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Ion-exchange equilibria between (Mn, Co)O solid solution and (Mn, Co) Cr_2O_4 and (Mn, Co) Al_2O_4 spinel solid solutions at 1100°C

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The compositions of the (Mn,Co)O solid solution with rock salt structure in equilibrium with (Mn,Co)Cr_2O_4 and (Mn,Co)Al_2O_4 spinel solid solutions have been determined by X-ray diffraction measurements at 1100° C and an oxygen partial pressure of 10^{-10} atm. The ion exchange equilibria are quantitatively analysed, using values for activities in the (Mn,Co)O solid solution available in the literature, in order to obtain activities in the spinel solid solutions. The $MnAl_2O_4$–$CoAl_2O_4$ solid solution exhibits negative deviations from Raoult's law, consistent with the estimated cation disorder in the solid solution, while the $MnCr_2O_4$–$CoCr_2O_4$ solid solution shows slightly positive deviations. The difference in the Gibbs free energy of formation of the two pure chromites and aluminates derived from the results of this study are in good agreement with recent results obtained from solid oxide galvanic cells and gas-equilibrium techniques.

1. Introduction

Electronically conducting cobalt chromite is a potentially useful material for interconnecting the cells of the high temperature, zirconia electrolyte, fuel cell battery. Its conductivity can be increased by doping with manganese. The high conductivity is probably caused by 3d electron interchange between chromium ions in adjacent octahedral positions because of their collinearity and small separation.

High temperature oxidation-resistant cobalt-base alloys contain chromium and aluminium for corrosion resistance. The growth rate of the chromite spinel is approximately 1000 times slower than that of Cr_2O_3. The addition of manganese to the alloy usually enhances the oxidation resistance, the inner protective layer of the oxide being a spinel solid solution. As a part of a larger programme of study of phase equilibria and thermodynamic properties of spinel solid solutions, with the dual object of exploring the possibility of using conducting oxide electrodes in fuel cells and understanding the formation of protective spinel solid solutions on cobalt alloys, the compositions of the conjugate phases in the ternary systems MnO-CoO-$Al_2O_3(\alpha)$ and MnO–CoO–Cr_2O_3 have been determined at 1100° C and an oxygen partial pressure of 10^{-10} atm by X-ray diffraction.

Activities in the binary CoO–MnO solid solutions have been determined by Aukrust and Muan [1] (1200° C) and Biggers and Muan [2] (1250° C) using gas-equilibrium techniques. Their results indicate ideal mixing in the solid solution. More recently, Seetharaman and Abraham [3] have re-examined the system using solid oxide galvanic cells and suggest small positive deviations from Raoult's law. They have confirmed the finding by

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acid-solution calorimetry [4]. An evaluation of all reported measurements on the system suggests that the thermodynamic properties of mixing at 1100° C can be expressed as,

$$\Delta G_M^E = W X_{CoO} X_{MnO} \text{ J mol}^{-1} \qquad (1)$$

where $W = 3375$ (± 1000) J mol^{-1}, and X_{CoO} and X_{MnO} represent the mole fractions of the constituent oxides. The selected value for W is the average of the mean values obtained from the three independent techniques, and agrees with our repetition of the emf measurement for $X_{CoO} = 0.5$. No previous thermodynamic or phase equilibrium measurements of the spinel solid solutions Mn(Co)Cr_2O_4 and Mn(Co)Al_2O_4 have been reported in literature. The results obtained in this study on the compositions of the conjugate phases of the spinel and rock-salt solid solutions can be analysed quantitatively, using information on the rock-salt phase given by Equation 1, and a method recently developed by Jacob and Jeffes [5], in order to yield the activities in the spinel solid solutions, and the differences in the standard free energies of formation of the chromites and aluminates of cobalt and manganese.

2. Experimental methods

2.1. Materials

Fine powders of α-Al_2O_3, Cr_2O_3 and CoO, each 99.99% pure, were supplied by Alfa Inorganics. Manganese oxide, MnO, were prepared by decomposing Analar $MnSO_4$ at 1000° C in air to a mixture of Mn_3O_4 and Mn_2O_3; the oxides were then reduced in hydrogen for 2 h to yield bright green MnO. The chromites and aluminates of cobalt and manganese were prepared by prolonged heating at 1100° C of pressed pellets containing an intimate, equimolar mixture of the component oxides at an oxygen partial pressure of 10^{-10} atm. The pellets for the synthesis of the aluminates were supported on alumina crucibles and the pellets for the synthesis of chromites were held in Cr_2O_3-lined alumina supports. The formation of the ternary compounds was confirmed by X-ray diffraction analysis.

