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Reactive Interdiffusion: A Method for Making Composition Graded Metal-ceramic Composites

S. N. S. Reddy,[1] **K. T. Jacob**[2,*] **and G. Rajitha**[2]

[1] Microelectronics Division, IBM, East Fishkill Facility, Hopewell Junction, New York, USA

[2] Department of Materials Engineering, Indian Institute of Science, Bangalore, India

Abstract. Presented is a new method for making composition graded metal-ceramic composites using reactive interdiffusion between a metal and a complex ceramic. Composition variation in both metal and ceramic phases with distance along the direction of diffusion is achieved. The design criteria for developing such composites are discussed. The system should exhibit extensive solid solubility in both metallic and ceramic phases, a defined gradation in the stabilities of the oxides, and mobility of electrons or holes in the oxide solid solution. The complex ceramic used for making the composite should be polycrystalline with sufficient porosity to accommodate the volume expansion caused by alloy precipitation. An inert atmosphere to prevent oxidation and high processing temperature to facilitate diffusive transport are required. The process is illustrated using the reaction couples Fe-$NiTiO_3$, Fe-(Mg,Co)TiO_3 and Fe-(Ni,Co)TiO_3.

Keywords. Composition-graded composites, metal-ceramic composite, diffusion, interfaces, microstructure.

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1 Introduction

Implementation of the concept of functionally graded materials (FGM) has enabled designers to meet more stringent specifications and create novel structures for advanced technologies since material properties can be changed as a function of spatial coordinates [1, 2]. FGMs are superior to monolithic or homogeneous materials for many applications such as armor [3], thermal barrier coatings (TBC) [4], slurry erosion resistant surfaces [5], and thermo and pyro-electric devices [6–8]. FGMs are usually prepared by the powder metallurgy technique [3, 6, 9]. Cui and Zhao have prepared $(PbTe)_{1-x}$-$(SnTe)_x$ based FGMs using pressure-less sintering [7]. Plasma spraying has also been used for the preparation of metal-ceramic composite FGMs [1,10,11]. For use in the plasma spraying technique, a mixture of metal and ceramic powders is usually ball-milled in argon atmosphere. This ball-milled mixture is then plasma sprayed on to a suitable substrate to get a uniform layer of coatings. By changing the metal to ceramic ratio in the feed material, layers of different compositions can be deposited. The composite coating will have a graded structure. Sabatello et al. [2] have fabricated graded TiC-based cermets by infiltration of porous ceramic preform with molten metal. Using laser-based direct material deposition, Yarrapareddy et al. [5] have deposited an FGM consisting of Ni and WC powders on AISI 4140 steel plate. The FGM had a high percentage of discrete WC particles in a Ni matrix, with the percentage of WC varying in each layer of the deposit [5]. Put et al. [12] have processed WC-Co ceramic-metal FGMs by electrophoretic deposition (EPD) by applying a voltage of 800 V between two parallel flat stainless steel electrodes placed in a polytetraflourethylene cell containing organic acetone/n-butylamine medium in which particles to be deposited were suspended The composition of the deposit was varied by continuously pumping concentrated slurry into the deposition cell. The surface of the deposition electrode was coated with graphite to facilitate the removal of the deposit after EPD and to avoid cracking of the deposit during drying. After drying, the green WC-Co bodies were cold isostatically pressed at 300 MPa and sintered in a graphite furnace at 1563 K in vacuum ($\sim$10 Pa) [12].

The purpose of this communication is to report a new method – reactive interdiffusion – for the fabrication of graded metal-ceramic composites, albeit over smaller length scales. All the fabrication methods for composition-graded metal-ceramic composites produce materials in which the ratio of metal to ceramic can be varied in one or more directions. No method is available in which the composition of each phase in the composite can be varied simultaneously with distance. The main advantage of reactive interdiffusion is its ability to affect spatial variation in composition of the constituent phases. The microstructure can consist of either alloy particles embedded in ceramic matrix or alloy deposits along grain boundaries of the ceramic matrix. The ceramic matrix may be a single crystal or poly-crystalline, single-phase or multi-phase. The

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* **Corresponding author:** K. T. Jacob, Department of Materials Engineering, Indian Institute of Science, Bangalore 560 012, India; E-mail: katob@materials.iisc.ernet.in.

