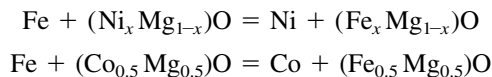# Internal Displacement Reactions in Multicomponent Oxides: Part II. Oxide Solid Solutions of Wide Composition Range

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As models of internal displacement reactions in oxide solid solutions, the following reactions were studied at 1273 K as a function of time:

$$Fe + (Ni_x Mg_{1-x})O = Ni + (Fe_x Mg_{1-x})O$$

$$Fe + (Co_{0.5} Mg_{0.5})O = Co + (Fe_{0.5} Mg_{0.5})O$$

In both reactions, Ni or Co in the starting oxide is displaced by Fe and the γ-(Ni-Fe) or (Co-Fe) alloy is precipitated. In the reaction zone, composition gradients develop in both product phases, *viz.*, the oxide and the alloy precipitate. The Ni (or Co) concentration of the alloy precipitate increases towards the reaction front. In the product oxide, the "inert" Mg diffuses toward the reaction front along with the Fe, while the Ni (or Co) diffusion is in the opposite direction, towards the Fe/boundary. The shape of the composition profiles for Mg and Fe in the product oxide suggests that cross-coefficient terms in the generalized flux equations contribute significantly to the cation flux. The parabolic rate constants of reactions involving Fe/(Ni$_x$Mg$_{1-x}$)O decrease by nearly four orders of magnitude when x decreases from 1 to 0.1.
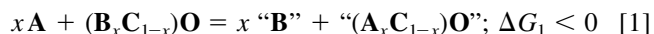
I. INTRODUCTION

PREVIOUS studies of solid-state displacement reactions have identified different reaction morphologies and their relationship to the thermodynamic and diffusional transport properties of product phases.[1,2] In the case of simple displacement reactions between a metal and a binary oxide, Rapp *et al.*[1] have predicted the morphologies and reaction rates from a knowledge of the thermodynamic and diffusion data of product phases; the predictions were verified for the following reaction couples: Cu_2O/Ni, Cu_2O/Co, Cu_2O/Fe, and NiO/Fe. Depending on the diffusional rate control in the product phases, the reactive interface is either stable (layered morphology) or unstable (aggregate morphology). The reactive interface is morphologically stable when the rate-controlling diffusion flux is in the same direction as the interface motion (*e.g.*, Cu_2O/Ni and Cu_2O/Co); the interface is unstable when it moves against the rate-determining flux (*e.g.*, Cu_2O/Fe and NiO/Fe). Tangchitvittaya *et al.*[2] have studied the reaction mechanism and the development of an interwoven product morphology for the reaction between Fe and NiO (single-crystal oxide). Internal displacement reactions occur inside a metal or ceramic matrix. The only published internal displacement reaction is between MoO_2 and Cr in a Ni-base alloy matrix by Shook *et al.*[3] As part of a study of internal displacement reactions in multicomponent oxides, a previous study (Part I) considered the reaction between a metal and a ternary oxide compound with a narrow homogeneity range.[4] A study of the internal displacement reaction between a metal and an initially
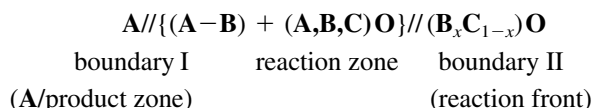
homogeneous single-phase ternary oxide solid solution with a wide composition range, at a constant temperature and pressure, is the subject of this article. In a following article (Part III), oxide solid solutions involving ternary line compounds will be considered.[5]

II. AN INTERNAL DISPLACEMENT REACTION IN AN OXIDE SOLID SOLUTION

Consider the oxides **AO**, **BO**, and **CO**, which have the same crystal structure and which form solid solutions in the entire composition range. The thermodynamic stability of the oxides is such that, $\Delta G^o_{CO} \ll \Delta G^o_{AO} < \Delta G^o_{BO}$. The oxide $(B_x C_{1-x})O$ is not stable when in contact with metal **A** at elevated temperatures, and the following internal displacement reaction occurs:

$$x\mathbf{A} + (\mathbf{B}_x\mathbf{C}_{1-x})\mathbf{O} = x\text{ ``}\mathbf{B}\text{''} + \text{``}(\mathbf{A}_x\mathbf{C}_{1-x})\mathbf{O}\text{''}; \Delta G_1 < 0 \quad [1]$$

The ΔG_1 is the Gibbs energy change for Reaction [1]. During the reaction, cation **B** is displaced by **A** in the oxide without changing the crystal structure of the oxide. The cation **C** does not participate in the chemical exchange reaction. The reaction product phases are typically: "**B**" is an (**A-B**) alloy and "$(A_x C_{1-x})O$" is $(A,B,C)O$ solid solution. As the reaction progresses, the reactants are spatially separated from each other by the product phases, as follows:

$$\mathbf{A}//\{(\mathbf{A}-\mathbf{B}) + (\mathbf{A,B,C})\mathbf{O}\}//(\mathbf{B}_x\mathbf{C}_{1-x})\mathbf{O}$$

boundary I	reaction zone	boundary II
(**A**/product zone)		(reaction front)

Both the product phases exhibit composition gradients in the reaction zone. If the reaction occurs in a single-crystal or polycrystalline oxide with very large grains, the alloy precipitates are isolated when the value of x is small and interconnected for large x values, depending on the morphology.

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