Thermodynamic Evaluation of Amorphism on Film Breakdown and Pitting

Desmond Tromans
Dept. of Materials Eng., University of British Columbia
Vancouver, British Columbia V6T 1Z5, Canada

It is generally recognized that regions of amorphism in passive films are likely sites for film breakdown and pit initiation in aqueous environments. However, there is a dearth of information on the thermodynamic stability of amorphous solids relative to the crystalline phase. Much of this is due to the difficulty of quantifying amorphous structures in a satisfactory manner, because they have varying degrees of short range order that require quantification in terms of atom distribution (frequency) functions, changes in local geometry and changes in local symmetry. An estimation of the maximum chemical free energy difference $(\Delta G_{a-c})_T$ between the amorphous phase (*a*) and the crystalline phase (*c*) at temperature *T* may be obtained by assuming a basic structural similarity between the amorphous and liquid phases, together with the following conditions:[1]

1. The amorphous phase behaves as a glass-type solid where the atom disorder is similar to that of the liquid phase, except that the atom positions are fixed (apart from thermal vibrations) and unable to undergo long range diffusion movements characteristic of liquids.

2. The temperature (T) dependent variations of the molar heat capacities C_P of the corresponding amorphous and crystalline solids are assumed to be similar. This follows from condition 1, supported by observed similarities in C_P behaviour between corresponding crystalline and amorphous phases in glass-forming minerals where both phases occur in the solid state, *e.g.*, anorthite, diopside, amphibole and quartz [1].

3. At all T, the entropies of the amorphous and crystalline phases are such that $S_a > S_c$. This is consistent with the general concept that the entropy of a disordered solid phase must always be larger than its crystalline counterpart.

4. The value of S_a must have a finite value at 0 K. This follows from condition 3 together with the thermodynamic requirement that S_c for a perfect crystal is zero at 0 K.

Conditions 1 to 4 lead to the relationship:

$$(\Delta G_{a-c})_T = \left(\frac{H_F}{T_m}\right)(T_m - T) \qquad [1]$$

from which $(G_a)_T$ is readily calculated from known values of $(G_c)_T$, where H_F is the enthalpy of fusion and T_m (K) is the melting point (all parameters being in absolute values of the standard state for *G*, *H* and *S*).

Equation 1 is applicable to those crystalline phases that are stable between T and T_m. If polymorphous crystal phase transitions occur between T and T_m, Eq. 1 may be modified accordingly to take into account the enthalpy of these transitions.[1] Values of $(\Delta G_{a-c})_T$ for several oxides at 298 K, based on Eq. 1, are listed in Table I.

Table I Estimated $(\Delta G_{a-c})_T$ at 298 K

Mineral	Formula	T_m K	H_F kJ/mol	$(\Delta G_{a-c})_T$ kJ/mol
Magnetite	Fe_3O_4	1870	138.072	116.07
Corundum	Al_2O_3	2327	111.085	96.859
Ilmenite	$FeTiO_3$	1658	90.793	74.474
Rutile	TiO_2	2130	66.944	57.578
Periclase	MgO	3105	77.822	70.353
Bunsenite	NiO	2228	54.392	47.117
Zincite	ZnO	2248	54.393	47.182
Cuprite	Cu_2O	1516.7	64.768	52.042

The degree to which Eq. 1 and Table I provide reasonable estimates of $(\Delta G_{a-c})_T$ may be assessed by examining the few systems where thermodynamic data are available for the corresponding amorphous (glassy) and crystalline phases at 298 K, as shown in Table II for quartz (SiO_2) and anorthite ($CaAl_2Si_2O_8$):

Table II Comparison of ΔG_{a-c} values

Mineral	$(\Delta G_{a-c})_{298}$, kJ/mol	
	Data	Equation [1]
SiO_2	5.9	8.14*
$CaAl_2Si_2O_8$)	58.6	67.9

*10 kJ/mol when polymorphic transitions are included.[1]

Thus, Eq. 1 appears to overestimate the maximum ΔG_{a-c} by no more than a factor of 2, from which it is proposed that 50% of each value in Table I is a reasonable estimate of $(\Delta G_{a-c})_T$ at 298 K. Accordingly, the difference between the aqueous stability of fully amorphous and crystalline Al_2O_3 (corundum) is shown on a conventional E-pH diagram in Figure 1 after assigning a value of 48.43 kJ/mol for ΔG_{a-c}.

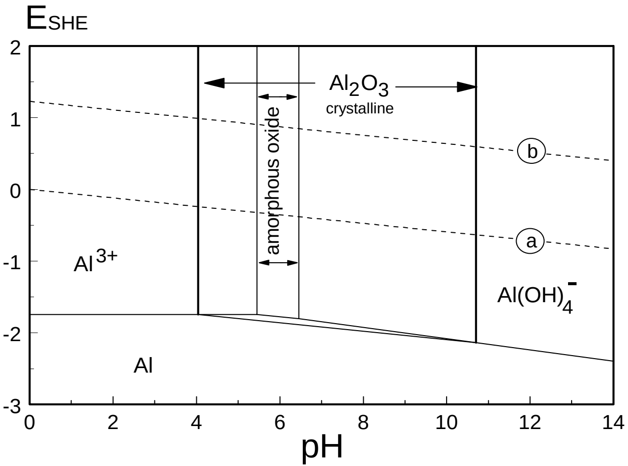

Figure 1 Al-H_2O equilibria; 10^{-3} activity soluble species

Clearly, the amorphous oxide has a diminished region of pH stability and it is likely that localized regions of amorphism in passive oxide films provide sites for easier film dissolution and pit initiation. Similar considerations and E-pH equilibria may be applied to the oxide systems listed in Table I and to hydrated oxides.

References

1. D. Tromans and J.A. Meech, *Minerals Engineering*, **14**(11), 1359-1377 (2001).