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method evolved from studies on internal displacement reactions in ternary and higher order oxides which have been published [13–16]. The results suggested a new method for making composition-graded metal-ceramic composites. In this review a more general approach from an engineering point of view is presented. The system requirements for engineering such graded metal-ceramic composites are discussed and the process illustrated with examples. Thermodynamic and kinetic constraints on systems that can generate graded composites are analyzed from a theoretical angle.

2 Design Criteria for Engineering a Composition-Graded Metal-ceramic Composite

The method is based on a displacement reaction between a metal (M) and an oxide component (NO_c) of a complex ceramic ($N_aX_bO_p$). The complex ceramic may be visualized as an inter-oxide compound formed from binary oxides NO_c and XO_d, such that $ac + bd = p$. The metal and ceramic are initially mated at an interface, where the reaction occurs. The process is carried out in an inert atmosphere. The reaction involves the reduction of the oxide component NO_c of the complex ceramic by metal M, which can be represented either as

$$(\mathrm{M}) + [\mathrm{NO}_c] \rightarrow [\mathrm{MO}_c] + (\mathrm{N}), \tag{1}$$

were the binary oxides in bracket are oxide components of the complex oxide, or as

$$a\mathrm{M} + \mathrm{N}_a\mathrm{X}_b\mathrm{O}_p \rightarrow \mathrm{M}_a\mathrm{X}_b\mathrm{O}_p + a\mathrm{N}. \tag{2}$$

The reaction results in a microstructure consisting of an alloy (M_xN_{1-x}) and an oxide solid solution $(M_yN_{1-y})_aX_bO_p$, where the composition of the alloy designated by x and of the solid solution designated by y vary in the direction of diffusion. The fabrication of such a composition graded metal-ceramic composite by reactive interdiffusion requires that the ionic and metallic radii of M and N be close $r_{\mathrm{M}^{2c+}} \approx r_{\mathrm{N}^{2c+}}$ and $r_\mathrm{M} \approx r_\mathrm{N}$, differing by less than $\sim$12%, in order that a single-phase oxide solid solution and alloy are obtained at high temperature. Further, the crystals structures of the two metals, and the two ternary oxide phases should be similar. Electron affinities of the pure metals and acidity or basicity of the oxides should be comparable. The phase diagrams for the binary alloy system M-N and pseudo-binary oxide system M_aX_bO- N_aX_bO would then show continuous solid solubility.

The production of such a composite also requires that the normalized standard Gibbs free energy of formation of the different binary oxides should be in the order $\Delta G_f^\circ(\mathrm{XO}_d)/d \ll \Delta G_f^\circ(\mathrm{MO}_c)/c < \Delta G_f^\circ(\mathrm{NO}_c)/c$. The Gibbs free energies of formation of oxides are assessed for one oxygen atom in the oxide for comparison of relative stability. With the indicated order of oxide stabilities, the component XO_d of the complex oxide will not be reduced by metal M, but component NO_c will be reduced to form an alloy M-N.

Since the reaction involves oxidative dissolution of metal M as M^{2c+} into the complex oxide at the metal/oxide interface and the reduction of N^{2c+} to metal N inside the oxide matrix, electronic conduction in the oxide phase is required for the reaction to proceed. If the transport number of electrons is close to unity, the reaction rate will be controlled by cation transport. The displacement reaction cannot proceed to any significant extent if the oxide phase is predominantly an ionic conductor.

The process temperature should be sufficiently high to permit diffusion in both metal and oxide phases. The duration of the process and the length scale of the composite formed are dependent on the process temperature. Under the conditions specified above, the formation of compositionally-graded metal-ceramic composite $(M_xN_{1-x}) + (M_yN_{1-y})XO_p$ can take place. The design criteria are based on theoretical considerations, tempered by experimental observations.