2.2. Synthesis of solid solutions

The CoO–MnO solid solutions with rock-salt structure were synthesized by heating pressed pellets made of intimate mixtures of component oxides at an oxygen partial pressure of 10^{-10} atm and a temperature of 1100° C for 3 to 4 days. The compositions of the pellets were obtained from the weights of the component oxides in the mixture. The solid solution was cooled to room temperature, ground under acetone, repelletized and heat-treated again for 3 days to ensure the complete formation of the solid solution. Spinel solid solutions, with atomic ratios of cobalt to manganese the same as in the rock-salt phases, were also prepared in a similar manner. Volatilization of manganese from the samples under the CO + CO_2 gas mixture corresponding to an oxygen partial pressure of 10^{-10} atm at 1100° C was insignificant, since the pellets showed no change in weight during the heat-treatment. An X-ray powder diffractometer was used for d-spacing measurements. Vegard's law was obeyed in the spinel solid solutions, while a small negative deviation similar to that reported by Biggers and Muan [2] was found in the rock salt solid solution with the maximum deviation occurring at $0.8 > X_{CoO} > 0.7$. The synthetic solid solutions were used as standards for the determination of the composition of oxide phases after equilibration.

2.3. Procedure

Weighed quantities of the spinel and rock-salt solid solutions with identical ratios of cobalt to manganese in each phase, were intimately mixed and the pelletized. The pellets were heated at 1100° C in a three-zone kanthal wound, horizontal furnace, with an even temperature (± 2° C) zone of 6 cm, under a flowing stream of CO + CO_2 gas mixture for 230 h. The ratio of CO to CO_2 in the mixture was 0.06, the flow rate of the mixture was 400 cm^3 min^{-1}, and the linear velocity was approximately 65 cm min^{-1}. Darken and Gurry [6] have experimentally demonstrated that at this linear gas velocity thermal segregation in the CO + CO_2 mixture can be avoided. Preliminary experiments indicated that equilibrium is attained in approximately 150 h, larger periods of equilibration causing no further change in the lattice parameter of the oxide solid solutions. At the end of equilibration, the samples were quenched by dropping into liquid nitrogen. The pellets were ground under acetone. Fine powders (50 μm or less) so obtained were used for measurement of the d-spacing of indexed high-θ lines by diffractometry using Cu$K\alpha$ radiation. The compositions of the solid solutions were obtained from the measured d-spacings corresponding to the 4 4 0 and 2 2 0 peaks of the spinel phases and the 2 0 0 peak of the rock salt phase. The precision was improved by admixture with pure silicon, which served as an internal standard of θ on the diffractometer trace. The unit cell dimensions of silicon are very precisely known. The 1 1 1 and 2 2 0 peaks of silicon with $d = 3.138$ and $d = 1.920$ were used for internal standardization. The amount of silicon in the diffractometer sample was adjusted by trial and error until the peaks from silicon and the solid solutions were of comparable height, so that uncertainties in scanning and chart speeds have minimal effect. The diffractometer was run at least six times over the peaks at a scanning speed of 0.2° 2θ per min and the average separations between the peaks of the oxide phases and silicon were measured. The uncertainty in the composition of the rock-salt phase obtained by this method was less than 1%. Because of the small difference in the lattice parameters of the pure spinel phases, the accuracy in the analysis of spinel composition was only ± 3%. A more accurate value for the compositions of the spinel solid solution was obtained by extending the line joining the points representing the total composition of the pellet and the composition of the rock-salt phase on the ternary diagram.

3. Results

The compositions of the conjugate phases at 1100° C and an oxygen partial pressure of 10^{-10} atm are summarized in Table I (see also Figs. 5 and 6). The activity coefficients (γ) in the spinel solid solution are calculated using the following equations [5], which are based on fundamental thermodynamic principles;

$$\log \gamma_{\mathrm{MnAl_2O_4}} = \int_1^{X_{\mathrm{MnAl_2O_4}}} X_{\mathrm{CoAl_2O_4}} \, \mathrm{d} \log \left(\frac{\gamma_{\mathrm{MnAl_2O_4}}}{\gamma_{\mathrm{CoAl_2O_4}}}\right)$$

$$= \int_1^{X_{\mathrm{MnAl_2O_4}}} X_{\mathrm{CoAl_2O_4}} \, \mathrm{d} \log \left[\frac{X_{\mathrm{CoAl_2O_4}} \, X_{\mathrm{MnO}}}{X_{\mathrm{MnAl_2O_4}} \, X_{\mathrm{CoO}}}\right]\left(\frac{\gamma_{\mathrm{MnO}}}{\gamma_{\mathrm{CoO}}}\right).$$

