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K.T. Jacob*, R. Adharsh

Thermodynamics of Congruent Oxidation

Abstract: Congruent oxidation occurs when an alloy oxidizes at constant oxygen chemical potential and temperature to an oxide in which the ratio of metallic components is the same as in the alloy. In alloys that undergo congruent oxidation concentration gradients near the surface are minimized. In this work thermodynamic conditions for congruent oxidation of binary and ternary alloys are formulated using the regular solution model to describe thermodynamic mixing properties. The conditions under which congruent oxidation can occur are identified. Congruent oxidation of a binary alloy X-Y will occur only if difference in oxygen potential for the oxidation of the two pure metals is less than twice the difference in regular solution parameters for the oxide and alloy phases ($\Omega^O - \Omega^A$). In the case of ternary alloys, congruency requirements for both two-phase and three-phase equilibria are discussed. Since the conditions for congruent oxidation of ternary alloy X-Y-Z depends on many parameters, the effect of systematic variation of the binary sets of regular solution parameters on the congruent composition is explored by numerical solution of the governing equations.

Keywords: congruent oxidation, congruent reduction, thermodynamics, oxygen potential maxima/minima, miscibility gap

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***Corresponding author: K.T. Jacob:** Department of Materials Engineering, Indian Institute of Science, Bangalore 560012, India
E-mail: katob@materials.iisc.ernet.in
R. Adharsh: Department of Materials Science and Metallurgical Engineering, Maulana Azad National Institute of Technology, Bhopal 462051, India, E-mail: adharsh_r@live.com

1 Introduction

In the normal course of oxidation of alloys, one of the component elements in the alloy is preferentially oxidized to form an oxide layer. The cationic fraction of any element in the oxide is generally different from the corresponding mole fraction of the same element in the alloy. The preferential oxidation leads to concentration gradients in the alloy and the oxide. If the alloy is depleted in an element that contributes significantly to its strength, mechanical properties at the surface can be degraded leading to more rapid propagation of cracks initiated at the surface either due to stress or environmental factors. It is therefore useful to explore if congruent oxidation alloys can be designed to prevent preferential loss of alloying elements near the surface. Congruent oxidation occurs when the composition of the oxide and alloy is the same when expressed in terms of the composition variable $\eta_Y/(\eta_x + \eta_Y + \eta_Z)$, where η_i denotes moles of metal *i*. At the congruent composition, oxidation of the alloy occurs at a fixed oxygen potential and constant temperature. The phenomenon of congruent oxidation is akin to more common congruent vaporization and congruent melting. In this communication, the thermodynamic conditions for congruent oxidation are formulated. The situations in which one can expect congruent oxidation are identified. The oxygen potential and composition corresponding congruent oxidation are related to the stability of oxides and thermodynamics of alloy and oxide solid solutions. Although the discussion is confined to binary and ternary alloys, the principles outlined are valid for broader application to situations such as congruent oxidation of lower oxides to higher oxides or heterogeneous reaction of a metal and an oxide solid solution at alloy/oxide interface to form a more complex oxide solid solution.

2 Congruent oxidation in the system X-Y-O

The generalized condition for congruent oxidation and reduction in the system X-Y-O is discussed at some length in this section. Oxidation of solid or liquid alloy at constant temperature and oxygen partial pressure, to a solid or liquid oxide solution without any change in the ratio of metallic constituents is termed congruent oxidation; the reverse is congruent reduction. The condition for extremum (minimum or maximum) in oxygen potential can be expressed in terms of composition variable (ξ) as

$$\xi_Y^A = \xi_Y^O \tag{1}$$

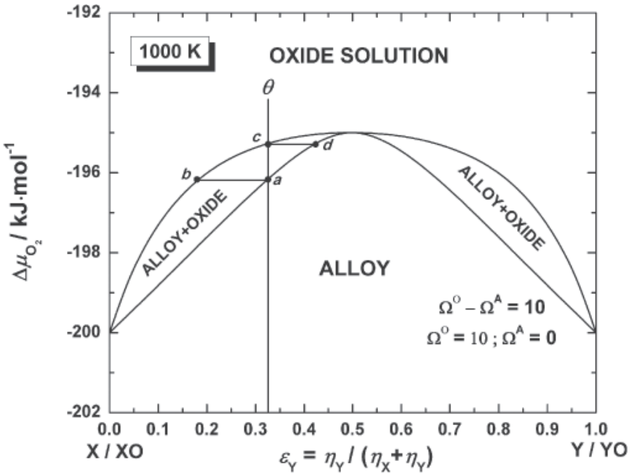

Fig. 1: Oxygen potential-composition diagram at constant temperature illustrating the oxidation of a binary alloy X-Y to an oxide solid solution XO-YO.

where ξ_Y^A is the mole fraction of Y in the alloy and ξ_Y^O is the cationic fraction of Y in the oxide solid solution. In general the composition variable can be defined as:

$$\xi_Y = \frac{\eta_Y}{\eta_X + \eta_Y} \tag{2}$$

Consider a case where alloy X-Y exists in the form of continuous solution and oxides XO and YO also form a continuous solution phase. At constant temperature, pure metals X and Y form their respective oxides at fixed oxygen partial pressures. The alloys generally oxidize over a range of oxygen partial pressure, except at the congruent composition, as shown in Fig. 1. An alloy of composition θ will start to oxidize at an oxygen potential marked as *a* in the figure. In this case component X is preferentially oxidized, giving an oxide solution rich in XO. The tie line *ab* gives the compositions of the alloy and oxide solution in equilibrium at the start of the oxidation process; the composition of the initial oxide phase is *b*. Alloy completes oxidation at an oxygen potential *c*. Assuming equilibrium oxidation, the composition of the oxide phase at the end of the oxidation process is the same as the initial alloy composition. The tie line *cd* gives the composition of the alloy (*d*) and oxide solution (*c*) at the termination of the oxidation process. On reducing the oxygen potential over an oxide solution, the reverse process will take place. The upper curve containing point *b* and *c* may be termed as 'oxidus' and the lower curve on which points *a* and *d* are located may be designated as 'reductus' by analogy with solidus and liquidus in conventional *T-X* diagrams.

The equilibrium between alloy and oxide solution can be represented by the exchange reaction,

$$\mathrm{XO} + \mathrm{Y} \rightarrow \mathrm{YO} + \mathrm{X} \tag{3}$$

for which the equilibrium constant can be written as,

$$\begin{aligned} K_3 &= \mathrm{e}^{-[(\Delta G^{\mathrm{o}}_{\mathrm{YO}} - \Delta G^{\mathrm{o}}_{\mathrm{XO}})/\mathrm{R}T]} \\ &= \left(\frac{(1-\xi_{\mathrm{Y}}^{\mathrm{A}})}{\xi_{\mathrm{Y}}^{\mathrm{A}}}\right)\left(\frac{\gamma_{\mathrm{X}}}{\gamma_{\mathrm{Y}}}\right)_{\xi_{\mathrm{Y}}^{\mathrm{A}}}\left(\frac{\xi_{\mathrm{Y}}^{\mathrm{O}}}{(1-\xi_{\mathrm{Y}}^{\mathrm{O}})}\right)\left(\frac{\gamma_{\mathrm{YO}}}{\gamma_{\mathrm{XO}}}\right)_{\xi_{\mathrm{Y}}^{\mathrm{O}}} \end{aligned} \tag{4}$$

In this equation $\Delta G^{\mathrm{o}}_{\mathrm{XO}}$ and $\Delta G^{\mathrm{o}}_{\mathrm{YO}}$ are the standard Gibbs free energies of formation of oxide XO and YO, and γ_i represents the activity co-efficient of component *i*.

