

# Thermochemical Reactions and Equilibria between Fluoromicas and Silicate Matrices: A Petromimetic Perspective on Structural Ceramic Composites

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A petromimetic (geological–analog) approach is applied to the design of alumina–fiber–reinforced glass–ceramic–matrix composites that use a refractory, trioctahedral fluoromica fiber–matrix interphase and feldspar matrixes. Studies of the solid-state reaction couples between these silicate phases are pursued to address the chemical tailorability of the interphase/matrix interface from an engineering perspective. The minimization of alumina and silica activities within polyphase, feldspar-based matrixes via MgO buffering is shown to be an effective route toward a stable fluoromica interphase. An anorthite–2-vol%–alumina ( $\text{CaAl}_2\text{Si}_2\text{O}_8 + \alpha\text{-Al}_2\text{O}_3$ ) substrate, chemically buffered with MgO, is shown to exhibit thermodynamic stability against fluorokinoshitalite ( $\text{BaMg}_3[\text{Al}_2\text{Si}_2]\text{O}_{10}\text{F}_2$ ), up to temperatures potentially as high as 1460°C. The key to the approach is the reduction of alumina activity via the formation of  $\text{MgAl}_2\text{O}_4$  spinel. Similarly, the formation of forsterite ( $\text{Mg}_2\text{SiO}_4$ ) stabilizes the mica in contact with matrix compositions otherwise containing excess silica. The cationic interdiffusion between solid-solution feldspars and fluoromicas also is characterized. Coupled interdiffusion of  $\text{K}^+$  and  $\text{Si}^{4+}$  in exchange for  $\text{Ba}^{2+}$  and  $\text{Al}^{3+}$  was observed between K–Ba solid-solution celsian and the barium-rich solid-solution end-member fluorokinoshitalite at 1300°C. A similar cationic exchange also is observed against the potassium-rich end-member fluorophlogopite ( $\text{KMg}_3[\text{AlSi}_3]\text{O}_{10}\text{F}_2$ ), although in a reverse direction, at temperatures of <1280°C. The interfacial compositions identified via electron microprobe analysis specify one set of local equilibrium conditions from which global ceramic composite equilibrium can be achieved.

## I. Introduction

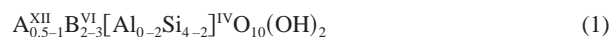
FIBER-REINFORCED ceramic composites must fulfil two general criteria to be effective structural materials for high-temperature aerobic environments. First, long-term thermochemical stability must be established between each of the ceramic component phases (i.e., fiber, matrix, and interphase) and the oxidizing environment. Second, useful ceramic composite systems must exhibit significant toughness at elevated temperatures and rapid loading rates. Achievement of this second requirement is largely dependent on the debonding characteristics of the fiber/matrix

interface. Both of these criteria emphasize the importance of engineering thermodynamically and mechanically functional interfaces or interphases between the fiber and the matrix phase.

In considering these interfacial requirements, one realizes that the achievement of effective ceramic composite materials will be predicated on polyphase ceramic equilibria possessing high mechanical-behavior contrast among phases. Therefore, one approach toward the fulfillment of these general design criteria is to consider the wealth of data and understanding in the geologic record: present right below our very feet is evidence of polyphase ceramic equilibria of phases—specifically silicates—with a wide variation of mechanical behavior. The combined disciplines of igneous and metamorphic petrology and geochemistry indicate the plethora of multicomponent silicate and oxide assemblages that exhibit high-temperature stability over geologic time scales. Thus, one can consider the design of environmentally robust, elevated-temperature ceramic composites from a petromimetic perspective.

Silicates possess a vast structural diversity, emanating from the degree of Si–O–Si polymerization, that can provide the necessary mechanical contrast (i.e., intrinsic fracture toughness) to achieve debonding in fiber-reinforced ceramic composites as articulated, for example, by the bimaterial interfacial crack-deflection criterion developed by He and Hutchinson.<sup>1</sup> Silicate mechanical behavior ranges from extremely strong but brittle framework silicates (fully polymerized, almost covalently bonded structures) to flexible sheet silicates (phyllosilicates) such as micas and clays (less-polymerized structures that incorporate notably weak ionic or van der Waals bonding on specific crystallographic planes). Thus, a refractory ceramic composite that uses micas as a thin, thermodynamically stable interphase to protect alumina fibers mechanically from cracks in an oxide/silicate matrix becomes a very real possibility.

Micas have a tetrahedral-cation-to-oxygen-anion (T:O) ratio of 1:2.5 and can be described by the structural formula



where the Roman-numeral superscripts refer to the cation coordination with  $\text{O}^{2-}$  and/or  $\text{OH}^-$  anions, A represents a 12-coordinated (i.e., large-diameter) alkali or alkaline-earth cation (known as the interlayer cation), and B represents a divalent or trivalent octahedral (6-coordinated) cation. The T:O ratio requirement means that the relative amounts of Al and Si on the tetrahedral sites are affected by the specific occupancy of the octahedral and interlayer cation sites; for the above-described formula, with 10  $\text{O}^{2-}$  anions, the sum of the tetrahedral Al and Si ions must total 4. Cation-site occupancy defines the adjectives used to describe the micas. For example, the mineral muscovite, which has the formula  $\text{KA}_2[\text{Al}_1\text{Si}_3]\text{O}_{10}(\text{OH})_2$ , is described as a dioctahedral (i.e., only two of the three available octahedral sites are occupied), trisilicic (i.e., three of the four tetrahedral sites contain Si), true (or flexible; i.e., the interlayer cation is an alkali) mica; the mineral kinoshitalite ( $\text{BaMg}_3[\text{Al}_2\text{Si}_2]\text{O}_{10}(\text{OH})_2$ ) is a trioctahedral, disilicic, brittle (i.e., the interlayer cation is an alkaline-earth element) mica.

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