The quantity in the first bracket is obtained from the results of this study, while the quantity in the second bracket is obtained from Equation 1 as,

$$\log \left(\frac{\gamma_{\mathrm{MnO}}}{\gamma_{\mathrm{CoO}}}\right) = 0.128 \, (X_{\mathrm{CoO}} - X_{\mathrm{MnO}})$$

since $\Delta G^{\mathrm{E}}_{\mathrm{CoO}} = W(1 - X_{\mathrm{CoO}})^2 = 19.14 T \log \gamma_{\mathrm{CoO}}$, etc. The modified Gibbs–Duhem integration plots for the aluminate and chromite solutions are shown in Figs. 1 and 2. The plot of

$$X_{\mathrm{CoAl_2O_4}} \text{ versus } \log \left[\frac{X_{\mathrm{CoAl_2O_4}} \, X_{\mathrm{MnO}} \gamma_{\mathrm{MnO}}}{X_{\mathrm{MnAl_2O_4}} \, X_{\mathrm{CoO}} \gamma_{\mathrm{CoO}}}\right]$$

is a straight line with a negative slope, which indicates that the aluminate spinel solid solution is "regular", and is characterized by negative excess

TABLE I Composition of conjugate phases of the rock salt and spinel solid solutions at 1100° C

$(\mathrm{Mn,Co})\mathrm{O} \rightleftharpoons (\mathrm{Mn,Co})\mathrm{Al_2O_4}$		$(\mathrm{Mn,Co})\mathrm{O} \rightleftharpoons (\mathrm{Mn,Co})\mathrm{Cr_2O_4}$	
at.% MnO in rock-salt phase	at.% $\mathrm{MnAl_2O_4}$ in spinel phase	at.% MnO in rock salt phase	at.% $\mathrm{MnCr_2O_4}$ in spinel phase
10.0	17.2	9.0	18.7
23.8	31.5	24.0	43.9
41.8	43.4	40.0	62.6
56.0	53.3	52.0	73.6
69.8	62.1	63.8	82.5
82.5	74.0	79.7	90.9
93.0	86.1		

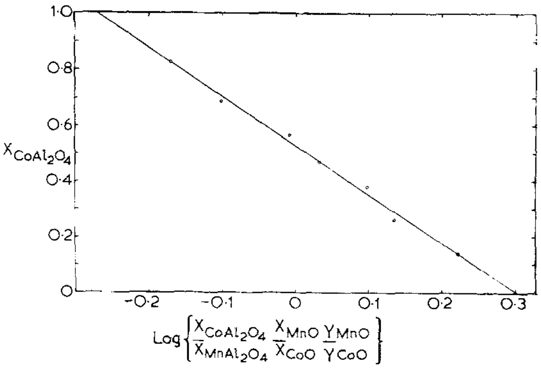

Figure 1 Integration plot for $\mathrm{MnAl_2O_4}$–$\mathrm{CoAl_2O_4}$ solid solution at 1100° C.

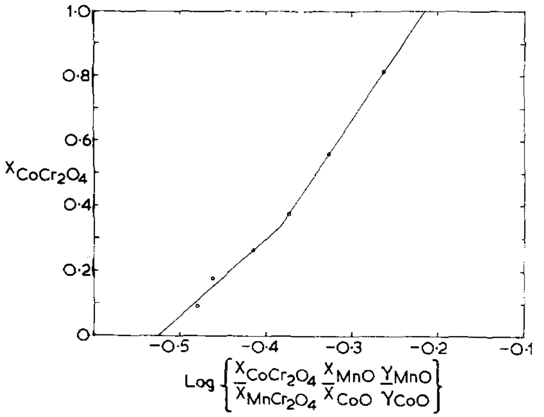

Figure 2 Integration plot for $\mathrm{MnCr_2O_4}$–$\mathrm{CoCr_2O_4}$ solid solution at 1100° C.

free energy of mixing which is a symmetric function of composition. A vertical line on the integration plot would characterize an ideal solution. From the area under the curve or the slope of the line in Fig. 1, the following parameters are calculated:

$$\log \gamma_{\mathrm{MnAl_2O_4}} = -0.285\, X^2_{\mathrm{CoAl_2O_4}} \qquad (4)$$

$$\log \gamma_{\mathrm{CoAl_2O_4}} = -0.285\, X^2_{\mathrm{MnAl_2O_4}} \qquad (5)$$

$$\Delta G^{\mathrm{E}}_{\mathrm{M}} = -7490\, X_{\mathrm{CoAl_2O_4}} X_{\mathrm{MnAl_2O_4}}\ \mathrm{J\,mol^{-1}}. \qquad (6)$$