Since during congruent oxidation compositions of the alloy and oxide solutions are the same, Eq. (1) can be incorporated in Eq. (4), resulting in

$$\ln K_3 = \ln \gamma_{\mathrm{X}} - \ln \gamma_{\mathrm{Y}} + \ln \gamma_{\mathrm{YO}} - \ln \gamma_{\mathrm{XO}} \tag{5}$$

In general γ is a complex function of composition. Eq. (5) can be solved only when explicit relation between activity co-efficient and composition are known for both solution phases. For a simplified generic discussion, assume that the behavior of both oxide solution and alloy can be represented by the regular solution model. Activity co-efficient of components X and Y in the alloy can then be written as:

$$\mathrm{R}T \ \ln \gamma_{\mathrm{X}} = \Delta \bar{G}^{\mathrm{E}}_{\mathrm{X}} = \Omega^{\mathrm{A}}(\xi_{\mathrm{Y}}^{\mathrm{A}})^2 \tag{6}$$

$$\mathrm{R}T \ \ln \gamma_{\mathrm{Y}} = \Delta \bar{G}^{\mathrm{E}}_{\mathrm{Y}} = \Omega^{\mathrm{A}}(1-\xi_{\mathrm{Y}}^{\mathrm{A}})^2 \tag{7}$$

In terms of the regular solution parameters Ω^{O} and Ω^{A} for oxide and alloy phases, respectively, Eq. (5) for oxidation at congruent composition ($\xi_{\mathrm{Y}}^{\mathrm{C}}$) can be rewritten as,

$$\ln K_3 = [(\Omega^{\mathrm{O}} - \Omega^{\mathrm{A}})(1 - 2\xi_{\mathrm{Y}}^{\mathrm{C}})]/\mathrm{R}T \tag{8}$$

This equation defines the composition for congruent oxidation. The value of $(1 - 2\xi_{\mathrm{Y}}^{\mathrm{C}})$ can vary from 1 to –1. The following conclusions can be derived from Eq. (8):

I. No extremum is possible if,

$$\frac{|\Delta G^{\mathrm{o}}_{\mathrm{YO}} - \Delta G^{\mathrm{o}}_{\mathrm{XO}}|}{|(\Omega^{\mathrm{O}} - \Omega^{\mathrm{A}})|} > 1 \quad \text{or} \quad \frac{|-\mathrm{R}T \ \ln K_3|}{|(\Omega^{\mathrm{O}} - \Omega^{\mathrm{A}})|} > 1 \tag{9}$$

Within the framework of the regular solution, the value of Ω cannot exceed 2R*T*, if continuous solid solution exists between the two end members. Thus, one basic requirement for congruent oxidation is that the stability of the two oxides XO and YO should not differ significantly.

II. When the standard Gibbs free energies of formation of oxides XO and YO are equal (i.e. ln $K_3 = 0$ or $K_3 = 1$), there will always be an extremum at $\xi_Y^C = 0.5$ irrespective of the value of $(\Omega^O - \Omega^A)$.

III. When the standard Gibbs free energy of formation of the oxide YO is more negative compared to that of XO (i.e. positive values of ln K_3) extremum exist only if,
   a. both $(\Omega^O - \Omega^A)$ and $(1 - 2\xi_Y^C)$ are positive (i.e. congruent composition exists only in the range $0 < \xi_Y^C < 0.5$ when $(\Omega^O - \Omega^A)$ is positive).
   b. both $(\Omega^O - \Omega^A)$ and $(1 - 2\xi_Y^C)$ are negative (i.e. congruent composition exists only in the range $0.5 < \xi_Y^C < 1$ when $(\Omega^O - \Omega^A)$ is negative).

IV. In the reverse case, when XO is marginally more stable than YO (i.e. value of ln K_3 is negative), extremum exist only if,
   a. $(\Omega^O - \Omega^A)$ is positive and $(1 - 2\xi_Y^C)$ is negative (i.e. congruent composition exists only in the range $0.5 < \xi_Y^C < 1$).
   b. $(\Omega^O - \Omega^A)$ is negative and $(1 - 2\xi_Y^C)$ is positive (i.e. congruent composition exists only in the range $0 < \xi_Y^C < 0.5$).

The oxygen potential for the oxidation of an alloy X-Y to an oxide solid solution XO-YO must satisfy conditions for oxidation of each metal. For the oxidation of X,

$$X + \tfrac{1}{2}O_2 \rightarrow XO \tag{10}$$

$$\Delta G^o_{XO} = -RT\ \ln K_{10} = -RT\ \ln(a_{XO}/a_X.P_{O_2}^{1/2}) \tag{11}$$

Rearranging,

$$\Delta\mu_{O_2}(X \rightarrow XO) = RT \ln P_{O_2} = 2[\Delta G^o_{XO} + \Delta\bar{G}_{XO} - \Delta\bar{G}_X] \tag{12}$$

where $\Delta\bar{G}_X = RT \ln a_X$ and $\Delta\bar{G}_{XO} = RT \ln a_{XO}$ are the partial molar Gibbs energy of X in the alloy and XO in the oxide solution. The partial molar quantities can be expressed as a sum of ideal and excess contributions.

$$\Delta\bar{G}_i = RT \ln X_i + \Delta\bar{G}_i^E \tag{13}$$

The excess partial free energy of the regular solution is given by,

$$\Delta\bar{G}_i^E = \Omega(1 - X_i)^2 \tag{14}$$

Substituting for partial properties in the Eq. (12) in terms of composition variable (ξ) and the regular solution parameter (Ω), one obtains:

$$\Delta\mu_{O_2}(X \rightarrow XO) = 2\left[\Delta G^o_{XO} + \Omega^O(\xi_Y^O)^2 - \Omega^A(\xi_Y^A)^2 + RT \ln\left(\frac{1-\xi_Y^O}{1-\xi_Y^A}\right)\right] \tag{15}$$

Similarly, for the oxidation of Y to YO

$$Y + \tfrac{1}{2}O_2 \rightarrow YO \tag{16}$$

one can obtain:

$$\Delta\mu_{O_2}(Y \rightarrow YO) = 2\left[\Delta G^o_{YO} + \Omega^O(1-\xi_Y^O)^2 - \Omega^A(1-\xi_Y^A)^2 + RT \ln\left(\frac{\xi_Y^O}{\xi_Y^A}\right)\right] \tag{17}$$

An alloy in equilibrium with oxide solution must satisfy both the Eqs. (15) and (17) simultaneously. For a fixed composition of the alloy, the composition of the oxide phase in equilibrium and oxygen potential are uniquely defined. Fig. 1 shows the variation of oxygen potential with composition for alloy/oxide equilibrium at 1000 K. The diagram is calculated assuming that the Gibbs energies of formation of XO and YO are the same (condition II above). Consequently oxygen potential for oxidation of pure metals X and Y are identical and the congruent composition is $\xi_Y^C = 0.5$. The difference in the regular solution parameter for the oxide solution and the alloy $(\Omega^O - \Omega^A)$ is taken as 10 kJ·mol^{-1}, with $\Omega^O = 10$ and $\Omega^A = 0$. The curves are symmetric with respect to composition.

