EQUILIBRIUM CRYSTAL SHAPES AND SURFACE PHASE DIAGRAMS AT SURFACES IN CERAMICS

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1. Background.

The character of interfaces in engineering materials is frequently the controlling factor in materials fabrication and performance. Due to increasing demands placed on materials in service, it is necessary to understand how these interfaces change in response to changes in processing variables, such as temperature, pressure, and chemical potential. From the time of Gibbs [1],...
the general thermodynamic principles describing these changes have been known. However, the specific details of the structures and energies of surfaces and interfaces in real materials are required in order to use the surface thermodynamics in a predictive mode.

In this paper, we describe one approach we have taken in the study of how the relative energies and equilibrium morphologies of surfaces change with temperature and chemical potential. We present the results of an experimental study of equilibrium crystal shapes as a function of composition in the $MgO-NiO$ system and use these results to construct equilibrium surface phase diagrams describing the transitions between crystal shapes.

2. Equilibrium crystal shapes.

The equilibrium shape of a crystal is the shape which minimizes the total surface free energy of the crystal. The relationship between the surface free energy per unit area, $\gamma$, and the equilibrium crystal shape is shown straightforwardly from the Wulff plot, the polar plot of $\gamma$ as a function of orientation of the normal vectors, $\hat{n}$ [2]. The inner envelope of planes perpendicular to the vectors $\gamma(\hat{n})$ defines the equilibrium shape [3]. Although this construction is useful from a pedagogical point of view, in nature we observe the crystal shape, not the plot of $\gamma(\hat{n})$. However, by using the Wulff plot several important characteristics of equilibrium crystal shapes become clear: (1) The equilibrium shape is convex. (2) It may contain any or all of the following features: facets, sharp edges, smoothly curved surfaces, and corners. (3) By changing the relative values of $\gamma$ for certain orientations, the equilibrium shape can change.

Cabrera, Cahn, and Rottman and Wortis [4-7] have described several convenient ways to view the equilibrium shape and its change with temperature. The transitions between adjacent crystal faces can be viewed as surface phase transitions. For example, at the intersection between two facet planes or at a nontangential intersection between a facet plane and a smoothly curved surface (Figure 1a and b), the surface energy changes discontinuously, corresponding to a first order transition. A second order transition occurs at the tangential intersection of a facet with a curved surface if the surface energy does not change discontinuously (Figure 1c). The smoothly curved (non-facetted) regions on the crystal shape are frequently referred to as being "rough". With these transitions defined in the same way we define bulk phase transitions, the change in the equilibrium shape with temperature, pressure, or chemical potential can be easily represented by a surface facetting transition diagram with axes relative top the crystal shape, in terms of angle from an arbitrary orientation, and the changing variable. The information which the surface facetting transition diagram contains is the orientation at which a transition occurs. The positions of first order transitions are indicated as dotted lines and second order transitions by solid lines, in accordance with the convention used by Rottman and Wortis, who calculated interface phase diagrams for cubic crystals as a function of temperature using statistical mechanics.

![Figure 1. Schematics of surface phase transition. (a) and (b) are first order. (c) is second order.](image-url)
A surface facetting phase diagram can then be constructed from the surface facetting transition diagrams and the crystal shapes. A surface facetting phase diagram shows the number of coexisting facet planes and rough surfaces as a function of the normal to the surface plane. This is directly analogous to a bulk phase diagram, with interface normal replacing composition and with facets corresponding to line compounds and rough surfaces on the equilibrium crystal shape corresponding to solid solutions. For example, when the equilibrium crystal shape is a cube, any surface whose normal is not normal to one of the six facets planes will decompose into a mixture of three \{001\} facets, except for surfaces with a \{100\} normal, which will decompose into two \{001\} facets. A surface facetting phase diagram for the cube will, thus, contain regions showing two-phase equilibrium and three-phase equilibrium. In this paper only the surface facetting transition diagram will be shown.

The change in the equilibrium shape of crystals with temperature is understood much better than with other variables. With increasing temperature, step energies decrease, facets shrink and a larger fraction of the area of the crystal becomes rough \[8,9-\]. With changes in chemical potentials, the change in the equilibrium shape depends on the details of adsorption and surface reconstructions.

While there have been several reports of changes in the equilibrium shape with annealing in different multi-component atmospheres \[10,11-\], there have been few studies where a single variable other than temperature is changed systematically.