3 Experimental Illustration

Reactive-interdiffusion process for the formation of the metal-ceramic composite can be illustrated using the system Fe-$NiTiO_3$, where metallic iron (Fe) is brought into contact with a ternary oxide $NiTiO_3$ with ilmenite structure at high temperature. In this case a displacement reaction occurs between Fe and $NiTiO_3$ at the interface because of the difference in the Gibbs free energies of formation of $NiTiO_3$ [17] and $FeTiO_3$ [18]:

$$\mathrm{Fe} + \mathrm{NiTiO_3} \rightarrow \mathrm{Ni} + \mathrm{FeTiO_3}. \tag{3}$$

The product Ni forms an alloy with reactant Fe, and similarly $FeTiO_3$ forms a solid solution with $NiTiO_3$ because of the close similarity in the metallic and ionic radii of Fe and Ni and identical crystal structures of the two metal and oxide phases. The phase diagram showing the direction of tie-lines connecting the alloy and the oxide solid solution with ilmenite structure has been determined recently [19]. Diffusion of Fe from the reaction interface into the initially continuous $NiTiO_3$ phase causes precipitation of Ni as an alloy phase. A product layer is formed between the initial reacting phases with the passage of time as shown in Figure 1.

The reaction–diffusion system can be divided into three zones; metallic Fe, reaction-diffusion zone or product layer consisting of Fe-Ni alloy and (Fe,Ni)TiO_3 solid solution, and unreacted $NiTiO_3$. At 1273 K, the length of the product layer is 560 μm after 129.6 ks. Reddy et al. [13] have

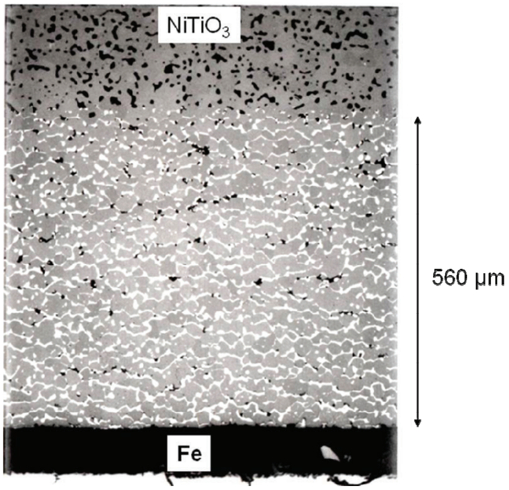

Figure 1. Cross-section through the reaction-diffusion couple Fe-$NiTiO_3$ along the diffusion direction showing the formation of metal-ceramic composite through the displacement reaction, Fe + $NiTiO_3$ = "Ni" + "$FeTiO_3$", at 1273 K after 129.6 ks. Bright phase is (Ni-Fe) alloy; grey phase is oxide solid solution with ilmenite structure; dark areas in $NiTiO_3$ and product layer are pores.

studied the reaction between Fe and polycrystalline $NiTiO_3$ and between Fe and single-crystalline $NiTiO_3$ at 1273 K. In each case, reaction resulted essentially in the formation of two-phase microstructure containing γ-(Fe–Ni) alloy and (Fe,Ni)TiO_3 solid solution in the reaction-diffusion zone. At higher magnification, a few specs of TiO_2 precipitate were seen inside the ilmenite grains when polycrystalline $NiTiO_3$ was reacted with Fe, suggesting very minor decomposition of the ilmenite phase. No TiO_2 precipitates were seen when single crystal $NiTiO_3$ was reacted with Fe. Compositions of the alloy and ilmenite solid solution were found to vary with distance along the direction of diffusion. The nature of distribution of the alloy phase in the two-phase microstructure depended on the initial microstructure of $NiTiO_3$. In the case of polycrystalline $NiTiO_3$, the alloy was mainly precipitated at triple grain junctions or near pores; the precipitates get connected along the grain boundary with time. When single-crystalline $NiTiO_3$ was used, the alloy precipitated as elongated ribbons, arranged in layers perpendicular to the diffusion direction.

There is significant volume expansion in the product layer, caused by the precipitation of the alloy in the oxide solid solution phase. In the case of single crystal $NiTiO_3$, the volume expansion results in the formation of cracks. In polycrystalline $NiTiO_3$, the volume expansion caused by alloy precipitation is largely absorbed by the pores present in the initial polycrystalline oxide microstructure. Hence, sintered complex oxide having sufficient porosity to absorb the volume expansion is required as the starting material to make composition-graded metal-ceramic composites for engineering applications.