Fig. 2 shows the effect of varying the value of the difference in regular solution parameters $(\Omega^O - \Omega^A)$ on the oxygen potential curves for alloy/oxide equilibrium, keeping all other parameters constant. For positive values of $(\Omega^O - \Omega^A)$, the curves display maxima at equiatomic composition. The value of the oxygen potential corresponding to the maxima increases with $(\Omega^O - \Omega^A)$. The separation between oxidus and reductus also increases with the value of $(\Omega^O - \Omega^A)$. For negative values the corresponding curves exhibit minima. The curves become more depressed with increasingly negative values of $(\Omega^O - \Omega^A)$. For computing the curves in Figs. 1 and 2, the value of Ω^A is taken as 0. In the oxygen potential diagram, it is useful to see the effect of changing the individual values of Ω^O and Ω^A, while keeping the difference constant $(\Omega^O - \Omega^A)$. In Fig. 3, results of computation are shown for (a) $\Omega^O = 15$ & $\Omega^A = 5$ and (b) $\Omega^O = 10$ & $\Omega^A = 0$, while keeping the difference $(\Omega^O - \Omega^A)$ as 10. Although the main features

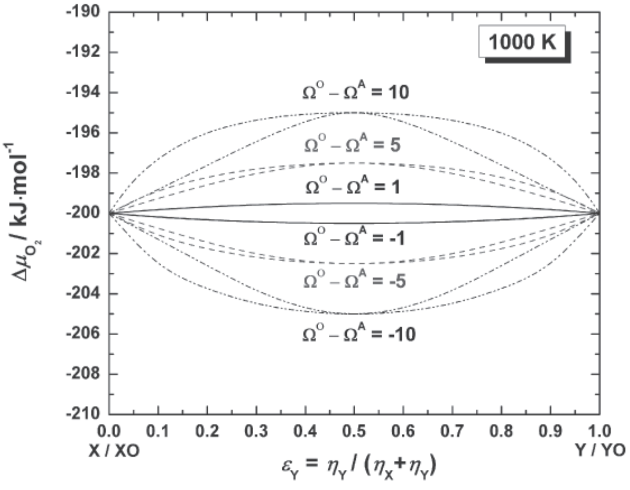

Fig. 2: Effect of varying ($\Omega^O - \Omega^A$) on extrema when the two end members X and Y have identical oxygen potentials for oxidation.

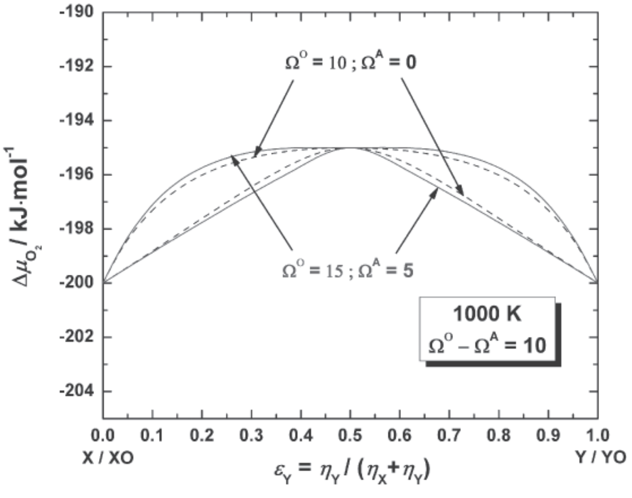

Fig. 3: Effect of individual values of the regular solution parameters composition of the alloy and oxide phases, when the difference in regular solution parameters for the two phases is kept constant.

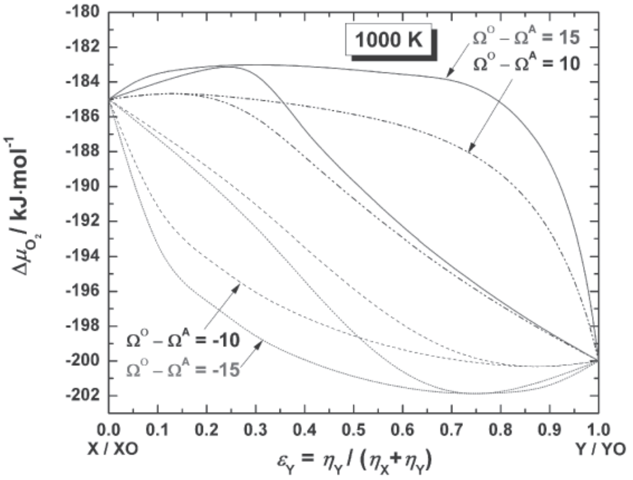

Fig. 4: Effect of varying ($\Omega^O - \Omega^A$) on extrema when two end members have different oxygen potentials for their oxidation.

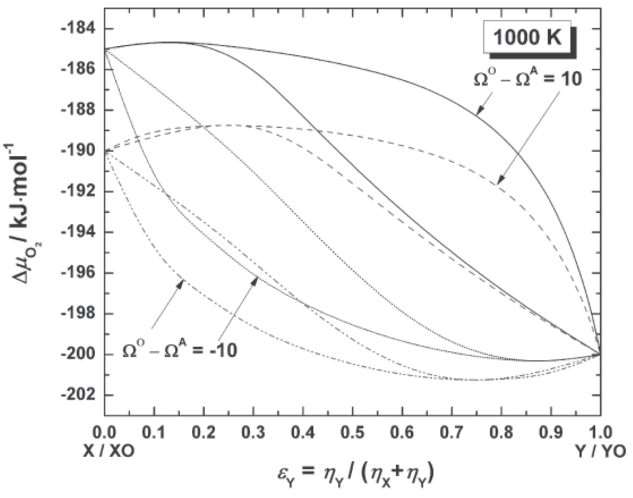

Fig. 5: Effect of difference in oxygen potential between the end members on extrema for identical set of values for ($\Omega^O - \Omega^A$).

of the curves are primarily controlled by the difference ($\Omega^O - \Omega^A$), individual values for each parameter does indeed make a minor difference in precise location of the curves. The larger the individual values, greater the separation between the oxidus and reductus.

The condition of equality for oxygen potential for the oxidation of pure X and Y assumed in Figs. 1–3 is relaxed in Fig. 4. Oxygen potential for oxidation of pure X is taken as –185 kJ·mol^{-1} and for pure Y as –200 kJ·mol^{-1}. Hence the difference in the oxygen potential of the two end members is 15 kJ·mol^{-1}. Condition (I) for the occurrence of extrema requires that the difference in oxygen potential should be less than twice the difference in regular solution parameters ($\Omega^O - \Omega^A$); $|\Delta\mu_{O_2}(Y+YO) - \Delta\mu_{O_2}(X+XO)| < 2(\Omega^O - \Omega^A)$. Because of the asymmetry in the oxygen potential of the end members, the congruent composition shifts to the left of the equiatomic composition when ($\Omega^O - \Omega^A$) is positive (condition III.a). Larger the positive value of ($\Omega^O - \Omega^A$), the maxima becomes more pronounced and the congruent composition shifts towards the equiatomic composition as shown in the figure. When ($\Omega^O - \Omega^A$) is negative, the congruent composition shifts to the right of the equiatomic composition (condition III.b). Larger the negative value of ($\Omega^O - \Omega^A$), more pronounced is the minima. Irrespective of the sign of ($\Omega^O - \Omega^A$), larger values result in greater separation between oxidus and reductus. However, the separation is more when ($\Omega^O - \Omega^A$) is positive than when it is negative. Fig. 5 shows the effect of varying

