

10 Ceramics and Glasses

In this chapters we will re-examine ceramics and inorganic glasses with a perspective informed by phase diagrams and phase transformations. We will also shed further light on the two classes of materials from the point of view of crystallization. We will conclude this chapter with a discussion of various engineering ceramics and their properties.

10.1 Phase Diagrams and Microstructure of Ceramics

In Chapters 2 and 3 we introduced ceramics as metal-nonmetal compounds, i.e. roughly speaking, combinations of elements from the left and right sides of the periodic table. Typical examples are metal halides such as LiF and CaF₂, metal oxides such as NiO, MgO, and Al₂O₃, and we also included SiO₂ in this category. The main characteristic of these types of materials is the strong ionic character of the atom-atom bonds. This in turn is the major determinant of their crystal structure. The structure of many of these compounds can be understood as the close packing of positive and negative ions.

For the microstructure of ceramics, basically the same principles apply as with metals and metal alloys. The equilibrium microstructure depends first of all on the number of components, and can be deduced from the phase diagram. We gave two examples of such phase diagrams before, namely in Fig. 8.16 for NiO-MgO as a binary system with complete miscibility, and in Fig. 8.17 for SiO₂-Al₂O₃ as a much more complex binary system.

Just as with metals, the simplest microstructure is observed for a pure, one-component ceramic (Fig. 10.1). However, even this relatively simple microstructure is somewhat more complicated than its metallic counterpart.

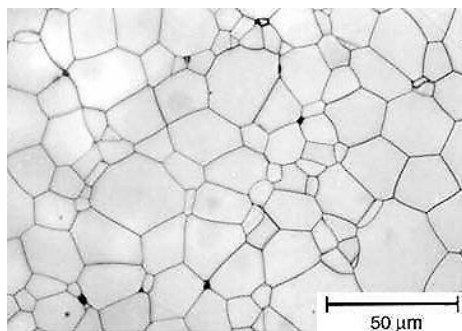


Figure 10.1:
Microstructure
of polycrystalline
Al₂O₃.

In Fig. 10.1 you can see individual grains, as in metals, but there are also a few dark spots visible. These are small voids which are related to the way ceramic materials are usually prepared.

Since ceramics are not ductile and thus difficult to machine, they must generally be prepared close to the shape in which they are needed. The raw material for a ceramic is often a powder, which is then pressed into a form and sintered. As noted in Chapter 5, sintering refers to a high-temperature treatment similar to annealing, but at a high enough temperature so that ions near the surfaces of the powder particle can diffuse around, equilibrate the particle shapes, bind particles together, and fill empty spaces between particles. During this process of sintering, the material becomes more dense, but it may not reach its full, theoretical density. That means that occasional small voids (the ellipsoidal dark areas mentioned above) may remain in the material. In addition, the boundary areas between the grains may not be fully crystalline but may consist of less dense, amorphous material.

In two-component ceramics, the microstructural phenomena you are familiar with can be seen again. The simplest cases are two-component metal-halide systems. They range from completely miscible (as for NiO-MgO in Fig. 8.16) to eutectic and completely immiscible, as e.g. in the CaF_2 -LiF system:

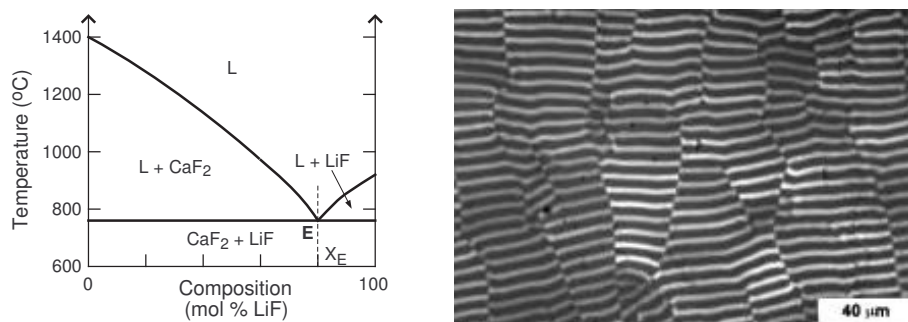


Figure 10.2: CaF_2 -LiF phase diagram (left panel) and eutectic microstructure (right panel).

The CaF_2 -LiF phase diagram shows a eutectic point at about 20 mol % of LiF and 767 °C (note that the composition is not in wt % here, but in mol %). The microstructure for the eutectic composition shows the usual lamellar appearance, consisting of alternating layers of CaF_2 and LiF. That is, the two low-temperature solid phases are essentially the two pure components.

A system with just one eutectic point is as simple as it gets for two components with limited solubility. It is also quite common, especially with metal oxides, that one or more intermediate phases (i.e. compounds) are formed. An example is SiO_2 - Al_2O_3 shown previously, where the phase diagram includes the intermediate compound mullite, with composition $3 \text{Al}_2\text{O}_3 - 2 \text{SiO}_2$, at about 28 wt % SiO_2 (cf. Fig. 8.17).

