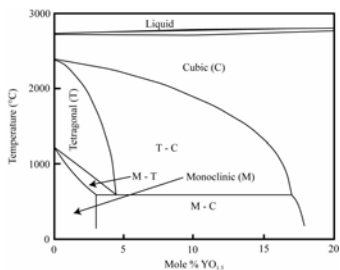


Class 6: Microstructure & Ceramic Phase Diagrams



Cut of ZrO₂-YO Phase Diagram: H. G. Scott, Phase relations in the zirconia-yttria system, *Journal of Materials Science*, 10 [9] 1527-1535 (1975)

PRIME Modules

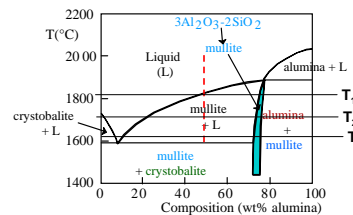
Project-based Resources for Introduction to Materials Engineering

The tie line can be used to determine the relative fraction of each phase

As you cool along the line shown here, you go from mostly liquid to mostly solid. That is, you convert liquid to solid.

As we showed last class, the tie line can be used at any temperature to give you the composition (%A and %B) of the liquid and solid.

We are also interested in knowing the fraction of liquid and solid you have at any temperature.



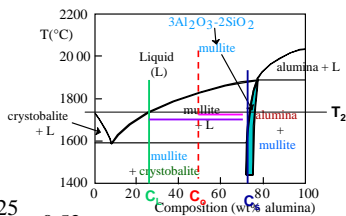
Adapted from Fig. 12.27, Callister 6e. (Fig. 12.27 is adapted from F.J. Klug and R.H. Doremus, "Alumina Silica Phase Diagram in the Mullite Region", *J. American Ceramic Society* 70(10), p. 758, 1987.)

The lever rule calculates the fraction of each phase present

The lever rule states that the fraction of the phase is the length of tie line opposite the phase divided by the whole tie line.

$$W_L = \frac{C_s - C_o}{C_s - C_L} = \frac{50 - 25}{73 - 25} = 0.52$$

$$W_S = \frac{C_o - C_L}{C_s - C_L} = \frac{73 - 50}{73 - 25} = 0.48$$



Adapted from Fig. 12.27, Callister 6e. (Fig. 12.27 is adapted from F.J. Klug and R.H. Doremus, "Alumina Silica Phase Diagram in the Mullite Region", *J. American Ceramic Society* 70(10), p. 758, 1987.)

Keep track of the important difference between composition and fraction of the phase

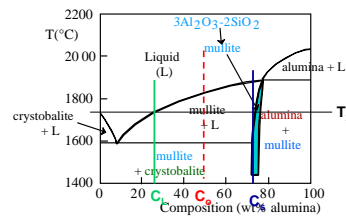
At T₂

The fraction of liquid is 0.52

The fraction of solid is 0.48

The liquid composition is 50 wt% alumina
50 wt% silica

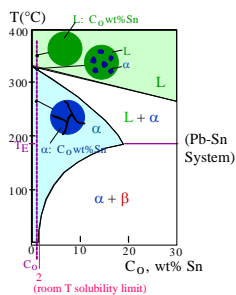
The solid (mullite) composition is 73 wt% alumina
27 wt% silica



Adapted from Fig. 12.27, Callister 6e. (Fig. 12.27 is adapted from F.J. Klug and R.H. Doremus, "Alumina Silica Phase Diagram in the Mullite Region", *J. American Ceramic Society* 70(10), p. 758, 1987.)

The phase diagram tells us about the microstructure based on what forms upon cooling

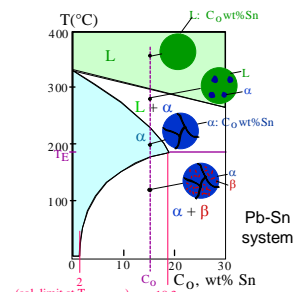
In the simplest case, liquid cools to a polycrystalline solid



Adapted from Fig. 9.9, Callister 6e.

The phase diagram tells us about the microstructure based on what forms upon cooling

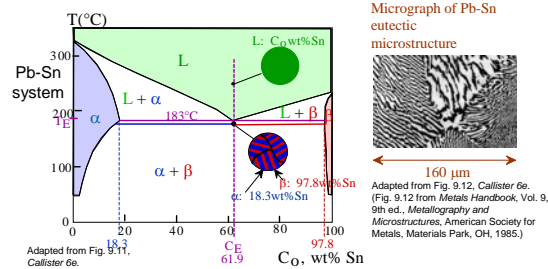
If we move over in composition (more Sn), first the liquid converts to all α and then some β forms



Adapted from Fig. 9.10, Callister 6e.

At the eutectic, the liquid all converts directly to α and β

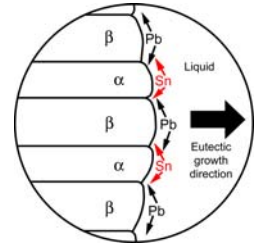
At the eutectic temperature and composition liquid converts directly (completely) to α and β



The eutectic lamellar structure forms to minimize diffusion

α is a Pb rich phase. It has to receive Pb, give off Sn, relative to the original C_0 .
 β is a Sn rich phase. It has to receive Sn, give off Pb, relative to the original C_0 .

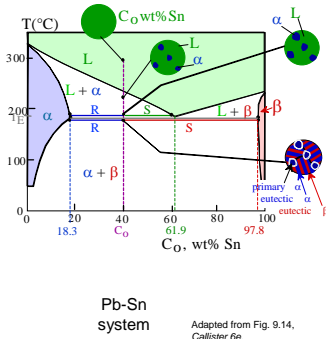
The alternating plates (lamellar structure) forms to minimize the distance Pb and Sn need to diffuse.