The compositions of both the alloy and the oxide solid solution vary continuously inside the reaction-diffusion zone. Reddy et al. [13] have determined the composition of the oxide and alloy phases accurately as a function of distance in the product zone using electron microprobe analysis (EPMA) of samples cooled from 1273 K after heat treatment for ~230 ks. The concentration of Fe in the alloy phase and $FeTiO_3$ in the oxide phase decrease, while those of Ni and $NiTiO_3$ increase in the direction of diffusion as shown in Figure 2. In the product oxide, the concentration Ti remains constant. The ilmenite structure can be visualized as the corundum structure with Ni/Fe and Ti ions alternating in layers along the c-axis of the unit cell. Since Ni and Fe ions diffuse on the same cation sub-lattice, their fluxes may be correlated.

The compositions of the two phases in the composite lie on the dotted inclined quadrilateral in the isothermal tetrahedral representation of phase equilibria in the quaternary system Fe-Ni-Ti-O shown in Figure 3, where the formation of higher oxides of Fe and their solid solutions are not shown for clarity. Tie-lines connect alloy compositions to composition of titanate solid solution. The two-phase region can exist over a range of oxygen potentials. However, since many other phases can form at higher and lower oxygen potentials in this quaternary system, it is important to conduct the reactive interdiffusion processes under inert conditions.

The growth of the product layer with graded composition follows parabolic rate law; the length (l) in the direction of diffusion increases linearly with the square root of time (t). The rate constant (k_p) defined by the relation, $l^2 = 2k_p \times t$, has been found to be $k_p = 1.3 \times 10^{-12}$ m^2 s^{-1} at 1273 K. The growth rate was almost the same when using single and polycrystalline $NiTiO_3$ as the starting material for the reaction. This indicates that the kinetics is controlled by the lattice diffusion of Fe and Ni, and that any contribution of diffusion along grain boundaries is negligible. The grain boundaries in polycrystalline oxide act as preferred nucleation sites for γ-alloy precipitates, as is evident in Figure 1. To calculate the magnitude of the rate constant a priori, information on transport properties (diffusion data for Ni and Fe) in (Ni,Fe)TiO_3 should be available.

One would not generally expect the direct solid-state displacement reaction (3) to proceed to equilibrium. However, careful analysis [14] shows that the compositions of the alloy and oxide in the composition-graded composite exhibit only minor deviations from local equilibrium. This can be explained by the occurrence of secondary reactions which push the compositions of the two phases towards equilibrium. If the displacement reaction (3) does not reach equilibrium, the activities of Ni in the alloy and $FeTiO_3$ in the oxide solid solution will be lower and those of Fe and $NiTiO_3$ higher than those at equilibrium. Because the ac-

