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Task 6.7.3 - Interfacial Mass Transport Effects in Composite Materials

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TASK 6.7.3 - INTERFACIAL MASS TRANSPORT EFFECTS IN COMPOSITE MATERIALS

INTRODUCTION

Advanced metal matrix composites (MMCs) consisting of titanium-based alloys possess some unique mechanical, physical, and chemical characteristics that make them highly desirable for aircraft and gas turbine engines. Tailoring MMC properties is essential for advanced product design in material processing. The main factor that affects material processing and, further, the nature of the metal-ceramic interface, its structure, and morphological stability is liquid surface mass transport related to adhesional wetting (physical effect) and reactive wetting (chemical effect).¹

The energetics of wetting driven by capillary imbalance forces are generally believed to control interfacial mass transport rather than the strong layering forces generated by the electrostatic contribution of adsorbed multilayers of a liquid phase on a substrate,^{2,3} and/or viscoelastic dissipation in the wetting ring of the substrate near the triple point.⁴ In practice, an increase in mass transport behavior in dissimilar materials is seen as the effect of liquid-solid reactions and/or alloying of either the substrate or adsorbate with other materials.⁵ However, attractive pairwise interactions between atoms in a liquid and solid via the well-known Lennard-Jones wall potential may be also involved in wetting of the solid.⁶ This effect can be understood in terms of the image interactions resulting from charges in the nonmetal.⁷ Interatomic force models and computer simulation are widely used in the study of image interactions in metal-ceramic systems.^{8,9}

Surfaces and interfaces dominate many of the technologically important processes in composite materials such as liquid-solid sintering and joining. The objective of this work is threefold: 1) to gain insight into the role of the nonstoichiometry of the chemical composition of ceramic materials used as reinforcing components in MMC in processing, 2) to extend the prior energetic analysis of mass transport phenomena to wetting behavior between liquid metal and the quasi-solidlike skin resulting from the presolidification of liquid on nonstoichiometric solids on a scale of interatomic distance, and 3) to provide experimental verification of our concept. The formation and stability of quasi-solidlike skins seem to depend on changes in the electronic states of the contacting surface layers of both the substrate and the liquid, which can be represented by a work function difference, $\Delta\phi$, between liquid and solid (or more rigorously, in the Fermi energy difference) and a difference in the electronic densities of states, Δn . These parameters are very sensitive to the stoichiometry and composition of the crystalline phase. The induced atomic layering transition to mass transport seems to be a small fraction of the total in solids with a stoichiometric composition; however, it may be large enough in solids with a nonstoichiometric chemical composition such as in carbides and nitrides of transition metals. The presence of gravitational forces that adds hydrostatic pressure to mass transport is not discussed in this report.^{10,11}

The concept of a stratified interface structure is derived from studies on density changes in liquids at free surfaces, premelting of certain crystalline facets, the double layer structure formed in metal-solvent systems, and the physics of wetting in three-dimensional systems with planar symmetry.¹²⁻¹⁵ Our concept of the role of nonstoichiometry and composition in surface

mass transport is being verified by performing wettability tests of liquid titanium on nonstoichiometric TiN_x and Ti(N,O)_x ceramics and correlating those results with the electronic state of the ceramic.

LIQUID-SOLID INTERFACES AND APPARENT SURFACE DIFFUSION

Generally, an ideal metal-ceramic interface should create a good joining to provide mechanical continuity and chemical neutrality to avoid formation of interphase(s), particularly, with different thermal expansion coefficient(s). At the present, no model is able to satisfactorily describe the processing of metal-matrix composites. It is our thesis that MMC processing is crucially dependent on surface diffusion in the wetting ring near the triple point, solid-liquid-vapor, and driven by 1) the energetics of wetting: $\gamma_{sv} - \gamma_{sl}$ introduced by liquid metal-substrate interaction (where, γ_{sv} and γ_{sl} represent the solid surface and solid-liquid interfacial energies, respectively), 2) the energetics of wetting arising at the liquid metal-quasi-solidlike skin interface (Figure 1, see details below), and 3) the intrinsic stresses at the interface resulting from the formation of the quasi-solidlike skin, which may change the interfacial surface energy of the substrate. The γ_{sl} energy balance suggests that it can either decrease or increase, depending on direct atomic interaction across the interface. For the sake of simplicity, we have chosen to consider the mass transport of liquid on flat surfaces. The role of the shape of substrates such as present in particles and/or fibers in mass transport was discussed in detail by Cahn and his coworkers.^{16, 17}

Figure 1. Schematic representation of wetting phenomena of liquid metal on a substrate indicating formation of the quasi-solidlike skin at the interface.