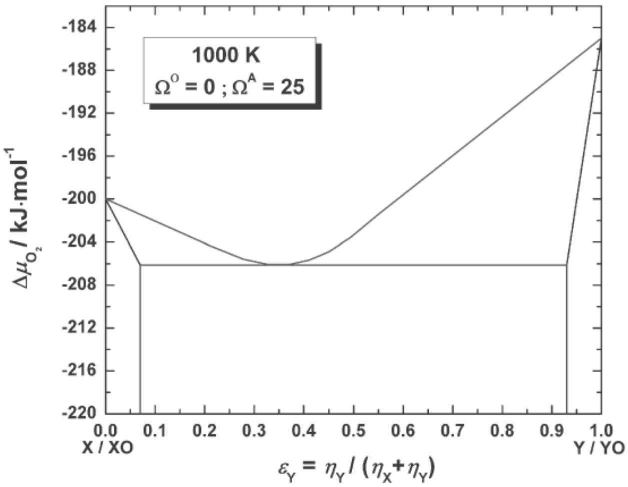

Fig. 6: Intersection of minimum in oxygen potential with immiscibility in the alloy phase, generating a eutectoid-type feature in the oxygen potential diagram at constant temperature.

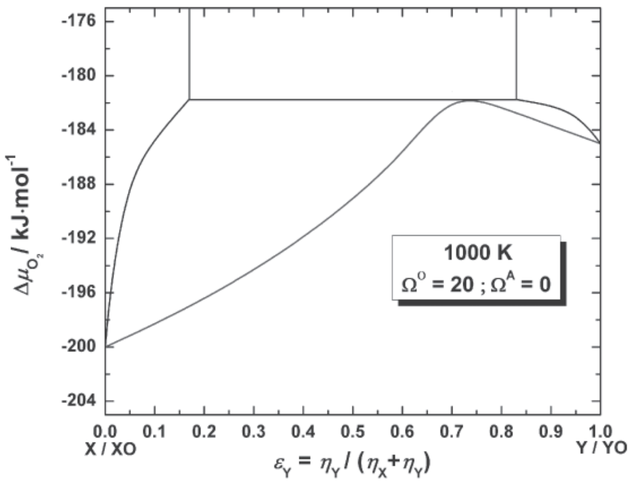

Fig. 7: Superimposition of maximum in oxygen potential on immiscibility in the oxide solid solution, generating a peritectoid-type phase diagram.

the difference in oxygen potential of end members $(\Delta\mu_{O_2}(X+XO)-\Delta\mu_{O_2}(Y+YO))$ on the diagram for a fixed value of $(\Omega^O - \Omega^A)$ both positive and negative. The congruent composition moves towards the equiatomic composition and the extrema become more pronounced, when the difference in oxygen potential is reduced.

When the value of the regular solution parameter exceeds 2R*T*, then the solution phase will exhibit a miscibility gap. The miscibility gap may impinge on the oxygen potential curve. For example, when $(\Omega^O - \Omega^A) = -25$ kJ·mol^{-1} and oxide solution is considered to be ideal $(\Omega^O = 0)$, the oxygen potential curve will exhibit a minima and the alloy phase exhibit a miscibility gap. The resulting eutectoid-type phase diagram is shown in Fig. 6. When $(\Omega^O - \Omega^A) = 20$ kJ·mol^{-1} and alloy phase is taken as ideal, the maxima in the oxygen potential will intersect miscibility gap of the oxide phase, giving a peritectoid-type diagram shown in Fig. 7. The oxygen potential diagrams at constant temperature obey all the rules of construction that are applicable for the more familiar temperature-composition (*T*-*X*) phase diagrams.

3 Congruent oxidation in the system X-Y-Z-O

3.1 Two-phase equilibria

Conditions for the congruent oxidation of a ternary alloy X-Y-Z are outlined in this section. Thermodynamic properties of a regular ternary solution can be expressed in terms of the regular solution parameters of the binaries constituting the ternary. The integral excess free energy of mixing can be written as [1]:

$$\Delta G^E_{XYZ} = \xi_X\xi_Y\Omega_{XY} + \xi_X\xi_Z\Omega_{XZ} + \xi_Y\xi_Z\Omega_{YZ} \tag{18}$$

where ξ_X, ξ_Y, ξ_Z for both alloy and oxide solid solutions are defined as:

$$\xi_X = \frac{\eta_X}{\eta_X+\eta_Y+\eta_Z}; \quad \xi_Y = \frac{\eta_Y}{\eta_X+\eta_Y+\eta_Z}; \quad \xi_Z = \frac{\eta_Z}{\eta_X+\eta_Y+\eta_Z} \tag{19}$$

η_i denoting moles of component *i*.

The corresponding partial excess free energy of mixing for component X is given by [1]:

$$\begin{aligned}\Delta\bar{G}^E_{X(XYZ)} = \Delta\mu^E_{X(XYZ)} &= \Omega_{XY}\xi_Y(\xi_Y+\xi_Z) \\ &+ \Omega_{XZ}\xi_Z(\xi_Y+\xi_Z) - \Omega_{YZ}\xi_Y\xi_Z\end{aligned} \tag{20}$$

Similar equations can be written for the other two components. The condition for congruent oxidation and reduction in the X-Y-Z-O system is given by:

$$\xi^A_Y = \xi^O_Y \quad \text{and} \quad \xi^A_Z = \xi^O_Z \tag{21}$$

Two independent exchange reactions are required to characterize alloy-oxide equilibrium in the system X-Y-Z-O. The reactions and their corresponding equilibrium constants may be formulated as:

$$XO + Y \rightarrow YO + X \tag{22}$$

$$K_{22} = e^{-\Delta G^O_{22}/RT} = \left(\frac{1-\xi^A_Y-\xi^A_Z}{\xi^A_Y}\right)\left(\frac{\gamma_X}{\gamma_Y}\right)\left(\frac{\xi^O_Y}{1-\xi^O_Y-\xi^O_Z}\right)\left(\frac{\gamma_{YO}}{\gamma_{XO}}\right) \tag{23}$$

and

$$\mathrm{ZO} + \mathrm{Y} \rightarrow \mathrm{YO} + \mathrm{Z} \tag{24}$$

$$K_{24} = e^{-\Delta G^{\circ}_{24}/RT} = \left(\frac{\xi^{\mathrm{A}}_{\mathrm{Z}}}{\xi^{\mathrm{A}}_{\mathrm{Y}}}\right)\left(\frac{\gamma_{\mathrm{Z}}}{\gamma_{\mathrm{Y}}}\right)\left(\frac{\xi^{\mathrm{O}}_{\mathrm{Y}}}{\xi^{\mathrm{O}}_{\mathrm{Z}}}\right)\left(\frac{\gamma_{\mathrm{YO}}}{\gamma_{\mathrm{ZO}}}\right) \tag{25}$$