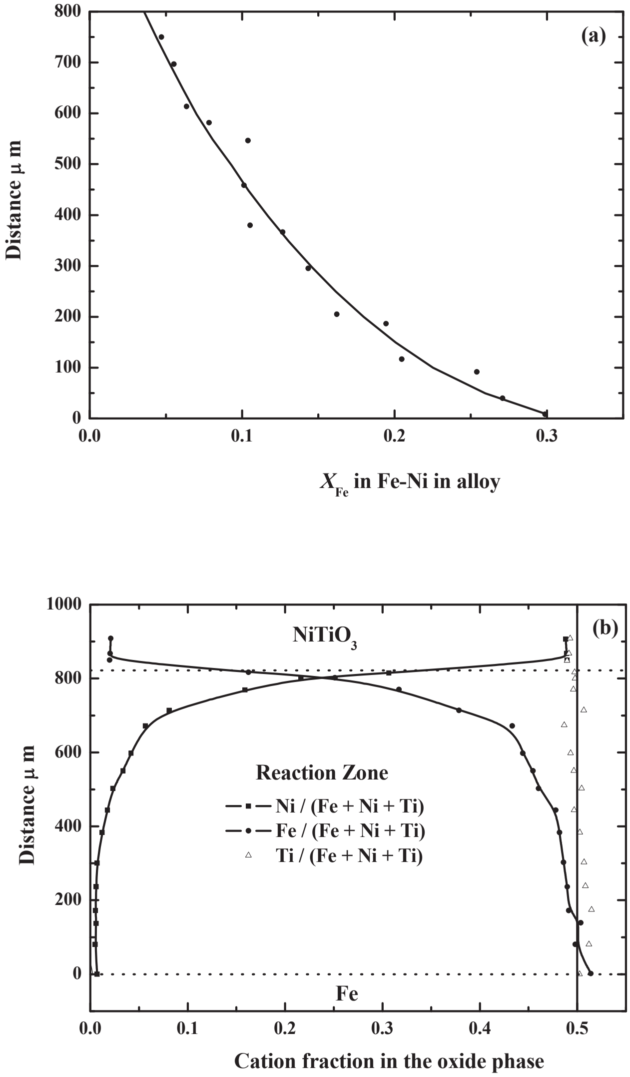

Figure 2. Composition of the (a) alloy and (b) oxide phases in the product layer formed by the reaction of Fe with polycrystalline $NiTiO_3$ at 1273 K after 230.4 ks

tivity of $NiTiO_3$ is higher and that of Ni lower than that at equilibrium, $NiTiO_3$ can dissociate according to the reaction:

$$NiTiO_3 \rightarrow Ni + TiO_2 + O_2. \qquad (4)$$

Similarly, since the activity of $FeTiO_3$ is lower and that of Fe higher when the displacement reaction is displaced from equilibrium, the formation of $FeTiO_3$ can occur by the reaction:

$$Fe + TiO_2 + O_2 \rightarrow FeTiO_3. \qquad (5)$$

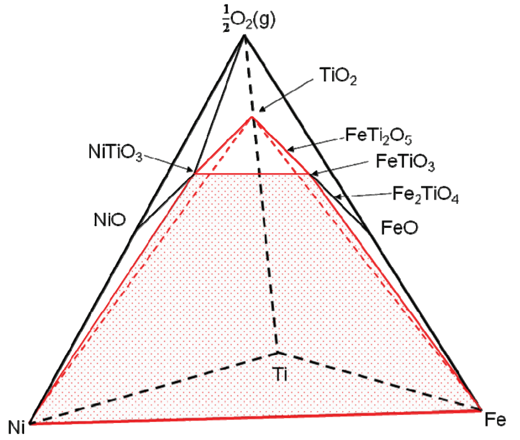

Figure 3. Isothermal section in the quaternary system Fe-Ni-Ti-O showing phase relations of the interest to reactive interdiffusion in the couple Fe: $NiTiO_3$.

Since the oxygen partial pressure corresponding to the dissociation reaction (4) would be higher than that corresponding to the formation reaction (5) when the displacement reaction (3) is displaced from equilibrium, the coupled reactions (4) and (5) move the compositions closer to equilibrium. When full equilibrium is achieved, the oxygen potentials corresponding to reactions (4) and (5) would be the same. If the rates of reactions (4) and (5) are equal, there will be no TiO_2 precipitate in the microstructure of the composite. Since only a limited number of small precipitates of TiO_2 were seen under high magnification when polycrystalline $NiTiO_3$ was reacted with Fe, it indicates that reactions (4) and (5) are almost compensating each other and the system is close to equilibrium. The absence of TiO_2 precipitates when single crystal $NiTiO_3$ was used is perhaps attributable to the higher energy required to nucleate TiO_2 inside the single crystal. This understanding is useful for designing more complex microstructures of composition-graded metal-ceramic composites.

4 Complex Microstructures

Microstructures of composition-graded metal-ceramic composites more complex than that illustrated in the previous section can be designed using reactive interdiffusion. Three examples are considered. First, one can conceive a three-phase metal ceramic composite consisting of *an alloy + oxide solid solution + oxide of constant stoichiometry*. Such a microstructure can be generated by reacting metallic iron with a two-phase sintered oxide pellet consisting of an intimate mixture of $NiTiO_3$ and TiO_2. Reactive interdiffusion will produce a three-phase microstructure consisting of Fe-Ni alloy and (Fe,Ni)TiO_3 solid solution of variable composition and TiO_2. The advantage of this microstructure is that the oxygen chemical potential is defined by three-phase equilibrium at all locations inside the composite at high temperatures. The three-phase region is shown by a volume element bounded by a quadrilateral and four triangles in Figure 3. For a fixed composition of the alloy or titanate solid solution, the three-phase equilibrium is depicted by a triangle joining the compositions of the two solid solution phases in equilibrium with that of TiO_2. Since the alloy and oxide solid solution compositions vary with distance, there will be a corresponding variation in the oxygen potential profile, from a low value at the Fe/product layer interface to a higher value at the product layer/$NiTiO_3+TiO_2$ interface. There will be an oxygen chemical potential gradient even in the absence of TiO_2 as a separate phase, but then the values at any location can vary over a range and are not well defined.