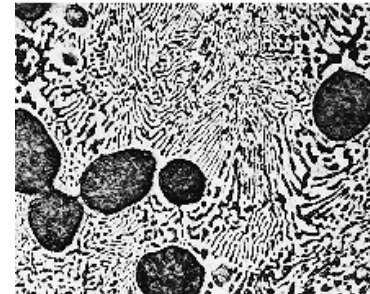
W.D. Callister, *Materials Science and Engineering An Introduction 5/e*, (John Wiley and Sons, New York, 2000).

When you are off the eutectic, solid forms first before the eutectic lamellar

- Just above T_E :
 $C_\alpha = 18.3 \text{ wt\% Sn}$
 $C_L = 61.9 \text{ wt\% Sn}$
 $W_\alpha = \frac{R}{R+S} = 50 \text{ wt\%}$
 $W_L = (1 - W_\alpha) = 50 \text{ wt\%}$
- Just below T_E :
 $C_\alpha = 18.3 \text{ wt\% Sn}$
 $C_\beta = 97.8 \text{ wt\% Sn}$
 $W_\alpha = \frac{S}{R+S} = 73 \text{ wt\%}$
 $W_\beta = 27 \text{ wt\%}$

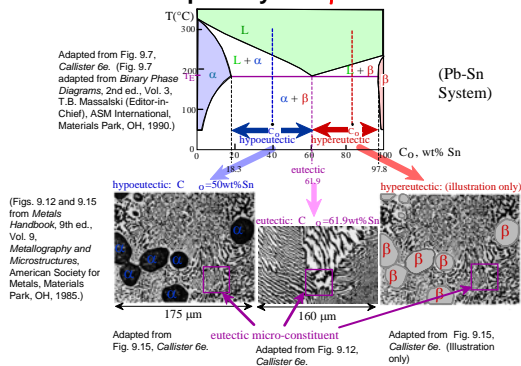


Microstructure of lead-tin alloy of composition 50 wt% Pb - 50 wt% Sn shows primary α and the eutectic structure

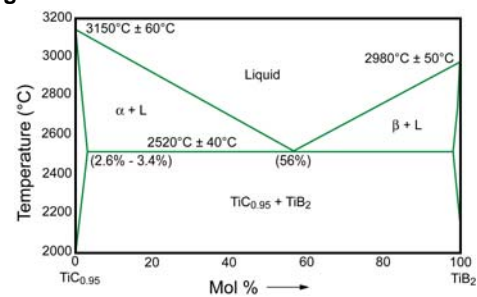


W.D. Callister, *Materials Science and Engineering An Introduction 5/e*, (John Wiley and Sons, New York, 2000).

HYPOEUTECTIC & HYPEREUTECTIC differ in whether it has primary α or β



Ceramics can have eutectic type phase diagrams

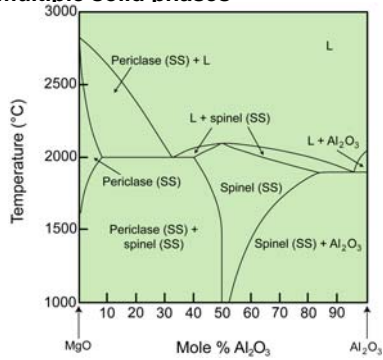


O.A. Graeve, *The Effect of an Electric Field on the Microstructural Development of Combustion Synthesized Ceramic Composites*, (Dissertation, University of California, Davis, 2001).

Many ceramic phase diagrams are complicated by multiple solid phases

Each solid phase has a different crystal structure

Spinel is an intermediate compound with ideal stoichiometry $MgO \cdot Al_2O_3$.

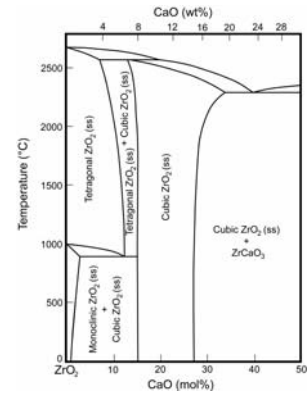


J.F. Shackelford, *Introduction to Materials Science for Engineers 5/e*, (Prentice Hall, New Jersey, 2000).

CaO is added to ZrO_2 to stabilize the cubic form

With the addition of CaO, other structures, aside from the monoclinic structure, become stable at room temperature.

The cubic phase becomes stable when 15-27 mol% CaO is added. The same effect occurs when Y2O3 is added.

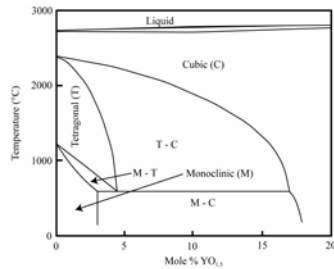


J.F. Shackelford, *Introduction to Materials Science for Engineers 5/e*, (Prentice Hall, New Jersey, 2000).

Adding Y to ZrO_2 stabilizes the cubic phase

Previously, it was determined that doped zirconia is optimum for the electrolyte in SOFC's. This is because the addition of the dopants produces oxygen vacancies, which then act as charge carriers that produce a working current.

Adding the yttrium also stabilizes the cubic form of zirconia



Cut of ZrO_2 -YO Phase Diagram: H. G. Scott, *Phase relations in the zirconia-yttria system*, *Journal of Materials Science*, 10 [9] 1527-1535 (1975)

In summary, phase diagrams can be used to tell the fraction of each phase and the microstructure

The lever rule is used to tell the fraction of each phase present.

Following each region of phase diagram you go through on cooling can be used to tell the microstructure of a given composition.

In ZrO_2 systems, adding species such as CaO or YO makes the cubic zirconia phase stable at lower temperatures