For the chromite solid solution, the integration plot (Fig. 2) has a positive slope, indicating positive deviations from Raoult's law. The data can be represented by two straight lines. The logarithm of the activity coefficients can, therefore, be represented by two quadratic equations, the coefficients of which are obtained from the slopes of the lines or the areas under them;

$$\begin{aligned}\log \gamma_{\mathrm{MnCr_2O_4}} &= 0.213\, X^2_{\mathrm{CoCr_2O_4}} \\ &\qquad 0.33 > X_{\mathrm{CoCr_2O_4}} > 0 \\ &= 0.127\, X^2_{\mathrm{CoCr_2O_4}} + 0.009 \\ &\qquad 1 > X_{\mathrm{CoCr_2O_4}} > 0.33\end{aligned} \qquad (7)$$

$$\begin{aligned}\log \gamma_{\mathrm{CoCr_2O_4}} &= 0.213\, X^2_{\mathrm{MnCr_2O_4}} - 0.039 \\ &\qquad 0.33 > X_{\mathrm{CoCr_2O_4}} > 0 \\ &= 0.127\, X^2_{\mathrm{MnCr_2O_4}} \\ &\qquad 1 > X_{\mathrm{CoCr_2O_4}} > 0.33.\end{aligned} \qquad (8)$$

The composition dependence of the activity of the component spinels in the aluminate and chromite solid solutions and their excess free energies of mixing at 1100° C are shown in Figs. 3 and 4.

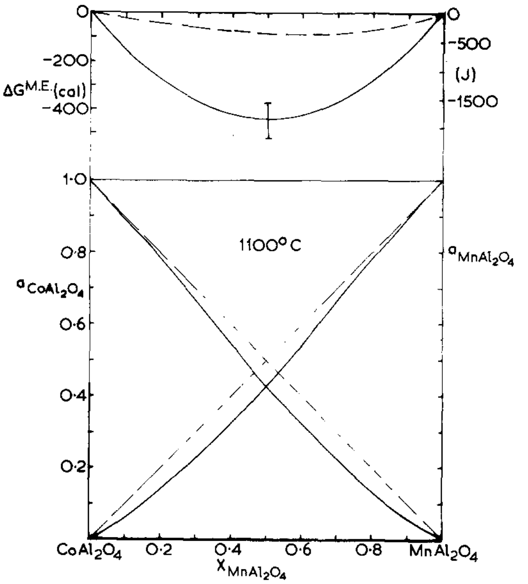

Figure 3 Activities and excess free energy of mixing in the system $\mathrm{CoAl_2O_4}$–$\mathrm{MnAl_2O_4}$ at 1100° C: —— experimental; – – – – calculated from cations distribution.

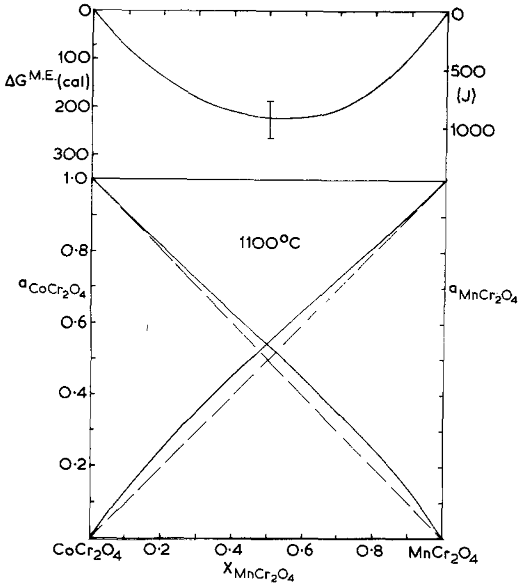

Figure 4 Activities and excess free energy of mixing in the system $\mathrm{CoCr_2O_4}$–$\mathrm{MnCr_2O_4}$ at 1100° C.