A third exchange reaction involving X and Z can also be written:

$$\mathrm{XO} + \mathrm{Z} \rightarrow \mathrm{ZO} + \mathrm{X} \tag{26}$$

However, only two exchange reactions are independent; the third can be obtained by combining the other two. Assuming alloy and oxide solid solution to be regular, we can rewrite the Eq. (23) and (25) in terms of regular solution parameters:

$$\Delta G^{\circ}_{22} = \left[\begin{array}{l} 2\Omega^{\mathrm{O}}_{\mathrm{XY}}\xi^{\mathrm{O}}_{\mathrm{Y}} + \xi^{\mathrm{O}}_{\mathrm{Z}}(\Omega^{\mathrm{O}}_{\mathrm{XY}} + \Omega^{\mathrm{O}}_{\mathrm{XZ}} - \Omega^{\mathrm{O}}_{\mathrm{YZ}}) - 2\Omega^{\mathrm{A}}_{\mathrm{XY}}\xi^{\mathrm{A}}_{\mathrm{Y}} \\ + \xi^{\mathrm{A}}_{\mathrm{Z}}(\Omega^{\mathrm{A}}_{\mathrm{YZ}} - \Omega^{\mathrm{A}}_{\mathrm{XY}} - \Omega^{\mathrm{A}}_{\mathrm{XZ}}) - \Omega^{\mathrm{O}}_{\mathrm{XY}} + \Omega^{\mathrm{A}}_{\mathrm{XY}} \\ -\mathrm{R}T\ln\left(\dfrac{\xi^{\mathrm{O}}_{\mathrm{Y}}}{1-\xi^{\mathrm{O}}_{\mathrm{Y}}-\xi^{\mathrm{O}}_{\mathrm{Z}}}\right) - \mathrm{R}T\ln\left(\dfrac{1-\xi^{\mathrm{A}}_{\mathrm{Y}}-\xi^{\mathrm{A}}_{\mathrm{Z}}}{\xi^{\mathrm{A}}_{\mathrm{Y}}}\right) \end{array}\right] \tag{27}$$

$$\Delta G^{\circ}_{24} = \left[\begin{array}{l} \xi^{\mathrm{O}}_{\mathrm{Y}}(\Omega^{\mathrm{O}}_{\mathrm{YZ}} + \Omega^{\mathrm{O}}_{\mathrm{XY}} - \Omega^{\mathrm{O}}_{\mathrm{XZ}}) + \xi^{\mathrm{O}}_{\mathrm{Z}}(-\Omega^{\mathrm{O}}_{\mathrm{YZ}} + \Omega^{\mathrm{O}}_{\mathrm{XY}} - \Omega^{\mathrm{O}}_{\mathrm{XZ}}) \\ - \Omega^{\mathrm{O}}_{\mathrm{XY}} + \Omega^{\mathrm{A}}_{\mathrm{XY}} + \Omega^{\mathrm{O}}_{\mathrm{XZ}} - \Omega^{\mathrm{A}}_{\mathrm{XZ}} \\ + \xi^{\mathrm{A}}_{\mathrm{Y}}(-\Omega^{\mathrm{A}}_{\mathrm{YZ}} - \Omega^{\mathrm{A}}_{\mathrm{XY}} + \Omega^{\mathrm{A}}_{\mathrm{XZ}}) + \xi^{\mathrm{A}}_{\mathrm{Z}}(\Omega^{\mathrm{A}}_{\mathrm{YZ}} - \Omega^{\mathrm{A}}_{\mathrm{XY}} + \Omega^{\mathrm{A}}_{\mathrm{XZ}}) \\ - \mathrm{R}T\ln\left(\dfrac{\xi^{\mathrm{A}}_{\mathrm{Z}}}{\xi^{\mathrm{A}}_{\mathrm{Y}}}\right) - \mathrm{R}T\ln\left(\dfrac{\xi^{\mathrm{O}}_{\mathrm{Y}}}{\xi^{\mathrm{O}}_{\mathrm{Z}}}\right) \end{array}\right] \tag{28}$$

The following expressions can be obtained by imposing the conditions for congruency [i.e. Eq. (20)] on Eqs. (27) and (28). Thus,

$$\Delta G^{\circ}_{22} = \left[\begin{array}{l} (\Omega^{\mathrm{A}}_{\mathrm{XY}} - \Omega^{\mathrm{O}}_{\mathrm{XY}}) - 2\xi^{\mathrm{C}}_{\mathrm{Y}}(\Omega^{\mathrm{A}}_{\mathrm{XY}} - \Omega^{\mathrm{O}}_{\mathrm{XY}}) \\ + \xi^{\mathrm{C}}_{\mathrm{Z}}(\Omega^{\mathrm{O}}_{\mathrm{XY}} - \Omega^{\mathrm{A}}_{\mathrm{XY}} - \Omega^{\mathrm{O}}_{\mathrm{YZ}} + \Omega^{\mathrm{A}}_{\mathrm{YZ}} + \Omega^{\mathrm{O}}_{\mathrm{XZ}} - \Omega^{\mathrm{A}}_{\mathrm{XZ}}) \end{array}\right] \tag{29}$$

$$\Delta G^{\circ}_{24} = \left[\begin{array}{l} \Omega^{\mathrm{A}}_{\mathrm{XY}} - \Omega^{\mathrm{O}}_{\mathrm{XY}} + \Omega^{\mathrm{O}}_{\mathrm{XZ}} - \Omega^{\mathrm{A}}_{\mathrm{XZ}} \\ + \xi^{\mathrm{C}}_{\mathrm{Y}}(\Omega^{\mathrm{O}}_{\mathrm{XY}} - \Omega^{\mathrm{A}}_{\mathrm{XY}} + \Omega^{\mathrm{O}}_{\mathrm{YZ}} - \Omega^{\mathrm{A}}_{\mathrm{YZ}} - \Omega^{\mathrm{O}}_{\mathrm{XZ}} + \Omega^{\mathrm{A}}_{\mathrm{XZ}}) \\ + \xi^{\mathrm{C}}_{\mathrm{Z}}(\Omega^{\mathrm{O}}_{\mathrm{XY}} - \Omega^{\mathrm{A}}_{\mathrm{XY}} - \Omega^{\mathrm{O}}_{\mathrm{YZ}} + \Omega^{\mathrm{A}}_{\mathrm{YZ}} - \Omega^{\mathrm{O}}_{\mathrm{XZ}} + \Omega^{\mathrm{A}}_{\mathrm{XZ}}) \end{array}\right] \tag{30}$$

Solving Eq. (29) and (30) simultaneously at constant temperature one can obtain the congruent composition ($\xi^{\mathrm{C}}_{\mathrm{Y}}$, $\xi^{\mathrm{C}}_{\mathrm{Z}}$).

