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# **Solders and Soldering**

**Materials, Design, Production, and Analysis  
for Reliable Bonding**

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state. Let us plot this temperature too, even though in the solder system it has little significance. Figure 3.1c yields the complete liquefaction temperature  $T_1$  and a lower solidification temperature  $T_2$ , which are plotted on the phase diagram, as does Fig. 3.1d. Finally, in Fig. 3.1e, we find the eutectic-temperature transformation of the system from a complete liquid to a complete solid at one temperature. Note that the temperature of the eutectic transformation is the same temperature as in Fig. 3.1d and c. We are now ready to complete the left side of the phase diagram by connecting all  $T_1$  temperatures and all  $T_2$  temperatures in the graphs as presented in the lower part of Fig. 3.1. More information is required to get the phase diagram in exactly the form shown in Fig. 3.1. In practice, it is customary to have cooling curves of many more alloys so as to have all the transformation temperatures that would give us an exact phase diagram. The right-hand side of this phase diagram can be obtained in a similar fashion.

Let us discuss in detail the various areas and lines which are found in the phase diagram. Starting from the top, we have the liquid region. The line which makes up the lower boundary of the liquid region is called the *liquidus*. The two triangular areas immediately beneath the liquid region represent the mushy stage, where the material has solid crystals floating in a liquid at equilibrium for that particular temperature. The lower border of this mushy region is the *solidus*, which in the tin-lead diagram lies between the melting points of the pure elements and 361°F (183°C). This is the temperature at which all the material changes into solid upon cooling, or upon heating starts forming a liquid phase. The area under the solidus is completely solid. The two triangular areas on both sides of the phase diagram are the regions of solid solution. The lower boundary of the solid solution region is the temperature at which the specific composition of the alloy changes from one solid homogeneous phase into two phases. A detailed account of the changes in the phase diagram and their corresponding importance to the tin-lead system is given in Sec. 3.7.

**3.3 Tin, Lead, and Their Alloys.** Both tin and lead have been known for thousands of years. *Oferet* (Hebrew for lead) and *bedil* (Hebrew for tin) are mentioned in the Bible. The Romans seemed to have been confused about the difference between tin and lead. They referred to tin as *plumbum album* (white lead) to separate it from *plumbum nigrum* (black lead), which stood for lead (note that *plumbum* is the modern chemical name for lead). Whereas lead was used by itself and in various alloyed forms for the manufacture of artifacts, tin was mainly used as an alloying addition to copper to make the alloy bronze, which was fairly widespread in ancient times. Today, both of

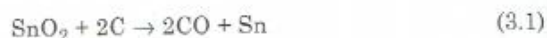


these metals are still used in an ever-increasing tonnage throughout industry, and the tin-lead alloys are the most widespread solder alloys. However, the use of lead may face some severe cutbacks as legislation and health concerns grow (see Sections 3.31 through 3.34).

Tin ores are found in Australia, Czechoslovakia, Bolivia, Cornwall, Malaya, Nigeria, Germany, South Africa, etc. Tin ores are usually found in what is called *tinstone* or *cassiterite*, which is a major source of commercial tin. This mineral,  $\text{SnO}_2$ , is usually found in crystals and is divided into *lode* or *vein tin*, which is cassiterite obtained from veins or lodes in primary deposits, and *stream tin*, which is cassiterite from alluvial secondary deposits that are usually rounded lumps. Small quantities of metallic tin are reported in various parts of the world, but these deposits are not large enough for production purposes.

Lead ores are usually found in nature as *galena*,  $\text{PbS}$ , which is the most common ore, although there are ores of lead carbonate,  $\text{PbCO}_3$ , called *cerussite*, and lead sulfate,  $\text{PbSO}_4$ , called *anglesite*. Lead ores are found in Australia, Belgium, Canada, Germany, Mexico, Russia, Spain, and the United States. The last is the world's largest producer of lead.

The extraction of tin from its ores is relatively simple. The ore is crushed and then concentrated by simple flotation methods, which are fairly easy because of the high specific gravity of tinstone (6.8 to 7.0). Unwanted impurities such as arsenic and sulfur are removed by an oxidizing roast and a dilute acid leach, while other impurities such as lead, bismuth, antimony, and silver are removed by a chloridizing roast and an acid leach. The ore is then ready for a reduction in either a blast furnace or a reverberatory furnace. The furnace is charged with the concentrated tinstone mixed with coal. The reduction reaction is



The molten tin collects on the bottom of the furnace and is drawn and cast directly into block tin. The average purity of the tin in this form is 99.5 percent. The tin is further refined by various methods.

Lead can be extracted by open-hearth smelting, by reverberatory-furnace smelting, and by blast-furnace methods. The most common today seems to be the last method, where the ore is subjected to preliminary roasting for the purpose of sintering the previously concentrated ore. During this roasting operation, most of the ore is converted into oxides. The oxidized ore is then charged together with the fuel into the furnace, where it is reduced by the carbon as well as by some of the unconverted lead sulfite. The quality of the lead obtained in this process is relatively poor, and further refining is necessary to remove the

**3.6 The Tin-Lead Alloy System.** To many people, the term *solder* has become synonymous with the tin-lead alloy system. There are many other useful soldering alloy systems and alloying additions to the tin-lead system itself, but since most soldering alloys actually are binary alloys of tin and lead, the tin-lead alloy system is discussed separately and thoroughly in this section. Figure 3.36 shows the variety of soldering alloys that can be used, and the shaded portion indicates the small temperature range in which all the tin-lead alloys fall. This narrow temperature range satisfies the requirements of most everyday soldering needs. Another important factor in their popularity is the relatively low price of tin-lead solders in relation to their wetting and strength properties.

Although much work has been done in the general investigation of the tin-lead system and the properties of the various alloys, it is difficult to find correlation among the figures published by the various workers. This can generally be attributed to the degree of purity of the alloys and materials used by these investigators. Most of this work was carried out when little or no attention was paid to minor alloying constituents and to the general condition of the sample. Recent advances in analytical methods, and especially in spectrographic and x-ray fluorescence techniques, make it possible today to gain much more information about the specimens under investigation than was possible when most of these studies were performed. Vacuum-melting techniques for the degassing of alloys and the removal of included oxides and nonmetallic impurities must be made part of these studies.

In a research study aimed at measuring certain physical parameters such as resistivity of tin-lead alloys and the effect of impurities on them, the author discovered the following interesting facts.<sup>5,6</sup> Calibration of the equipment for resistivity measurements on pure lead and pure tin proved difficult, because the results were not reproducible. The raw materials used were of 99.999 percent purity and were the best obtainable at the time. Only after these metals were vacuum-melted for degassing and also for oxide and inclusion removal was it possible to get repeatable measurements of the samples.

The inclusions and oxides present in the lead were removed by repeatedly vacuum-melting the lead specimen of 99.999 percent purity and cropping the head of the ingot. After three treatments, the alloy developed no further scum on the surface. The volume of the inclusions constituted nearly two percent of the volume of the specimen.

Thus, it becomes apparent that, although many technical data are available on the tin-lead system, the exact figures reported by various observers cannot be used without further investigation of the purity of the samples they used and correlation with the type of material to be used. In addition, the method of sample preparation and sample test-