4. Discussion

Since Equation 2 is not based on thermodynamic models or other assumptions, the derived activities may be used to calculate the equilibrium constants and the standard free energy changes at 1100° C for the reactions;

$$\mathrm{MnAl_2O_4 + CoO \rightarrow CoAl_2O_4 + MnO} \qquad (9)$$

$$K_9 = \frac{X_{\mathrm{CoAl_2O_4}}\gamma_{\mathrm{CoAl_2O_4}}}{X_{\mathrm{MnAl_2O_4}}\gamma_{\mathrm{MnAl_2O_4}}} \cdot \frac{X_{\mathrm{MnO}}\gamma_{\mathrm{MnO}}}{X_{\mathrm{CoO}}\gamma_{\mathrm{CoO}}} = 1.037\ (\pm 0.035)$$

$$\Delta G^\circ_9 = -RT\ln K_9 = -415\ (\pm 400)\ \mathrm{J\,mol^{-1}}$$

$$\mathrm{MnCr_2O_4 + CoO \rightarrow CoCr_2O_4 + MnO} \qquad (10)$$

$$K_{10} = \frac{X_{\mathrm{CoCr_2O_4}}\gamma_{\mathrm{CoCr_2O_4}}}{X_{\mathrm{MnCr_2O_4}}\gamma_{\mathrm{MnCr_2O_4}}} \frac{X_{\mathrm{MnO}}\gamma_{\mathrm{MnO}}}{X_{\mathrm{CoO}}\gamma_{\mathrm{CoO}}} = 0.444\ (\pm 0.01)$$

$$\Delta G^\circ_{10} = -RT\ln K_{10} = 9275(\pm 400)\ \mathrm{J\,mol^{-1}}.$$

The standard free energy changes for the above reactions represent the differences in the standard free energies of formation of the two pure aluminates or chromites from component oxides. Recent measurements by Jacob and Alcock [7] on the stability of pure spinel phases using solid oxide galvanic cells and gas equilibrium techniques suggest values of $-8\,\mathrm{J\,mol^{-1}}$ and $8400\,\mathrm{J\,mol^{-1}}$ for ΔG_9° and ΔG_{10}° in good agreement with the values calculated in this study. The manganese and cobalt aluminates have approximately the same stability, so that the conjugate lines between (Mn, Co)O and (Mn, Co)Al_2O_4 phases are roughly symmetrical (Fig. 5). Perfect symmetry of the conjugate lines is realised when ΔG_9 equals zero and

$$\frac{\gamma_{\mathrm{CoAl_2O_4}}\cdot\gamma_{\mathrm{MnO}}}{\gamma_{\mathrm{MnAl_2O_4}}\cdot\gamma_{\mathrm{CoO}}} = 1.$$

Manganese chromite is substantially more stable than cobalt chromite and this causes the conjugate lines between the (Mn, Co)O and (Mn, Co)Cr_2O_4 phases to be directed towards the $MnCr_2O_4$ corner (Fig. 6).

A normal spinel structure (MX_2O_4) can be described as a close-packed cubic arrangement of anions with one-eighth of the tetrahedral holes filled with M^{2+} cations and one-half of the octahedral holes filled with X^{3+} cations. A high temperatures, cations can exchange positions, the magnitude of cation mixing being determined by the difference in "site preference energies". In the aluminate solid solution there are three different cations, Co^{2+}, Mn^{2+}, and Al^{3+}, competing for the occupancy of the two interstitial positions. The cation distribution can be represented as,

$$\left(\mathrm{Co}_{x\alpha}\mathrm{Mn}_{(1-x)\beta}\mathrm{Al}_{2\lambda}\right)\left[\mathrm{Co}_{x(1-\alpha)}\mathrm{Mn}_{(1-x)(1-\beta)}\mathrm{Al}_{2(1-\lambda)}\right]\mathrm{O}_4$$

where ( ) denotes tetrahedral and [ ] denotes octahedral positions, $x = X_{\mathrm{CoAl_2O_4}}$ (mole fraction), and

$$2\lambda = 1 - x\alpha - (1-x)\beta. \qquad (11)$$

Dunitz and Orgel [8] have tabulated the crystal field stabilization energies of transitional metal