Since there are three groups of interaction parameters, it is not possible to derive an analytical condition for the occurrence of congruent oxidation in the case of ternary even for the simplest case. Hence, the effect of varying the binary sets of interaction parameters on the congruent composition will be explored by numerical solution of the equations. A special case may be considered first. When the standard Gibbs free energies of formation of three oxides XO, YO and ZO are identical (–100 kJ·mol^{-1}), then Gibbs energy changes for the exchange reactions (i.e. ΔG°_{22}, ΔG°_{24} and ΔG°_{26}) are zero. In such a case, by equating the right hand side of Eqs. (29) and (30) one obtains:

$$\frac{1-2\xi^{\mathrm{C}}_{\mathrm{Z}}}{\xi^{\mathrm{C}}_{\mathrm{Y}}} = \frac{(\Omega^{\mathrm{O}}_{\mathrm{XY}} - \Omega^{\mathrm{A}}_{\mathrm{XY}}) - (\Omega^{\mathrm{O}}_{\mathrm{YZ}} - \Omega^{\mathrm{A}}_{\mathrm{YZ}}) + (\Omega^{\mathrm{O}}_{\mathrm{XZ}} - \Omega^{\mathrm{A}}_{\mathrm{XZ}})}{(\Omega^{\mathrm{O}}_{\mathrm{XZ}} - \Omega^{\mathrm{A}}_{\mathrm{XZ}})} \tag{31}$$

The congruent composition is determined by the difference in the regular solution interaction parameters for the oxide and alloy phases for each of the three binaries. By holding two of the binary difference functions ($\Omega^{\mathrm{O}} - \Omega^{\mathrm{A}}$) constant, one can explore the effect of varying the third difference function on the congruent composition. Fig. 8 shows the variation of the congruent composition when two of the binary difference functions ($\Omega^{\mathrm{O}}_{\mathrm{YZ}} - \Omega^{\mathrm{A}}_{\mathrm{YZ}}$) and ($\Omega^{\mathrm{O}}_{\mathrm{XZ}} - \Omega^{\mathrm{A}}_{\mathrm{XZ}}$) are held constant (10 kJ·mol^{-1}) and the value of ($\Omega^{\mathrm{O}}_{\mathrm{XY}} - \Omega^{\mathrm{A}}_{\mathrm{XY}}$) is varied systematically from +20 to –20 kJ·mol^{-1}. It is to be noted that all the binaries will exhibit extrema at equiatomic composition: maxima when ($\Omega^{\mathrm{O}} - \Omega^{\mathrm{A}}$) is positive and minima when ($\Omega^{\mathrm{O}} - \Omega^{\mathrm{A}}$) is negative. When ($\Omega^{\mathrm{O}}_{\mathrm{XY}} - \Omega^{\mathrm{A}}_{\mathrm{XY}}$) = 20 kJ·mol^{-1}, much higher than the corresponding values along the other two binaries, the maxima of the binary X-Y is significantly more pronounced than along the other two binaries. As a result, there is no ternary congruent composition. When ($\Omega^{\mathrm{O}}_{\mathrm{XY}} - \Omega^{\mathrm{A}}_{\mathrm{XY}}$) is reduced, a ternary congruent compositions are obtained. The congruent compositions are plotted as discrete points in Fig. 8 for different values of ($\Omega^{\mathrm{O}}_{\mathrm{XY}} - \Omega^{\mathrm{A}}_{\mathrm{XY}}$). $\xi^{\mathrm{C}}_{\mathrm{Z}}$ increases with reducing values of ($\Omega^{\mathrm{O}}_{\mathrm{XY}} - \Omega^{\mathrm{A}}_{\mathrm{XY}}$), while the ratio $\xi^{\mathrm{C}}_{\mathrm{X}}/\xi^{\mathrm{C}}_{\mathrm{Y}}$ remains constant. The congruent composition moves away from the binary X-Y in a straight line towards Z as ($\Omega^{\mathrm{O}}_{\mathrm{XY}} - \Omega^{\mathrm{A}}_{\mathrm{XY}}$) is reduced. Further, all the ternary extrema indicated in Fig. 8 are maxima, since two binary regular solution parameter differences are positive. When two of the binaries have negative values for ($\Omega^{\mathrm{O}} - \Omega^{\mathrm{A}}$), one obtains minima. It is found that when the sum of two of the binary ($\Omega^{\mathrm{O}} - \Omega^{\mathrm{A}}$) terms is equal to the third one, the extrema lies on the third binary. For example when ($\Omega^{\mathrm{O}}_{\mathrm{XY}} - \Omega^{\mathrm{A}}_{\mathrm{XY}}$) + ($\Omega^{\mathrm{O}}_{\mathrm{XZ}} - \Omega^{\mathrm{A}}_{\mathrm{XZ}}$) = ($\Omega^{\mathrm{O}}_{\mathrm{YZ}} - \Omega^{\mathrm{A}}_{\mathrm{YZ}}$), there is no ternary congruent composition; extrema lies on the binary Y-Z.

A more general case where Gibbs free energies of formation of the three oxides are different ($\Delta G^{\circ}_{\mathrm{XO}}$ = –95 kJ·mol^{-1}; $\Delta G^{\circ}_{\mathrm{YO}}$ = –97.5 kJ·mol^{-1}; $\Delta G^{\circ}_{\mathrm{ZO}}$ = –100 kJ·mol^{-1}) can now be considered. In such cases, the binary extrema will not be at equiatomic composition. Fig. 9 shows the computed congruent compositions when two of the

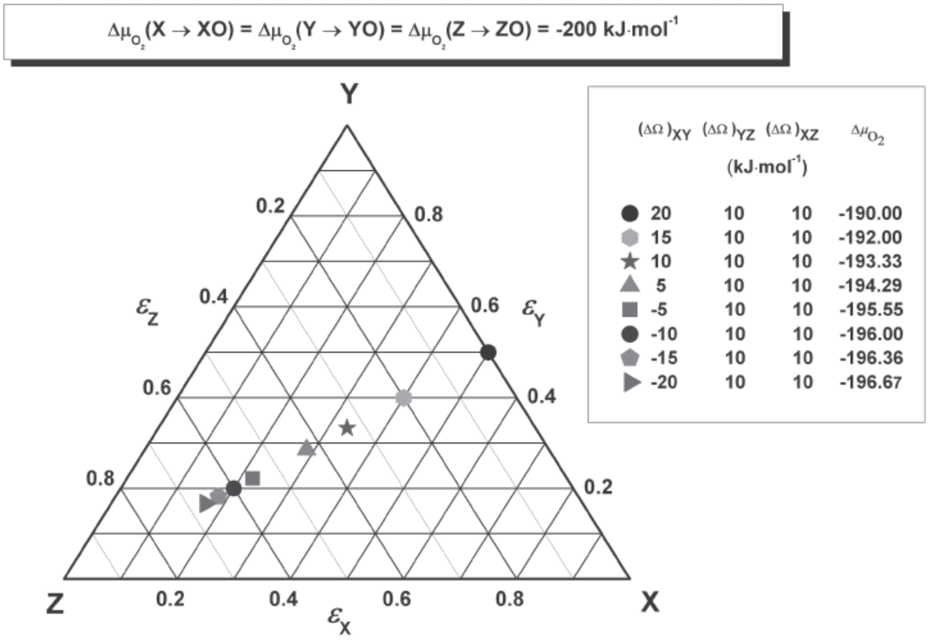

Fig. 8: Variation of congruent composition for oxidation of the ternary alloy X-Y-Z when difference in regular solution parameters of one binary (X-Y) is varied while keeping the others constant. The three pure metals are assumed to oxidize at the same oxygen potential. $(\Delta\Omega)_{ij}$ represents $(\Omega^{O}_{ij} - \Omega^{A}_{ij})$. The corresponding oxygen potentials are indicated in the legend.