A second example considered is a composition-graded composite consisting of a *binary alloy and a pseudo-ternary oxide solid solution*. Such a microstructure can be generated by reacting metallic Fe with a complex oxide solid solution (pseudo-binary) of fixed composition having the ilmenite structure. Consider the couple Fe-$(Mg_{0.5}Co_{0.5})TiO_3$. Because the Gibbs energy of formation of $MgTiO_3$ is very much more negative than those of $CoTiO_3$ [20] and $FeTiO_3$ [18], metallic Fe will not reduce $MgTiO_3$ component of the ilmenite solid solution. Metallic Fe will only displace Co in the ilmenite solid solution, resulting in a microstructure consisting of Fe-Co alloy and a ternary oxide solid solution $(Mg,Co,Fe)TiO_3$. No precipitation of TiO_2 was seen in the ilmenite phase, suggesting that the alloy-oxide equilibrium is close to equilibrium. Since $MgTiO_3$ is not reduced by Fe, one would expect its composition in the ilmenite phase to be unaffected by the displacement reaction, at least to a first approximation. Figure 4 shows the composition profile in the ilmenite phase of the composition-graded metal-ceramic microstructure obtained using the couple Fe-$(Mg_{0.5}Co_{0.5})TiO_3$. It is the seen that Mg profile exhibits a maximum in the reaction-diffusion zone, while the profiles for Fe and Co are as expected. The Mg profile can be explained in terms of variation of activity coefficients in the pseudo-ternary titanate solid solution and cross-coefficients in the transport coefficient matrix. A detailed description and analysis of transport processes in this reaction-diffusion couple is published elsewhere [15]. A similar pattern of composition profiles was also observed for the couple Fe:$(Mg,Ni)TiO_3$ [16]. The important finding is that composition profiles exhibiting maxima in the oxide solid solution can be generated in the composition-graded composite.

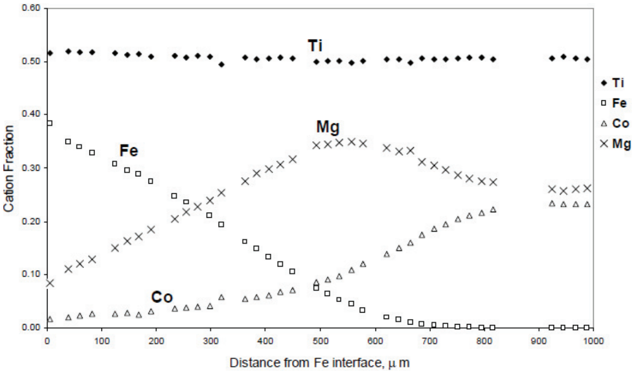

Figure 4. Composition profiles of the titanate solid solution formed by reaction of Fe with $(Co_{0.48}Mg_{0.52})TiO_3$ after 360 ks at 1273 K.

The third example is a composition-graded metal-ceramic composite in which the *alloy and oxide phases are ternary (or pseudo-ternary) solid solutions along with an oxide of fixed composition*. The microstructure consists of three phases, compositions of two ternary solutions varying with distance in the direction of diffusion. Such a composite can be generated by using the couple Fe-$(Ni,Co)TiO_3$. Here, both components of the initial titanate solid solution can be reduced by Fe, so that a ternary alloy (Fe,Ni,Co) is formed along with a ternary titanate solid solution $(Fe,Ni,Co)TiO_3$. The system is characterized by two displacement reactions, unlike in the two examples considered earlier. In addition to the displacement reaction (3), there is an additional displacement reaction,