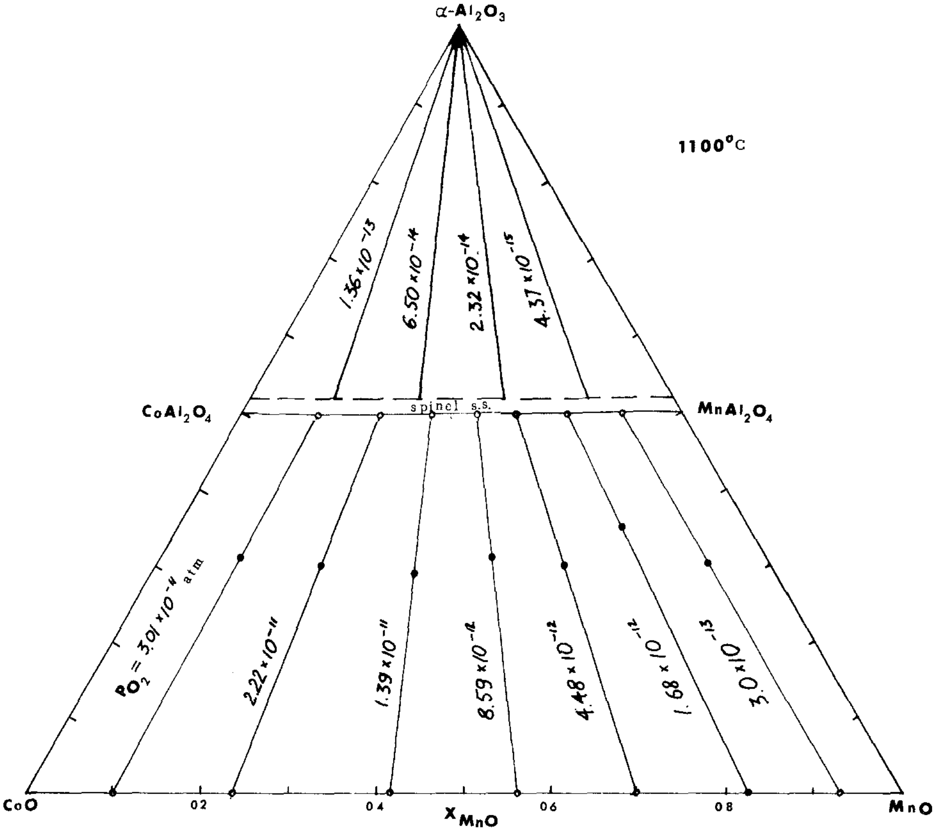

Figure 5 Compositions of conjugate phases in the system $CoO{-}MnO{-}Al_2O_3(\alpha)$ at 1100° C. Filled circles correspond to the total average compositions of the pellets containing the rock salt and spinel phases. The oxygen partial pressures below which metallic cobalt will appear are also indicated on the diagram.

TABLE II Cation distribution in $Co_xMn_{1-x}Al_2O_4$ system at 1100° C.

x or $X_{CoAl_2O_4}$	Estimated			Measured		
	α	β	λ	α	β	λ
1	0.84	–	0.08	0.83	–	0.085(±0.01) [10]
				0.95	–	0.025(±0.02) [11]
0.8	0.825	0.986	0.071			
0.6	0.804	0.984	0.062			
0.4	0.77	0.98	0.052			
0.2	0.715	0.974	0.039			
0	–	0.955	0.022	–	0.92	0.04(±0.02) [11]

ions in the octahedral and tetrahedral sites. The difference in energy of an ion between these two sites is termed "octahedral site preference energy". The values for Co^{2+}, Mn^{2+} and Cr^{3+} ions are −31, 0, and −158 kJ respectively [8]; the negative signs indicating octahedral preference. A value of −78 kJ for the octahedral site preference energy of the Al^{3+} ion was derived [9] from a number of direct high temperature cation distribution measurements on $NiAl_2O_4$ based on the value of −86 kJ for Ni^{2+} ion suggested by Dunitz and Orgel [8]. The differences in the octahedral site preference energies of Co^{2+} and Al^{3+} is equal to the enthalpy change for the exchange reaction,

$$(Co^{2+}) + [Al^{3+}] \rightarrow [Co^{2+}] + (Al^{3+})$$

where ( ) denotes tetrahedral and [ ] denotes octahedral sites. Assuming that the activities of the ions on each site are equal to their ionic fractions (Temkin ideal mixing [12]) on that site, the cation distribution can be related to differences in the octahedral site preference energies [9];