An even simpler example is displayed in Fig. 10.3 below with the phase diagram for the CaCl_2 -KCl system:

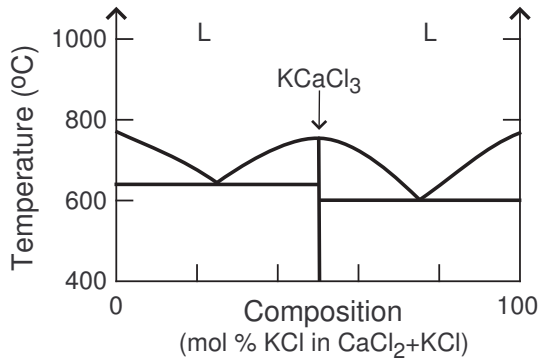


Figure 10.3:
Phase diagram
for the CaCl₂-
KCl system.

This phase diagram has an intermediate compound at 50 mol % KCl with composition KCaCl₃ and two eutectic points. Again, note that the composition is not given in wt % here, but in mol %.

Another interesting example is the CeO₂CoO system, a material under investigation for potential application in solid fuel cells (see the title picture at the beginning of the chapter). This system shows limited solubility in the solid state and has a eutectic point at around 1645 °C and 82 mol % CoO. In a directional crystallization experiment, the material showed various eutectic microstructures depending on the growth rate (i.e., basically, the time allowed for growth to occur). At very low growth rate the structure was fibrous: One solid phase had the form of fibers embedded in the matrix of the other solid phase. At higher growth rates the microstructure took on the layered shape typical for eutectics, which you have seen before with metals.

10.2 Ceramics, Glasses, and Crystallization

Given that both ceramics and inorganic glasses are in essence compounds of metals and non-metals, a question of great fundamental as well as practical interest is why some of these compounds tend to crystallize whereas others do not. Based upon what you learned in Chapter 8 on solidification, you realize of course that this is not so much a question of "either or", but rather "under what circumstances".

In Chapter 8 our tacit assumption was that the liquid would crystallize with a sufficient amount of undercooling, once nucleation got initiated. We can refine this view now with help of what you learned in Chapter 9 on the kinetics of phase transformations. Consider Fig. 10.4 below, which displays two generic time-transformation curves for crystallization vs. glass formation (cf. Fig. 8.25).

The parameter y once again denotes the extent of the transformation. The first of the time-transformation curves represents the beginning of crystallization and the other curve the completion. (When discussing crystallization, it is

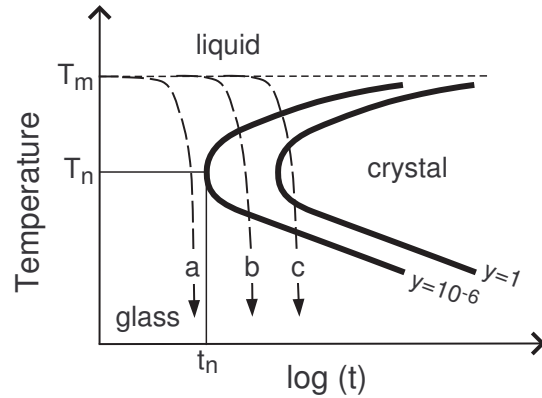


Figure 10.4: Generic time-transformation curves for crystallization and glass formation (solid lines), and three continuous cooling curves a, b, and c, corresponding to different cooling rates (dashed lines).

common to identify the beginning of the transformation with the point at which 10^{-6} of the total volume has crystallized). Thus, curve (a) among the three cooling curves indicates a cooling schedule which avoids any crystallization and thus leaves the sample as a glass. For curve (b) about half of the sample would end up crystalline, and for curve (c) the entire sample would have crystallized.

You can also see from Fig. 10.4 that if the objective is to avoid crystallization, then a decent estimate for the critical cooling rate can be obtained by taking the ratio T_n/t_n where T_n is the temperature of the "nose", and t_n is the time at the tip of the "nose".

The key to applying these arguments to a real system is, of course, to know the actual values of T_n and t_n , and these are often not known. What one can say is that among the ceramic compounds we have discussed, the alkali halides and their alloys are just as hard not to crystallize as are metals. On the other hand, silicates especially (i.e. SiO_2 -based compounds), and also some other oxides, are much easier to synthesize in glassy, amorphous form, even though with enough time crystals can certainly be prepared.

One clue as to why this is so can be gleaned from the viscosities of these types of materials in the liquid state, as listed on Table 10.1. The point of these data is that molten salts such as KCl and molten metals have similar, and very low, viscosities just above their melting points. A glass does not have a melting point but becomes practically molten over a temperature range. Still, at a viscosity where the glass flows much like a liquid, say at an η of the order of 1, or equivalently at a temperature much above the working point (Fig. 7.8), the typical viscosity for the glass is about a factor 10^3 higher than the viscosity of a molten metal or molten salt.