Introduction

A unique class of impurity-based quasi-liquid films has been widely observed at free surfaces, grain boundaries (GBs), and hetero-phase interfaces in ceramic and metallic materials (Figure 1). These nanometer-thick interfacial films can be alternatively understood to be: (a) quasi-liquid layers that adopt an "equilibrium" thickness in response to a balance of attractive and repulsive interfacial forces (in a high-temperature colloidal theory) or (b) multilayer adsorbates with thickness and average composition set by bulk dopant activities [1-2]. In several model binary systems, such quasi-liquid, interfacial films are found to be thermodynamically stable well below the bulk solidus lines, provoking analogies to the simpler interfacial phenomena of premelting in unary systems [3] and prewetting in binary de-mixed liquids [4]. These interfacial films exhibit structures and compositions that are neither observed nor stable as bulk phases, as well as transport, mechanical, and physical properties that are markedly different from bulk phases.

This overview article briefly reviews recent observations in this field with an emphasis on microscopy results. Reviews for specialists can be found elsewhere [1, 5].

Premelting in Unary Systems

Premelting, also known as "surface melting," refers to the stabilization of a thin surface liquid layer below the bulk melting temperature ($T_m$) in unary systems [3]. This can be conceived as if the increased free energy for forming an undercooled liquid film of thickness $h$ is more than compensated by the reduction in interfacial energies upon replacing a crystal-vapor interface with a crystal-liquid interface and a liquid-vapor interface:

$$\Delta S_{fusion}(T_m - T) \cdot h < \gamma_{CV} - (\gamma_{CL} + \gamma_{LV})$$

where $\Delta S_{fusion}$ is fusion entropy and the $\gamma$ parameters are excess interfacial energies. Convincing experimental evidence for premelting has been obtained in ice, lead, and other unary systems.

Premelting is the reason that ice is slippery. We often explain ice skating using a "pressure melting" theory. Quantitatively, however, an ice skater can exert a pressure to cause local melting at only a few degrees below zero [6]. Premelting, along with additional frictional heating, enables us to skate at as low as -35 °C [6]. Furthermore, ice premelting plays important roles in snow "sintering" and glacier motion (creep) [3].

Surficial Films in Binary Oxides

Impurity-based films of self-selecting (equilibrium) thickness form on the surfaces of various doped oxide nanoparticles [5]. These films are often termed as surficial amorphous films (SAFs), although they generally exhibit partial structural order. For $V_2O_5$-based SAFs on TiO$_2$ anatase {101} surfaces, the film thickness decreases monotonically with decreasing
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temperature in the subeutectic regime (Figure 2) and vanishes at a first-order surface transition [7].

For Bi$_2$O$_3$ on ZnO, SAF formation is anisotropic: while {1120} facets exhibit SAFs, {1100} facets are devoid of films (Figure 3) [8-11]. In the single-phase and subeutectic two-phase regimes, the thickness of SAFs on the {1120} facets decreases with deceasing temperature or Bi$_2$O$_3$ activity [9, 10]. Because of the presence of an attractive London dispersion force, nanoscale quasi-liquid SAFs persist into the solid-liquid two-phase regime, in equilibrium with partial-wetting bulk liquid drops [11]; yet, the average film composition is markedly different from that of bulk liquid [Figure 4a]. In a few cases, nanometer-thick SAFs are found to co-exist with nanoscale glass or liquid drops with non-zero contact angles [Figure 4b], directly demonstrating the self-limiting thickness. Interested readers are referred to a recent review article on SAFs [5].

**Intergranular Films in Ceramics and Metals**

Impurity-based nanoscale intergranular films (IGFs) have been widely observed in ceramics (Figure 1). Clarke originally proposed that these IGFs exhibit an equilibrium thickness [12]. A recent review article [1] summarizes the observations and theories of IGFs.

SAFs are considered as the free-surface counterparts to IGFs in ceramics. On the other hand, metallic counterparts to the ceramic IGFs have also been observed in Ni-doped W (Fig. 1) and explained as segregation-induced GB premelting [13]. It is worth noting that while the importance of GB premelting in unary materials is somewhat controversial, concurrent adsorption in binary or multicomponent systems can in principle stabilize the impurity-based quasi-liquid IGFs over greater undercooling ranges.