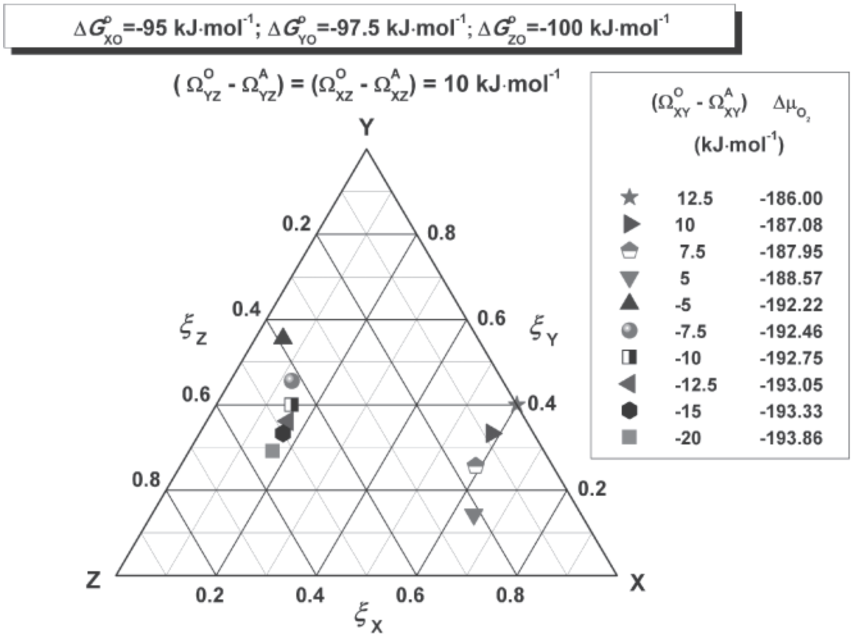

Fig. 9: Variation of congruent composition when difference in regular solution parameters of one binary (X-Y) is varied while keeping the others constant. Unlike in Fig. 8, the three pure metals oxidize at different oxygen chemical potentials.

binary $(\Omega^{O} - \Omega^{A})$ terms (Y-Z and X-Z) are kept constant at 10 kJ·mol^{-1} and the third (X-Y) is varied from +12.5 to –20 kJ·mol^{-1}. When the value of $(\Omega^{O}_{XY} - \Omega^{A}_{XY}) = 12.5$ kJ·mol^{-1}, the extrema lies on the X-Y binary at $\xi^{C}_{Y} = 0.4$. On decreasing the value of$(\Omega^{O}_{XY} - \Omega^{A}_{XY})$, the congruent composition moves away from the binary X-Y along a curved path towards binary X-Z. When the value of $(\Omega^{O}_{XY} - \Omega^{A}_{XY})$ become negative, the congruent composition shifts away from this trend. The congruent composition gets enriched in Y at the expense of X. All the congruent compositions for the negative values of $(\Omega^{O}_{XY} - \Omega^{A}_{XY})$ lie along another curved path moving away from the binary X-Y towards Z. For more complex situations, Eqs. (29) and (30) can be solved numerically to obtain the congruent compositions.

The oxygen potential for the oxidation of X-Y-Z alloy can be computed using reactions (10) and (16), with appropriate values for activities of metallic and oxide constituents. The oxygen potential for the oxidation of X to XO is defined by;

$$\Delta\mu_{O_2}(X \to XO) = 2\begin{bmatrix} \Delta G^{o}_{XO} + \Omega^{O}_{XY}(\xi^{O}_{Y})^2 + \Omega^{O}_{XZ}(\xi^{O}_{Z})^2 \\ + \xi^{O}_{Y}\xi^{O}_{Z}(\Omega^{O}_{XY} + \Omega^{O}_{XZ} - \Omega^{O}_{YZ}) - \Omega^{A}_{XY}(\xi^{A}_{Y})^2 \\ - \Omega^{A}_{XZ}(\xi^{A}_{Z})^2 - \xi^{A}_{Y}\xi^{A}_{Z}(\Omega^{A}_{XY} + \Omega^{A}_{XZ} - \Omega^{A}_{YZ}) \\ + RT\ln\left(\dfrac{1-\xi^{O}_{Y}-\xi^{O}_{Z}}{1-\xi^{A}_{Y}-\xi^{A}_{Z}}\right) \end{bmatrix} \tag{32}$$

Similarly, for the oxidation of component Y to YO and Z to ZO the oxygen potential is given by the following equations;

$$\Delta\mu_{O_2}(Y \to YO) \\ = 2\begin{bmatrix} \Delta G^{o}_{YO} + \Omega^{O}_{XY} - 2\Omega^{O}_{XY}\xi^{O}_{Y} + \xi^{O}_{Z}(-\Omega^{O}_{XY} + \Omega^{O}_{XY} - \Omega^{O}_{XZ}) \\ + (\xi^{O}_{Y})^2\Omega^{O}_{XY} + \Omega^{O}_{XZ}(\xi^{O}_{Z})^2 + \xi^{O}_{Y}\xi^{O}_{Z}(\Omega^{O}_{XY} - \Omega^{O}_{YZ} + \Omega^{O}_{XZ}) \\ - \Omega^{A}_{XY} + 2\Omega^{A}_{XY}\xi^{A}_{Y} + \xi^{A}_{Z}(\Omega^{A}_{XY} - \Omega^{A}_{YZ} + \Omega^{A}_{XZ}) - (\xi^{A}_{Y})^2\Omega^{A}_{XY} \\ - \Omega^{A}_{XZ}(\xi^{A}_{Z})^2 + \xi^{A}_{Y}\xi^{A}_{Z}(-\Omega^{A}_{XY} + \Omega^{A}_{YZ} - \Omega^{A}_{XZ}) + RT\ln\left(\dfrac{\xi^{O}_{Y}}{\xi^{A}_{Y}}\right) \end{bmatrix} \tag{33}$$

$$\Delta\mu_{O_2}(Z \to ZO) \\ = 2\begin{bmatrix} \Delta G^{o}_{ZO} + \Omega^{O}_{XZ} - 2\Omega^{O}_{XZ}\xi^{O}_{Z} + \xi^{O}_{Y}(-\Omega^{O}_{XY} + \Omega^{O}_{YZ} - \Omega^{O}_{XZ}) \\ + (\xi^{O}_{Y})^2\Omega^{O}_{XY} + \Omega^{O}_{XZ}(\xi^{O}_{Z})^2 + \xi^{O}_{Y}\xi^{O}_{Z}(\Omega^{O}_{XY} - \Omega^{O}_{YZ} + \Omega^{O}_{XZ}) \\ - \Omega^{A}_{XZ} + 2\Omega^{A}_{XZ}\xi^{A}_{Z} + \xi^{A}_{Y}(\Omega^{A}_{XY} - \Omega^{A}_{YZ} + \Omega^{A}_{XZ}) - (\xi^{A}_{Y})^2\Omega^{A}_{XY} \\ - \Omega^{A}_{XZ}(\xi^{A}_{Z})^2 + \xi^{A}_{Y}\xi^{A}_{Z}(-\Omega^{A}_{XY} + \Omega^{A}_{YZ} - \Omega^{A}_{XZ}) + RT\ln\left(\dfrac{\xi^{O}_{Z}}{\xi^{A}_{Z}}\right) \end{bmatrix} \tag{34}$$

At equilibrium the oxygen potential defined by the three equations should be identical. By numerical solution the locus of oxidus and reductus can determined as a function of alloy composition. It is difficult to display both surfaces touching tangentially at the congruent composition is a 3-D plot. In Fig. 10, the oxidus surface is shown as a function of composition for the ternary alloy X-Y-Z, where the standard Gibbs free energies of formation of all the three components are taken as –100 kJ·mol⁻¹ and $(\Omega^{O}_{XY} - \Omega^{A}_{XY}) = (\Omega^{O}_{XZ} - \Omega^{A}_{XZ}) = (\Omega^{O}_{YZ} - \Omega^{A}_{YZ}) = 10$ kJ·mol⁻¹. In this case the maxima occur at the equiatomic composition. The calculated oxygen potential corresponding to congruent compositions is also listed in Figs. 8 and 9. The value of oxygen potential is required to determine whether congruent composition corresponds to maxima or minima.