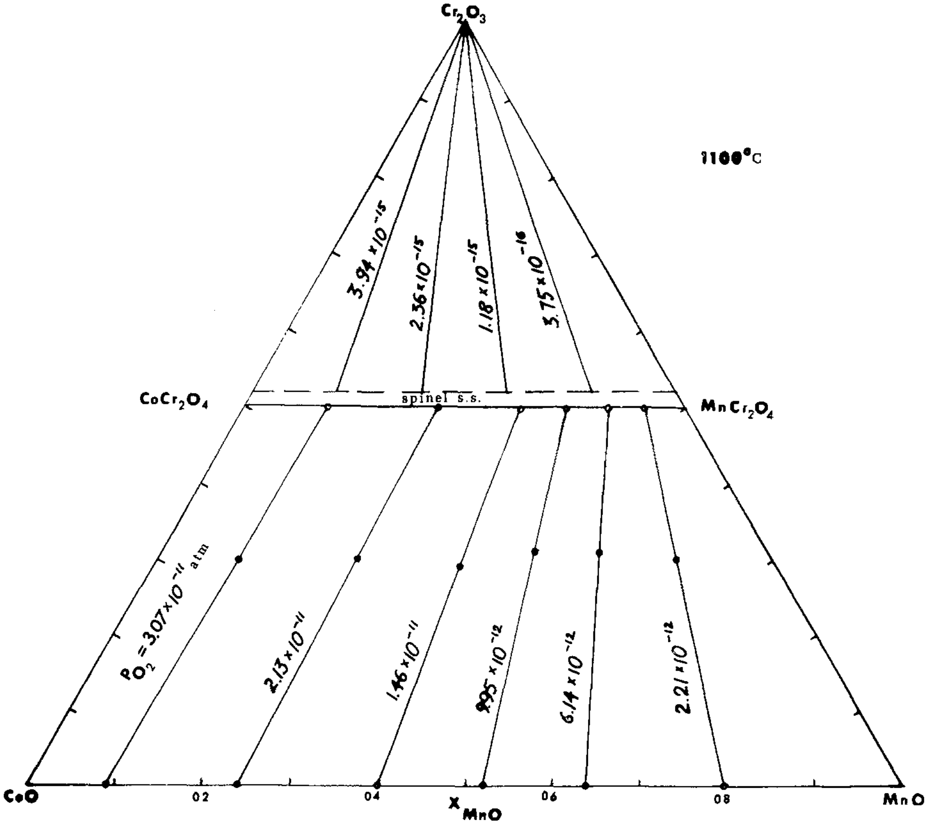

Figure 6 Composition of conjugate phases in the system CoO–MnO–Cr_2O_3 at 1100° C. Filled circles correspond to the total average compositions of the pellets containing the rock salt and spinel phases. The oxygen partial pressures below which metallic cobalt will appear are also indicated on the diagram.

$$H^{\mathrm{oct}}_{\mathrm{Co}^{3+}} - H^{\mathrm{oct}}_{\mathrm{Al}^{3+}} = 47\,000\,\mathrm{J} = -RT\ln\left[\frac{\lambda(1-\alpha)}{\alpha(1-\lambda)}\right] \qquad (12)$$

$$H^{\mathrm{oct}}_{\mathrm{Mn}^{2+}} - H^{\mathrm{oct}}_{\mathrm{Al}^{3+}} = 78\,000\,\mathrm{J} = -RT\ln\left[\frac{\lambda(1-\beta)}{\beta(1-\lambda)}\right]. \qquad (13)$$

The values of α, β and λ, which define the cation distribution, for different compositions (i.e. values of x) of the spinel solid solution obtained by solving the three simultaneous Equations 11, 12, and 13 are summarized in Table II. This table also contains the measured cation distributions in pure $CoAl_2O_4$ and $MnAl_2O_4$ for comparison. It has been shown earlier [9] that the cation distribution estimated from the site preference energies for a number of aluminate spinels is in good agreement with X-ray and neutron diffraction measurements.

The Temkin ideal cation mixing contribution to the total entropy of the spinel solid solution is given by,

$$\Delta S^{\mathrm{CM}} = -R\left[\Sigma(N_{\mathrm{i}})\ln(N_{\mathrm{i}}) + 2\Sigma[N_{\mathrm{i}}]\ln[N_{\mathrm{i}}]\right] \qquad (14)$$

where (N_{i}) represents the ionic fraction of the cation i among all the ions on the tetrahedral site, i.e. $(N_{\mathrm{Co}^{2+}}) = x\alpha$ etc, and $[N_{\mathrm{i}}]$ represents the ionic fraction on the octahedral site, i.e. $N_{\mathrm{Co}^{2+}} = x(1-\alpha)/2$, etc. The above equation can also be written in terms of α, β and λ as,

$$\begin{aligned}\Delta S^{\mathrm{CM}} = -R\Big[&\{x\alpha\ln x\alpha + (1-x)\beta\ln(1-x)\beta + 2\lambda\ln 2\lambda\}\\ &+\Big\{x(1-\alpha)\ln\left[\frac{x(1-\alpha)}{2}\right] + (1-x)(1-\beta)\ln\left[\frac{(1-x)(1-\beta)}{2}\right] + 2(1-\lambda)\ln(1-\lambda)\Big\}\Big]. \qquad (15)\end{aligned}$$

