

Intermetallics

Module β -2: SEM Study of binary alloys

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Objectives:

Determine the equilibrium phases and composition of the intermetallic compounds that can exist in the copper-tin binary system.

Summary of tasks:

- 1) Find the interface between the pure copper and the pure tin starting plates

Lessons to be learned: Regions of different composition in a metallic sample show different contrast when observed in a scanning electron microscope using back-scattered electrons to generate the image.

- 2) Determine the composition of the different phases present in the copper-tin binary system.

Lessons to be learned: The composition of different regions of a sample can be measured by analyzing the X-rays generated by the interactions of the electron beam and the atoms in the sample. The profile of the composition as a function of position along the interface can be used to determine the presence of intermetallic compounds.

Materials needed

Cu-Sn diffusion couple previously prepared

Equipment to be used

Scanning Electron Microscope (SEM) with an Energy Dispersive X-ray analysis (EDX) detector.

Sample Preparation

The surface of each a copper and tin plate were first polished flat by grinding using successive grits of grinding paper followed by polishing with alumina powder 0.3 μm in diameter suspended in water. The flat polished faces of the two metals were then pressed against each other and held together using a clamp. The entire assembly was heated up to 220°C in an argon atmosphere and held at temperature for 48h. The sample was then rapidly cooled to room temperature by quenching in water. The sample was then cut along a plane transverse to the Cu-Sn interface to reveal a cross-section of the interface and carefully polished to a mirror finish.

Background

Scanning electron microscope.

The size of the smallest feature that can be observed in a light microscope is limited by the wavelength of the light used in the microscope. In a scanning electron microscope an electron beam is used to image the sample. The wavelength of the electron beam is inversely proportional to the potential used to accelerate the electrons, and the wavelengths that can be obtained are smaller than those of visible or ultraviolet light. The wavelength can be calculated if relativistic effects are ignored by $\lambda = h/(2 m e u)^{1/2}$, where λ the wavelength, h is Planck's constant, m is the mass of the electron, e is the charge of the electron and u is the acceleration potential. The beam is rastered over the surface and the back-scattered or the secondary electrons are detected. Back-scattered electrons are detected in line with the electron beam and contain information about the sample chemistry, since the probability that an electron will bounce straight back to the back scatter detector is proportional to the atomic number of the atom it interacts with. Regions rich in high atomic number atoms in the sample will look brighter than regions with high concentrations of lower atomic number atoms. Secondary electrons are detected at an angle to the incident beam and can be used to generate an image of the sample topography.

Energy Dispersive X-ray analysis

A side effect of bombarding a surface with high energy electrons is that X-rays are generated by the inelastic collisions of the electrons with the atoms. The wavelengths of the X-rays generated are related to the energy difference of the different electronic shells in an atom, and are characteristic for each element. The fraction of a species in a sample can be related to the ratio of the integrated intensities of the characteristic wave lengths of the elements.

Phase Diagrams

A phase diagram is a map that shows, under equilibrium conditions, what phases will be present at a specific set of conditions. Phase diagrams can provide information on the melting temperatures of different systems and what phases will evolve as a given coordinate is changed in the system. They can also be used to determine what the relative fractions of two phases that evolve from a single phase will be.

The connection between a phase diagram and the free energy curves of a system is important in order to understand why certain phases coexist and how the equilibrium conditions change as temperature or concentration are varied.

For an ideal system, it is assumed that the enthalpy of mixing is zero, and the free energy of mixing of the system is only a function of the entropy of mixing, given by:

$$\Delta G_{mix} = RT(X_1 \ln X_1 + X_2 \ln X_2)$$

where R is the universal gas constant, T is the temperature of the system in absolute units and X_1 and X_2 are the mole fractions of components 1 and 2 in a binary system. For an ideal system, components 1 and 2 are completely miscible at all concentrations.

For a real system the enthalpy of mixing is non zero, and can be obtained to a first approximation from the probabilities of having atoms of the same species be next to each other and atoms of different species be next to each other and the bond energies of the 1-1, 1-2 and 2-2 bonds. In this case the free energy of the system is given by:

$$\Delta G_{mix} = zwX_1X_2 + RT(X_1 \ln X_1 + X_2 \ln X_2)$$

Where z is the number of nearest neighbors, and w is the difference of the bond energy for the 1-2 bonds and the average bond energy of the 1-1 and 2-2 bonds. If the bonds between similar atoms are favored by the system, immiscibility can result because it will be energetically favorable for the system to form two different phases. Each phase that forms will be rich in one of the components. Figure 1 shows the relation of the free energy curves and the phase diagram for a system with a miscibility gap. The common tangent of the two minima marks the boundaries of the miscibility gap. Each phase present in a system has its own free energy curve, and the competition between these free energies controls what phases will coexist at a fixed coordinate in the free energy diagram.

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Figure 1. Free energy curves and the corresponding phase diagram for a system with a miscibility gap. (From *Thermodynamics in Materials Science*, Robert T Dehoff)

In some metallic alloys phases may exist that are different than those of the pure components. These intermediate phases are called intermetallics. These intermetallics tend to have compound character; their composition can generally be described by a ratio of the component, like AB or A₂B, but the composition of these compounds can vary within a small range, leading to the formation of regions of finite width rather than just a single line on the diagram. Figure 2 shows the relation of the free energy curves and the phase diagram for a system with a miscibility gap and an intermetallic phase.

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Figure 2. Free energy curves and the corresponding phase diagram for a system with a miscibility gap and an intermetallic compound. (From *Thermodynamics in Materials Science*, Robert T Dehoff)

Figure 3 shows the phase diagram for the copper-tin system. Copper rich alloys of up to about 15% tin are commonly known as bronze. Below 350°C the system has a tin rich phase and a copper rich phase separated by two intermetallic compounds. Commercial bronzes are generally single phases alloys.

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Figure 3. Copper-tin phase diagram. (From the *ASM Handbook, volume 3, Alloy phase diagrams*)

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Copper-tin crystallographic data. (From the *ASM Handbook, volume 3, Alloy phase diagrams*)

Reading list

1. *Thermodynamics in materials science*, Robert T. Dehoff, (McGraw Hill , 1993) Chapter 10.
2. *Solid state Chemistry and its applications* , Anthony R. West, (Wiley, 1995), Chapter 3.
3. *Heat and Thermodynamics*, M. Zemansky and R. Dittman, (McGraw Hill, 1997)
4. *ASM Handbook Volume 3. Alloy phase diagrams*, Hugh Baker Editor, (ASM International. 1992)
5. *Scanning Electron Microscopy and X-ray Microanalysis*, J. Goldstein, D. Newbury, D. Joy et al. (Springer, 2003)