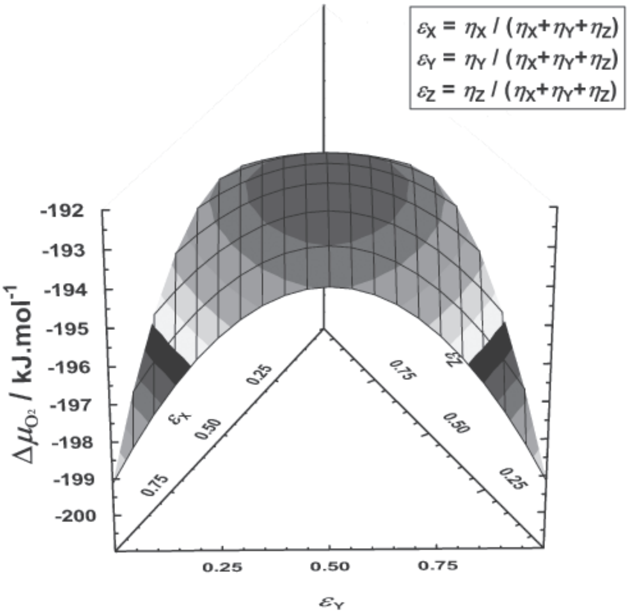

Fig. 10: "Oxidus" surface of a ternary alloy at constant temperature. In this case, the oxygen potential for the oxidation of all the three metals are identical.

3.2 Three-phase equilibria

In a quaternary system such as X-Y-Z-O, equilibrium between three phases is required to define the oxygen chemical potential. When two of the phases exist over a range of composition, then the oxygen potential surface for three-phase equilibria can also exhibit maxima or minima. An example is the metal-spinel-corundum equilibrium in system Ni-Cr-Al-O. The oxygen potential diagram for the decomposition of spinel solid solution [$Ni(Cr_xAl_{1-x})_2O_4$] to nickel [Ni] and corundum solid solution [$(Cr_yAl_{1-y})_2O_3$] at 1373 K is shown in Fig. 11 [2]. It exhibits a minimum corresponding to aluminum cationic fraction, $[\eta_{Al}/(\eta_{Al}+\eta_{Cr})] = 0.524$ at a constant oxygen partial pressure $P_{O_2}/P^{o} = 8.66 \times 10^{-12}$. Thus, the reduction of spinel solid solution or the oxidation of corundum solid solution in the presence of nickel is congruent at this composition. The diagram is relevant to the design of oxidation resistant nickel base alloys.

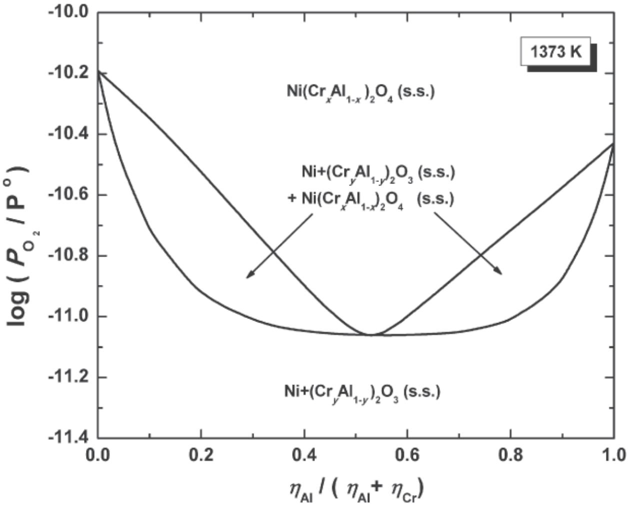

Fig. 11: Variation of oxygen partial pressure for three-phase equilibrium involving Ni, spinel solid solution [$Ni(Cr_xAl_{1-x})_2O_4$] and sesquioxide solid solution [$(Cr_yAl_{1-y})_2O_3$] with corundum structure as a function of composition of the oxide solid solutions in system Ni-Cr-Al-O at 1373 K [2].

In the system Fe-Cr-Al-O at 1373 K, the congruent composition associated with a minimum in oxygen potential occurs at a composition close to the end member $FeCr_2O_4$/Cr_2O_3 [3]. No congruent composition was identified in the system Co-Cr-Al-O at 1373 K corresponding to the phase equilibrium [4].

4 Conclusions

At congruent composition the alloy oxidizes at a fixed oxygen partial pressure to an oxide solution in which the ratio of metallic constituents is the same. The circumstances in which one can find congruent oxidation are identified. The thermodynamic conditions for congruent oxidation are formulated using the regular solution model to describe the mixing properties of solution phases. For a binary alloy X-Y, congruent oxidation will occur only if difference in oxygen potential for the oxidation of the two pure metals is less than twice the difference in regular solution parameters for the oxide and alloy phases $(\Omega^O - \Omega^A)$. Maxima in oxygen potential variation with composition occurs when $(\Omega^O - \Omega^A)$ is positive and minima when $(\Omega^O - \Omega^A)$ is negative. When oxygen potential for the oxidation of the two pure metals is the same, then extremum occurs at the equiatomic composition irrespective of the value of $(\Omega^O - \Omega^A)$. If the oxygen potentials corresponding to the end members are different, the maxima shifts towards the metal having a higher oxygen potential and minima shifts towards the metal having a lower oxygen potential. Maxima and minima become less pronounced with increasing difference in oxygen potential for the oxidation of pure metals and decreasing values of $(\Omega^O - \Omega^A)$. Although the topology of the oxygen potential diagram depends primarily on the value of $(\Omega^O - \Omega^A)$, individual values for the regular solution parameters do have a relatively minor effect on the location of the “oxidus” and “reductus”. When the value of regular solution parameter exceeds 2R*T*, superimposition of miscibility gap on the oxygen potential curve prevents the occurrence of congruent oxidation.

The conditions for congruent oxidation of a ternary alloy X-Y-Z are more complex since two independent exchange reactions and three sets of regular solution parameters are involved. Nevertheless, some trends in the variation of the congruent composition and oxygen potential with variation of $(\Omega^O - \Omega^A)$ and oxygen potentials for the oxidation of pure metals can be discerned by numerical solution of the governing equations for two-phase equilibrium. Congruent oxidation occurs at equiatomic composition when the oxygen potentials for the oxidation of the three metals are identical and the $(\Omega^O - \Omega^A)$ parameters of all three binaries are the same. When $(\Omega^O - \Omega^A)$ values for two or three binaries are positive, maxima occur in the oxygen potential variation with composition. In the reverse case when two or three binaries have negative values of $(\Omega^O - \Omega^A)$, minima occur in the oxygen potential variation with composition. Extension of the congruency requirement to three-phase equilibria in quaternary systems is outlined.

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