\frac{\beta\, D_a \nabla \phi_a}{\alpha\, D_b \nabla \phi_b} = 1 \qquad (3)$$

where D = diffusion coefficient. C_a variation with co-ordinates may, evidently, be neglected if in any matrix point

$$\frac{\nabla\phi_a}{C_a} \ll \frac{\nabla\phi_b}{C_b}$$

which occurs, as is seen from 3, when

$$\beta D_a C_a \gg \alpha D_b C_b \quad (4)$$

C_b variation may be neglected if

$$\beta D_a C_a \ll \alpha D_b C_b \quad (5)$$

The critical values of $C_a{}^*$ and $C_b{}^*$, corresponding to the equality sign in 4 and 5, will then be

$$C_a{}^* = \left(\frac{\alpha D_b}{\beta D_a}\right)^{\beta(\alpha+\beta)^{-1}} K^{(\alpha+\beta)^{-1}}$$

$$C_b{}^* = \left(\frac{\beta D_a}{\alpha D_b}\right)^{\alpha(\alpha+\beta)^{-1}} K^{(\alpha+\beta)^{-1}}$$

where K may be considered equal to K_0 assuming minimum values of $1/m$ in the system studied to be much greater than $2\sigma V/RT$ (see equation 1), which generally applies [3].

Thus if rate constant of mass transport is proportional to CD (C = concentration and D = diffusion coefficient of the element transported) in the element/element system, then in a similar element/oxide system (B is oxygen) rate constant at $C_b \ll C_b{}^*$ will be proportional to $C_b D_b$, and at $C_b \gg C_b{}^*$ will be proportional to $C_a D_a$, which is equal to $C_b{}^{-\beta/\alpha} D_a K_0{}^{1/\alpha}$. In the last case the process activation energy is determined by the activation energy of diffusion of A, the free energy of compound formation from elements dissolved in the matrix, and the free energy of solution of B in M. If it is this case ($C_b \gg C_b{}^*$) that occurred in [1], then it explains the high value for the activation energy of the groove growth process obtained in the range 1410 to 1540°C and rules out the supposition that diffusion through the oxide proceeds faster than through the metal.

Different forms of dependence of the rate constant on solid oxygen solution concentration in the matrix at $C_b > C_b{}^*$ and $C_b < C_b{}^*$ gives in principle the possibility to determine which of these cases apply to the present (or other) experimental conditions.

It should be noted that the problem of mass transport in the element/compound system was discussed in detail in [4] which suffers from the same mistake as was pointed out in [5]: the principle of minimum entropy production is used to determine thermodynamic forces associated with j_a and j_b, while these forces are already set by the boundary conditions (A and B concentrations on the metal/compound interface in [4]). Such application of the principle contradicts its contents [6].

References

1. M. MCLEAN and E. D. HONDROS, *J. Mater. Sci.* **6** (1971) £9.
2. F. A. NICHOLS and W. W. MULLINS, *Trans. Met. Soc. AIME* **233** (1965) 1840.
3. C. WAGNER, *Z. Electrochem.* **65** (1961) 581.
4. CHE-YU LI, J. M. BLAKELEY, and A. H. FEINGOLD, *Acta Met.* **14** (1966) 1397.
5. J. W. CAHN and W. W. MULLINS, discussion in "Decomposition of Austenite by Diffusional Processes", edited by V. F. Zackay and H. I. Aaronson (Interscience, New York, 1960) p. 123.
6. S. R. DEGROOT, "Thermodynamics of Irreversible Processes" (North Holland, Amsterdam, 1952).

A. SEREBRYAKOV
Solid State Physics Institute,
USSR Academy of Sciences,
Chernogloovka, Moscow, USSR

Authors' Reply

Dr Serebryakov's comments refer to only a small part of the discussion in our paper, in which we distinguished, because of a kink in the Arrhenius plot (fig. 6), betwen a low-temperature and a high-temperature process in the kinetics of mass transport at a platinum/alumina interface. On the basis of a comparison between the observed activation energies and values in the literature, we speculated that diffusion of either Al or O in Pt is rate-controlling at low temperatures and that diffusion of either Al or O in Al_2O_3 is rate-controlling at high temperatures. Although Dr Serebryakov chooses to ignore the low-temperature results, we think that in a detailed analytical interpretation, equal weight should be given to them.