In previous work, we attempted to understand the physical and chemical origins of surface mass transport in capillarylike media,^{18,19} metal-metal and metal-carbide systems.¹ We introduced the apparent surface diffusion parameter given by

$$D_s + D_r = (\gamma_{LV}/\eta) L \lambda \cos\theta_e \quad [\text{m}^2/\text{s}] \quad \text{at } T = \text{constant} \quad [1]$$

where D_s and D_r represent diffusion driven by adhesional forces and reaction-enhanced diffusion of atoms from a liquid, respectively; γ_{LV}/η is the surface tension-to-viscosity ratio for liquid metal; λ is the geometrical factor when anisotropic properties of a substrate result mostly from the roughness of the solid surface; L represents the average atomic/ionic distances in a solid; and θ_e corresponds to a wettability angle at thermodynamic equilibrium in a liquid-solid system. The equation provides a good estimation of surface diffusion for liquid metal-solid metal systems; however, some large $D_s + D_r$ values for liquid metals on carbides seem to be suspect and are likely caused by the large difference in L between a solid and liquid (Table 1). The L in carbides corresponds to the distance between either carbon or metal atoms in the B1 structure calculated in two crystallographic directions [110] and [100] (Figure 2) and in liquid metals related to the nearest-neighbor distance.¹ A straightforward strategy to correct the $D_s + D_r$ property is to assume that the layering transition in liquid metal on a substrate occurs with the formation of the quasi-solidlike metal interface. It is expected that the new L for the quasi-solidlike interface will be between that of a liquid metal and a solid substrate and will not depend on crystallographic directions. In liquid metal-solid metal systems, the misfit in L from metal to metal is low; however, it is high between metal and oxide/carbide/nitride. Thus, the layering transition at the interface will reduce the misfit between the substrate and liquid phase.

LAYERING TRANSITIONS AT THE LIQUID-SOLID INTERFACE

To understand the wetting phenomena at the liquid metal-solid interface, one must consider metal liquid structure at melting temperature. Liquid metals are considered a two-component fluid, one composed of ion cores and another composed of nearly free conduction electrons. The conduction electrons penetrate the ion cores and experience an attractive potential. The ion-electron forces constructed from pseudopotentials strongly depend on changing electron density at the Fermi energy level.²⁸ The partial delocalization of electrons near an interface caused by electron transfer either from solid to liquid or liquid to solid leads to a change in effective pairwise interaction between ions. The energy of this process is not conserved. In transition metals, electrons from the d-bands seem to play a crucial role.²⁹

As a consequence of the partial delocalization of conduction electrons from a substrate near the ion cores, atoms from the liquid phase near the interface possess a lower vibration amplitude than those in the bulk. If a close-packed liquid layer with higher packing density forms on a substrate, it exhibits layering transition, which will extend into the bulk liquid with an exponential decay. This process leads to the ordering of atoms near the interface and a sudden change in melt structure such as observed in a quasi-solidlike skin in a solid metal near its premelting temperature. The structure of a thin, coherent phase can be either amorphous or similar to that of a superlattice in alloys.³⁰ In this process, a fraction of the full entropy is liberated. It is likely that the ordering

TABLE 1

Contact Angles, Apparent Surface Diffusion Parameters of Liquid Cobalt and Copper, and Work Function for Selected Carbides and Metals

Liquid Co and Cu at T_m and Carbide	θ_e , deg Refs. 7,8	L (min.), nm [110] Refs. 9,10	L (max.), nm [100] Refs. 9,10	$D_s + D_r$ (min.) $m^2/s \times 10^{-8}$	$D_s + D_r$ (max.) $m^2/s \times 10^{-8}$	ϕ , eV for clean surfaces MC_x , MN_x ($x = 0.8 - 1.0$) face (100) Refs. 11-13	ϕ , eV at an exposure of 10 L* of O_2 , MC_x ($x = 0.8 - 1.0$) face (100) Ref. 11
Co Liquid	-	0.256	0.256	-	-	5.0	-
TiC	30	0.308	0.437	11.8	16.6	4.1	5.8
ZrC	35	0.334	0.472	12.1	17.0	3.5	4.7
HfC	35	0.318	0.450	11.5	16.2	4.63	NA
VC	10	0.298	0.422	13.0	18.2	4.3	5.8
NbC	11.5	0.319	0.449	13.8	19.3	4.1	4.6
TaC	10	0.317	0.449	13.8	19.4	4.38	NA
Cu Liquid	-	0.257	0.257	-	-	4.7	-
TiC _{0.98}	110	0.308	-	-	-	-	-
TiC _{0.70}	95	0.306	-	-	-	-	-
TiC _{0.60}	50	0.305	0.434	6.5	9.3	-	-
TiC _{0.50}	5	0.304	0.433	10.1	14.4	-	-

* 1 L (Langmuir) = 10^{-6} Torr sec.