A quantitative model has been developed to forecast the thermodynamic stabilization of subsolidus quasi-liquid IGFs in binary alloys [14, 15]. An example computed for Co-doped W is shown in Figure 5. This model calculates the maximum thickness of a stable quasi-liquid IGF without considering interfacial forces, and the computed $\lambda$ values scale the actual IGF thickness. For ceramic IGFs, additional van der Waals London dispersion forces and electrostatic double-layer interactions can significantly change the film appearance and thickness.

**Interface Transitions and Complexions**

Tang, Carter and Cannon demonstrated that GBs in binary alloys can exhibit first-order or continuous transitions that can be interpreted as coupled premelting and prewetting transitions [16].
Recently, six distinct GB “complexions” (i.e., interfacial “phases”) with increasing structural disorder were discovered in doped Al₂O₃ [17, 18]. As shown in Figure 6, Complexion I represents “Langmuir-McLean-like” submonolayer adsorption, Complexion II is clean crystalline GBs, Complexion III is ~ 0.35 nm thick adsorption double-layers, Complexion IV is ~ 0.6 nm IGFs, Complexion V is ~ 1-2 nm thick IGFs, and Complexion VI is wetting films. By this scheme, the complexions have been labeled in order of increasing boundary mobility, which varies by 4 orders of magnitude at a particular temperature. Furthermore, the concept of GB complexions and their transitions helps solve an outstanding scientific problem regarding the origin of abnormal grain growth [17, 18].

In a phenomenological thermodynamic model [14, 15], a finite atomic effect can produce a series of discrete GB transitions, leading to the formation of multiple distinct complexions (Figure 7). The concepts of interface transitions and complexions are also applicable to free surfaces, whereas a first-order surface transition from monolayer adsorption to nanoscale SAFs (i.e., a coupled surface premelting and prewetting transition) has indeed been revealed (Figure 2) [7].

**Technological Importance**

Nanoscale (equilibrium or meta-stable) SAFs can control the shape, coarsening, and properties of oxide nanoparticles. For example, formation of TiO₂-based SAFs can convert polyhedral CeO₂ into spherical nanoparticles, which is significant for applications as abrasives for chemical-mechanical planarization [19]. In another recent extraordinary example, nanoscale SAFs on LiFePO₄ nanoparticles are credited as a “fast ion-conducting surface phase,” producing “beltways” for ultrafast charging and discharging of Li ion batteries (in seconds) [20]. Understanding and control of SAFs and their self-selecting thicknesses are also important for tailoring supported oxide catalysts [7] and ultra-thin dielectric films, among many other application areas [1, 5].

In addition to controlling microstructure evolution (e.g., sintering and grain growth), IGFs and presumably other GB complexions can play critical roles in determining the mechanical properties of Si₃N₄, SiC, Al₂O₃, ZrO₂, and B₄C based structural ceramics. GB complexions have been exploited to reproducibly grow single crystal sapphire by controlled abnormal grain growth [21]. Furthermore, IGFs control the electronic properties of RuO₂ based thick-film resistors and ZnO-based varistors, and they affect the thermal conductivity of AlN substrates and the critical current of high Tc superconductors [1]. Liquid-like GB complexions can also exist in metals (e.g., W-Ni [13] and Cu-Bi [22]) and metal matrix composites (e.g., WC-Co) and critically impact on their embrittlement, sintering, creep, oxidation and corrosion properties. The technological importance of SAFs and IGFs has been reviewed [1].

**Concluding Remarks: A Long-Range Scientific Goal**

Nanoscale liquid-like interfacial films can exhibit thermodynamic stability and properties that are strikingly different from their bulk counterparts. Furthermore, interfaces can undergo
first-order and continuous transitions. Thus, a long-range scientific goal is to develop quantitative interface complexion (phase) diagrams as a new tool for realizing predictable fabrication of materials by design. For example, the necessity of developing GB diagrams is demonstrated by studies of activated sintering in ceramics [23] and metals [13], showing that short-circuit diffusion in the subsolidus quasi-liquid IGFs leads to accelerated sintering when a bulk liquid phase is not yet stable, with phenomenological similarities to liquid-phase sintering. Thus, bulk phase diagrams are not adequate for designing optimal activated sintering recipes; on the other hand, onset sintering temperatures can indeed be predicted by computed GB diagrams (see, e.g., Figure 5) [14]. The computation shown in Figure 5 represents the first step towards the development of quantitative GB diagrams. Related concepts are elaborated in a recent Current Opinion article [15].

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References
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