$$Fe + CoTiO_3 \rightarrow Co + FeTiO_3, \qquad (6)$$

because the Gibbs free energy of formation of $CoTiO_3$ [20] is less negative than that of $FeTiO_3$ [18]. When the two displacement reactions are away from equilibrium, in addition to the dissociation of $NiTiO_3$ according to reaction (4), there is an additional titanate dissociation reaction involving $CoTiO_3$:

$$CoTiO_3 \rightarrow Co + TiO_2 + O_2. \qquad (7)$$

The formation reaction (5) will use the TiO_2 and oxygen generated by the two dissociation reactions to form $FeTiO_3$. However, the single formation reaction cannot compensate for the two dissociation reactions, with the result that a three-phase microstructure will invariably result with significant amount of TiO_2 precipitated inside the titanate solid solution phase. It is important to note that unlike in the first example, TiO_2 was not a component of the starting materials used to form the composite; it is formed in situ by reaction. Further, the excess oxygen released by the two dissociation reactions will cause an oxygen flux towards the metal Fe (the low oxygen potential side) and cause the formation of oxygen-rich phases (FeO or FeO-rich solid solution) adjacent to the metal. The composition profile of Co in the titanate solid solution exhibits a maximum along the direction of diffusion because of the higher activity coefficient of $CoTiO_3$ in the $(Fe,Ni,Co)TiO_3$ solid solutions formed by the displacement reaction compared to the initial $(Ni,Co)TiO_3$ solid solution, and possible interaction between the diffusion of Fe, Co and Ni on the same sublattice of the ilmenite structure.

The similarities and differences between the three examples of composition-graded metal-ceramic composites with complex microstructures discussed above are summarized in Table 1. The principles outlined here can be

Example	Starting Materials	Reaction	Product Characteristics	Special Features
1	Metal + Complex (ternary) oxide + Binary oxide	Displacement reaction between metal and ternary oxide	Three-phase microstructure. (Binary alloy + Pseudo-binary complex oxide ss + Binary oxide)	Compositions of alloy and oxide ss vary with distance. At high temperature, oxygen potential is defined at all locations inside the composite.
2	Metal + Complex oxide ss (pseudo-binary)	Displacement reaction between metal and one component of the oxide ss.	Two-phase microstructure. (Binary alloy + Pseudo-ternary complex oxide ss)	Compositions of alloy and oxide ss vary with distance. Composition profile of one component of the oxide ss exhibits maxima.
3	Metal + Complex oxide ss (pseudo-binary)	Displacement reaction between metal and both components of the oxide ss.	Three-phase microstructure. (Binary alloy + Pseudo-binary complex oxide ss + Binary oxide). The binary oxide is produced by reaction.	Compositions of alloy and oxide ss vary with distance. Composition profile of one component of the oxide ss exhibits maxima. At high temperature, oxygen potential is defined at all locations inside the composite.

Solid solution is abbreviated as ss

Table 1. Similarities and differences between three composition-graded metal-ceramic composites with complex microstructures prepared by reactive interdiffusion.

readily extended to design a variety of microstructures of composition-graded metal-ceramic composites with more components and differing profiles of composition.

5 Summary

Reactive interdiffusion has been introduced as the effective method for the preparation of composition-graded metal-ceramic composites in which the composition of each phase can be varied simultaneously with distance. The method is based on one or more displacement reactions between the metal and a complex oxide. The conditions for reactive interdiffusion to generate a two phase microstructure consisting of an alloy (M-N) and a ceramic solid solution $(M,N)_aX_bO_p$ are (i) extensive solid solubility in the metallic and ceramic phases, (ii) a defined gradation in the stabilities of the oxides, (iii) mobility of electrons or holes in the oxide solid solution, (iv) sufficient porosity in the initial complex oxide to absorb volume expansion caused by alloy precipitation, (v) inert atmosphere to prevent oxidation of the metal and reduction of the oxide, and (vi) high processing temperature to facilitate diffusive transport. The process is illustrated using the reaction couple Fe-$NiTiO_3$ system, which generates a product layer in which an Fe-Ni alloy coexists with $(Fe,Ni)TiO_3$. Compositions of both phases vary with distance. More complex three-phase microstructures with composition profiles exhibiting maxima can be designed by suitable choice of starting oxide compositions.

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