** Not available.

mechanism of atoms in a liquid phase at the interface is opposite to the disordering or deconstruction transition in metal crystals below their melting temperature.³¹⁻³⁵ The existence of layering transitions for metals with low-index faces has already been predicted with density functional calculations. For these systems, the interface states have identical structure parameters. However, at a liquid-solid interface in dissimilar materials, electrons behave as if they belong with two different phases composed of two different structure parameters with some lattice misfit. The

Figure 2. The atomic geometry of a carbide (001) surface.²⁷

misfit energy per unit area of an interface tends to reduce the mismatch of lattice parameters depending on bond strength, interlayer thickness, and the elastic properties of the substrate. The lattice misfit may introduce stresses and structural defects.

The transition from a disordered liquid to an ordered one in quasi-solidlike skins should be initiated by the electronic states of contacting phases of both the substrate and liquid, described by a work function difference, $\Delta\phi$, and the difference in the electronic densities of states, Δn . The difference in their work function, $\Delta\phi = W_m - W_s$ (where W_m and W_s represent work functions of the liquid metal and substrate, respectively), gives rise to an electric dipole layer. The charging is determined from the $\Delta\phi$, while the energy change accompanying the electron transfer is proportional to both $-(\Delta\phi)^2$ and $(\Delta n^{1/3})^2$.³⁴ The $\Delta\phi$ sign, either + or -, indicates the electron's transfer either from substrate to metal or vice versa. The quasi-solidlike skin can support a potential difference, but will be transparent to the flow of electrons between liquid metal and substrate such as it is in a metal-semiconductor junction with an interfacial layer and interface states. However, the quasi-solidlike skin may reduce the $\Delta\phi$ of a substrate. It has already been demonstrated that the work function of α -SiC can be reduced from 4.5 to 2.9 eV when the thickness of deposited europium increases from 0 to 20 Å.³⁵ Electron work functions usually decrease as temperature rises, mainly as a result of lowering the material's density. Unfortunately, no measured values for work functions in liquid metals, except for alkalis, are available in the literature. Therefore, in this discussion, we use values of ϕ determined for solid phases.

Generally, work function is highly sensitive to perturbation at a material's surface resulting from crystallographic orientation, nonstoichiometry, and adsorption of gases. Transition metal carbides and nitrides typically exist in nonstoichiometric form, with either ordered or disordered vacancies in the nonmetallic sublattice. The presence of nonmetal vacancies results in an increase in

the density of states at the Fermi energy level. When carbon vacancies are formed, some charge is transferred to the vacancy sphere from the C2p bands, lowering the Fermi energy. Therefore, the vacancies cannot be considered electron traps.³⁶ However, they can control the interface potential and donate electrons to other materials. The decreasing copper contact angle, θ_c , on nonstoichiometric TiC_x ceramics with increasing apparent surface diffusion parameters is good evidence of the role of electron transfer in the wettability process (Table 1).

The increase in work function in carbides with oxygen content (Table 1) creates new energies in the surface state, which in particular cases may reduce the probability of layering transitions and simultaneously, of the wetting ability of oxidized carbides. Usually, oxygen atoms occupy carbon vacancies and are involved in the increase in the ionic character of bonds.³⁷ Also, it has been suggested that thin oxide films formed on liquid metals inhibit wettability of ceramic surfaces by these metals.³⁸

EXPERIMENTAL

A series of TiN_x and Ti(N,O)_x films formed from a TiCl_4 , N_2 , H_2 , and $(\text{N}_2 + \text{O}_2)$ gas mixture was deposited on alumina ceramics at 1073 K for 5 hr at atmospheric pressure, according to the procedure described in Dekker et al.³⁹ These conditions were selected because they offer a reasonable deposition rate and low chlorine content in films. The TiN_x films, with two different nonstoichiometries controlled by the ratio of N_2 to H_2 and two Ti(N,O)_x films with different nitrogen and oxygen content were prepared. The N_2 and H_2 gases were first purified in alkaline pyrogallol and dried over silica gel and further over a copper and palladium catalyst. TiCl_4 concentration in flowing N_2 and H_2 (70/30) corresponded to its vapor pressure over liquid at 300 K. Film thickness was determined using a multiple interferometer. All of the films obtained were thicker than 1000 nm. Phase analysis and interatomic distances were determined by x-ray diffraction analysis (XRD) at room temperature.

FUTURE WORK

The films will be characterized by electron spectroscopy for chemical analysis (ESCA) using a PHI 595 multiprobe, depth profiling. A Mg $K\alpha$ x-ray source and a double-pass cylinder mirror electron analyzer will be used for excitation. Peak positions will be corrected by assuming that the very weak C1s photoelectron line present for each sample was at 284.6 eV. All measurements will be taken at room temperature. Scanning electron microscopy will be applied for morphology tests.

Wettability tests of liquid titanium on TiN_x and Ti(N,O)_x films will be done using the sessile drop technique in high-purity Ar at 1973 K.

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