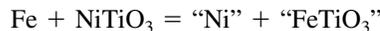


Internal Displacement Reactions in Multicomponent Oxides: Part I. Line Compounds with Narrow Homogeneity Range

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As a model of an internal displacement reaction involving a ternary oxide “line” compound, the following reaction was studied at 1273 K as a function of time, t :



Both polycrystalline and single-crystal materials were used as the starting NiTiO_3 oxide. During the reaction, the Ni in the oxide compound is displaced by Fe and it precipitates as a γ -(Ni-Fe) alloy. The reaction preserves the starting ilmenite structure. The product oxide has a constant Ti concentration across the reaction zone, with variation in the concentration of Fe and Ni, consistent with ilmenite composition. In the case of single-crystal NiTiO_3 as the starting oxide, the γ alloy has a “layered” structure and the layer separation is suggestive of Liesegang-type precipitation. In the case of polycrystalline NiTiO_3 as the starting oxide, the alloy precipitates mainly along grain boundaries, with some particles inside the grains. A concentration gradient exists in the alloy across the reaction zone and the composition is >95 at. pct Ni at the reaction front. The parabolic rate constant for the reaction is $k_p = 1.3 \times 10^{-12} \text{ m}^2 \text{ s}^{-1}$ and is nearly the same for both single-crystal and polycrystalline oxides.

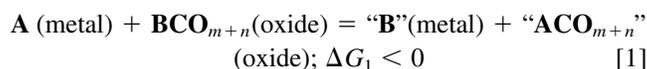
I. INTRODUCTION

A displacement reaction between a metal and an oxide involves the reduction of a noble oxide by a reactive metal. Previous studies of solid-state displacement reactions between metals and oxides^[1–6] have identified several types of reaction morphologies and their relationship to the thermodynamic and diffusional transport properties of product phases. Some of the reaction couples considered were $\text{Cu}_2\text{O}/\text{Co}$,^[1] $\text{Cu}_2\text{O}/\text{Ni}$,^[1] $\text{Cu}_2\text{O}/\text{Fe}$,^[1,2] $\text{Cu}_2\text{O}/\text{Co}_{1-x}\text{Fe}_x$,^[3] NiO/Fe ,^[1,4] NiO/Al ,^[5] and NiO/Mg .^[6] In particular, Rapp *et al.*^[1] have considered the reactive interface stability as a function of the diffusional rate control in the product phases. Internal reactions occur inside a metal or ceramic matrix; an example is the well-known internal oxidation of alloys.^[7] Schmalzried^[8,9] has considered internal oxidation and reduction reactions in multicomponent oxides and an extensive review is given by Schmalzried and Backhaus-Ricoult.^[10] Shook *et al.*^[11] have considered the internal displacement reaction in a metal matrix by studying the reaction between Cr and MoO_2 inside a Ni matrix. As part of a study of the internal displacement reactions in multicomponent oxides, the reaction between a metal and ternary oxide compound of a narrow homogeneity range (a line compound) is considered in this article, along with the results for a model reaction between Fe and NiTiO_3 at 1273 K. Reactions involving solid solutions of oxide compounds will be considered in Part II of this series of articles.^[12] These reactions can

be exploited to manufacture metal-ceramic composites having unique physical and mechanical properties.

II. DISPLACEMENT REACTIONS INSIDE A LINE COMPOUND

An internal displacement reaction in an oxide compound of a narrow homogeneity range is defined by the following chemical reaction:



where ΔG_1 is the Gibbs energy change for the reaction. In Reaction [1], cation **B** is displaced by cation **A** in the oxide, without changing the crystal structure of the oxide, and cation **C** does not participate in the chemical exchange reaction. During the reaction, “**B**” is typically precipitated as **A-B** alloy and the product oxide, “**ACO** _{$m+n$} ”, is usually **(A,B)CO** _{$m+n$} . The reaction is associated with a volume increase in the product zone, mainly due to the volume of “**B**” precipitate. The oxide systems in which Reaction [1] is possible are illustrated in Figure 1 and discussed in the following.

Consider three binary oxides, **AO** _{m} , **BO** _{m} , and **CO** _{n} ; **AO** _{m} and **BO** _{m} have the same crystal structure (different from that of **CO** _{n}) and form a continuous series of solid solutions. Also, the thermodynamic stability of the binary oxides is such that $\Delta G^\circ(\text{CO}_n) \ll \Delta G^\circ(\text{AO}_m) < \Delta G^\circ(\text{BO}_m)$. The binary oxides combine to form ternary line compounds of narrow homogeneity range, *e.g.*, **ACO** _{$m+n$} and **BCO** _{$m+n$} , and having the same crystal structure. The meaning of line compound is that the ratio **A:C** or **B:C** has a constant value (equal to 1:1)* and any deviation from it will result in the

*Other ternary line compounds, such as **(A or B)₂CO** _{$2m+n$} or **(A or B)₂CO** _{$m+2n$} , referred to as (2:1) or (1:2), respectively, are not considered for the sake of simplicity. However, reactions in these compounds follow the same technical arguments that are applied to (1:1) compounds.

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