We welcome Dr Serebryakov's interest in this work and his attempts to make a more detailed analysis of the high-temperature process, in which he points out the importance of the free energies of compound formation and element solution. We would, however, like to make the following comments on his analysis:

(1) He maintains that the flux conservation condition $j_a/j_b = \alpha/\beta$ applies to all points in the metal matrix. Although for purposes of conservation of stoichiometry the above is plausible at the interfaces, it is not immediately obvious why this should apply everywhere in the bulk: indeed, in this situation, we suggest that the appropriate condition is

$$\frac{j_a}{j_b} = \frac{C_a\,(\text{bulk})}{C_b\,(\text{bulk})}$$

(2) It is not clear how relations derived from the Gibbs-Thompson equation, and which strictly apply to interface phenomena, can be substituted in his equations 4 and 5 which refer to the bulk.

Finally, we agree with his misgivings concerning the application of the principle of minimum entropy production in the interpretation of mass transport kinetics in such complex systems, and indeed, this was the reason why we hesitated to analyse our results along these lines.

M. MCLEAN
E. D. HONDROS
National Physical Laboratory
Teddington, Middlesex, UK

Wrought Cobalt-Chromium Surgical Implant Alloys

The two most popular alloys now used for the repair or replacement of damaged bone in human patients are molybdenum-containing wrought austenitic stainless steel and precision cast cobalt-chromium-molybdenum-carbon alloys [1]. Unfortunately, neither of the above alloy systems can be regarded as ideally suitable implant material. Stainless steel tends to pit and crevice corrode in body fluids [2, 3], while precision cast cobalt-chromium-molybdenum-carbon alloys such as Vitallium, Vinertia, Haynes Stellite 21, etc., possess insufficient ductility to withstand short-comings in design, fabrication or use [4]. The stronger and more ductile wrought Co-Cr-W-Ni alloy Haynes Stellite 25, sometimes used in conjunction with, or as a replacement for cast HS 21, although vastly more resistant to crevice corrosion than stainless steel, has been found inferior to cast Vitallium [5, 6] (HS 21, Vinertia, etc.). Crevice corrosion of this alloy has also been found to lead to corrosion fatigue failure [7].

In our studies of the hot and cold deformability of Co-Cr-Mo-C alloys of varying composition we have found that the mechanical properties of a number of such cast alloys if hot worked either by extrusion or press forging at 1100 to 1200°C can be improved. By subsequent heat-treatment it was found possible to more than double the as-cast percentage elongation. Such an increase in ductility permitted cold reductions of 35% (RA) by cold swaging and about 26% by cold rolling. The same techniques were used to improve the mechanical properties of as-cast HS 21 as shown in table I.

Orthodox electrochemical measurements [8] such as critical potential, resting potential versus time, and corrosion current density versus time at passive potentials were carried out in isotonic salt solutions and in such of higher chloride and hydrogen ion content [9]. Since such measurements are but of limited usefulness in assessing crevice corrosion resistance [10] of alloys, accelerated crevice corrosion tests in a 10% HCl plus 1% $FeCl_3$ solution at 37°C were also made. These accurately machined and finely finished alloy specimens tightly fitted with accurately machined and finished teflon washers, were compared with non-gasketed samples of the same alloys. Gasketed samples of Mo stainless steel in this solution were found to exhibit visible evidence of crevice corrosion in the first hour after immersion, wrought HS 25 specimens in four to six days, cast HS 21 specimens in not less than fourteen days. The corrosion rates listed in table II indicate crevice corrosion was not observed in the wrought and heat-treated specimens of HS 21 in four weeks.

The superior mechanical properties, as well as corrosion resistance of the wrought HS 21 alloy as compared to the cast alloy of the same composition can be attributed to the more homogenised finer grained matrix structure and more uniform distribution of carbides achieved by hot working and heat-treatment as indicated by the photomicrographs of figs. 1a and b.