3. Experimental Procedures.

The system \textit{MgO-NiO} forms an fcc solid solution at temperatures below the melting point of \textit{NiO}, 1990°C. The equilibration studies were performed using \textit{MgO-NiO} powder mixtures with \textit{MgO:NiO} molar ratios of 100:0, 99:1, 95:5, 90:10, 80:20, 50:50, 40:60, 20:90, 10:90, 0:100. The background impurity concentrations of the \textit{MgO} powder, determined by induction coupled plasma emission spectroscopy, were 750 Ba, 400 Ca, 80 Mn, 3540 Na, 450 Sr (\(\mu g/g\) \textit{Mg} metal basis) and of the \textit{NiO} powder, as provided by the manufacturer, were 6 Cu, 1 Ca, and 1 Si (\(\mu g/g\) \textit{Ni} metal basis). The powders were mixed for two minutes in a vibratory mill, using plastic balls. The powders were placed in high purity \textit{Al}_2\text{O}_3 or Pt crucibles and annealed at 1500°C for 55 h to homogenize the mixtures. The morphologies of the powder surfaces were examined by SEM.

4. Facetting Transitions and Surface Phase Diagrams.

The morphologies of the \textit{MgO-NiO} powders are shown in Figure 2 and the corresponding 3-D equilibrium shapes and the projected views along the \{001\} and \{011\} zone axes are shown in Figure 3. Major changes in equilibrium shape occur with changes in the \textit{Ni} concentration. The equilibrium shapes at low fractions of \textit{Ni} \(\textit{MgO:NiO} = 100:0, 99:1, 99:5\) are cuboidal with \{100\} facets and rough regions separating the \{100\} facets. The areas of the facets are large relative to the rough areas separating them. The intersections between the \{100\} facets and the rough regions appear to be continuous; the surface energy changes continuously where the facets and the rough areas join and the transition is second order. The second order transition is seen in the \{001\} zone axis (Figure 2(b)). The \{90:10\} powders show a minimum in the size of the \{001\} facets and the rough regions are almost spherical. For powders with higher \textit{Ni} concentrations (80:20, 50:50, 40:60), the size of the \{100\} facets increases. The transitions between the \{100\} facets and the rough regions are clearly first order, as indicated in the SEM micrographs by the well-defined edge at the intersection. At higher concentrations of \textit{Ni} (20:80, 10:90), \{111\} facets appear, the size of \{100\} facets decreases, and a rough region still exists separating facets. The intersections between the \{111\} and the \{100\} facets, between the \{100\} facets and the rough regions, and between the \{111\} facets and the rough regions are all first order. For pure \textit{NiO} (0:100), the rough regions are
Figure 2. SEM micrographs of MgO-NiO powders annealed at 1500°C for 55 h: MgO:NiO (a) 100:1; (b) 99:1; (c) 95:5; (d) 90:10; (e) 80:20; (f) 50:50; (g) 40:60; (h) 20:80; (i) 10:90; and (j) 0:100.
very small and the relative areas of the (100) and the (111) facets have increased. In pure NiO, all of the intersections are also first order transitions.

The shapes and their transitions described above are plotted in the surface phase transition diagrams for the (001) and the (011) zone axes, Figure 4a and b. The upper parts of both curves show that, at low Ni concentrations, the size of the (001) facets decreases with increasing Ni concentration. The size of the (001) facets increases with Ni concentration for Ni concentrations greater than 10% (90:10). The appearance of (111) facets occurs between 60% and 80% Ni. There are no data between these two compositions to determine the exact composition where (111) facets first appear. The hypothetical construction on the diagram between these two compositions corresponds to the appearance of a (111) facet surrounded by rough regions, that is, all facet planes are separated by rough regions. For Ni concentrations greater than 80%, the (100) and the (111) facets intersect but small rough regions remain separating facets of the same type.
5. Summary.

The equilibrium crystal shapes and the surface phase diagrams for the MgO-NiO system at 1500°C in air have been determined. The equilibrium crystal shape changes with composition, indicating major changes in the Wulff plot, $\gamma(\hat{a})$. These results emphasize that interfaces which are initially stable may become unstable as the composition of the interface changes during processing and service. This effect is not limited to vapor-solid interfaces, as discussed here, but is applicable to all interfaces, including grain boundaries.

While reporting these equilibrium crystal shapes and phase transition diagrams for the MgO-NiO system, we warn the reader that the equilibrium shapes are extremely sensitive to the background impurity level. A wide variety of equilibrium shapes are found in undoped MgO derived from different sources. Cubes of MgO with sharp edges and corners are formed by burning Mg metal and by decomposition of magnesium hydroxochlorides in air; rough, unfaceted surfaces are formed on MgO powders by the decomposition of ultra-clean hydrated magnesium carbonate. In a continuation of this study, ultra-clean powder and clean room processing techniques are being used to limit sources of chemical contamination and to make it easier to identify how $\gamma(\hat{a})$ is changing with composition.
Figure 4. Surface facetting transition diagrams for MgO-NiO: (a) along the (001) zone axis (b) along the (011) zone axis.

References