The entropy of mixing of the spinel solid solution may be obtained by subtracting from the cation mixing entropy of the solid solution the mole fraction weighted sum of the cation mixing entropy of the two pure component spinels;

$$\Delta S_{\mathrm{M}} = S^{\mathrm{CM}}_{\mathrm{S.S}} - x\,S^{\mathrm{CM}}_{\mathrm{CoAl_2O_4}} - (1-x)\,\Delta S^{\mathrm{CM}}_{\mathrm{MnAl_2O_4}}\,. \qquad (16)$$

Similarly, the heat of mixing of the spinel solid solution due to cation rearrangement can be calculated from the octahedral site preference energies:

$$\begin{aligned}\Delta H_{\mathrm{M}} = {}&(\alpha_{\mathrm{S.S}} - \alpha_{\mathrm{CoAl_2O_4}})x\,.\,31\,000 + 2\{\lambda_{\mathrm{S.S}} - x\lambda_{\mathrm{CoAl_2O_4}} -\\ &(1-x)\lambda_{\mathrm{MnAl_2O_4}}\}\cdot 78\,000\,\mathrm{J}. \qquad (17)\end{aligned}$$

Since the octahedral site preference energy of Mn^{2+} ion is zero, there is no heat effect associated with the redistribution of the Mn^{2+} ions in the solid solution. The excess free energy of mixing of the spinel solid solution is then given by

$$\Delta G^{\mathrm{E}}_{\mathrm{M}} = \Delta H - T\Delta S - RT\{x\ln x + (1-x)\ln(1-x)\}. \qquad (18)$$

The calculated values for $\Delta G^{\mathrm{E}}_{\mathrm{M}}$ are shown in Fig. 3. Similar calculations for the chromite solid solution suggests an almost ideal behaviour. This may be expected from the high octahedral stability of Cr^{3+} ion and the negligible cation mixing in the pure chromites. The measured excess free energy of mixing in aluminate solid solution is approximately 1400 J more negative than the estimated values, while in the chromite solid solution the measured excess free energy is approximately 900 J more positive than the estimated value at equimolar composition. Formation of an ideal solution would require that the ionic radii of the cations be the same on structurally equivalent sites. Since the ionic radius of Mn^{2+} ion is approximately 12% higher than that of Co^{2+} ion, it is reasonable to anticipate a positive strain energy contribution to the excess free energy of mixing. If the Madelung energy of the solid solution does not vary linearly with composition, there would be an additional electrostatic contribution to the heat of mixing, which is difficult to evaluate in the absence of accurate values for the oxygen parameter, u, for the spinel solid solutions.

Another factor to be considered is the presence of Mn^{3+} and Co^{3+} ions in the spinel phase. From the standard free energy change for the reaction,

$$3\mathrm{MnO} + \tfrac{1}{2}\mathrm{O_2} \rightarrow \mathrm{Mn_3O_4}$$

it can be shown that the activity of Mn_3O_4 in the spinel phase at an oxygen partial pressure of 10^{-10} atm is:

$$a_{\mathrm{Mn_3O_4}} \leqslant 8.8 \times 10^{-4}.$$

Similarly it can be shown that Co^{3+} ion is unstable in the presence of Mn^{2+} ion.

Phase equilibria in the ternary systems MnO–CoO–Al_2O_3(α) and MnO–CoO–Cr_2O_3 at 1100° C are shown in Figs. 5 and 6. The oxygen partial pressures below which metallic cobalt would precipitate by the reduction of the spinel or rock salt solid solutions are calculated from the standard free energy changes [7] for the reactions,

$$Co + \tfrac{1}{2}O_2 \rightarrow CoO$$

$$\Delta G^\circ = -234\,620 + 71.02\,T\,\mathrm{J\,mol^{-1}} \qquad (19)$$

$$Co + \tfrac{1}{2}O_2 + \alpha\text{-}Al_2O_3 \rightarrow CoAl_2O_4$$

$$\Delta G^\circ = -166\,295\,\mathrm{J\,mol^{-1}}\ (1100^\circ\,C) \qquad (20)$$

$$Co + \tfrac{1}{2}O_2 + Cr_2O_3 \rightarrow CoCr_2O_4$$

$$\Delta G^\circ = -186\,900\,\mathrm{J\,mol^{-1}}\ (1100^\circ\,C), \qquad (21)$$

and activities in the rock salt and spinel solid solutions. Owing to the large difference in the stabilities of MnO and CoO, the metallic phase that precipitates on reduction is essentially pure cobalt.

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