PLASTICITY OF TIN – LEAD ALLOYS DURING CONTACT
MELTING WITH BISMUTH, CADMIUM, AND INDIUM

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The derivation of a theory for the onset of brittleness in metals and alloys exposed to melts would be aided by a study of the role played in this phenomenon by the chemical composition of the solid material. Moreover, even though complicated alloys rather than pure metals are usually used in applications, the effect of the chemical composition of alloys on their behavior under stress in a liquid-metal medium has not been studied adequately. The effect of alloying on the occurrence of this effect is usually treated as an indirect effect, operating through a change in the mechanical properties of the material. For example, it was concluded in [1] that the tendency of copper to suffer a loss in strength and plasticity when exposed to mercury was independent of the impurity elements in the copper being governed instead primarily by the yield point. We believe that this approach to the problem is of limited value.

Since polycrystalline materials exposed to liquid metals suffer destruction primarily along grain boundaries, the appearance of this effect must depend strongly on the state of the grain boundaries, particularly on their chemical composition. In view of the special physical properties of grain boundaries, particularly their high adsorptivity, due to their defective nature, grain boundaries may contain a large impurity content, even when the impurity content in the metal is low. In this regard the role of alloying is more important in the case in which the impurities are relatively insoluble in the solid state; highly soluble impurities should not significantly affect the plasticity or strength of metals in liquid-metal media, particularly if this medium can cause brittleness of the pure metal. In [2], e.g., a study was made of the strength of Ni—Cu, Pd—Ag, Pd—Cu, and Ni—Pd alloys, which have unlimited mutual solubility in the solid state, during deformation in contact with molten lithium; it was found that the strength of the alloys under these conditions was essentially independent of the composition, grain size, and preliminary cold working.

We report here a study of the role played by the composition of binary alloys of the tin—lead system in the onset of the sharp decrease in plasticity which occurs when the alloys are subjected to a bending stress while under conditions corresponding to contact melting with bismuth, cadmium, and indium. Since tin and lead have a limited mutual solubility, we would expect a strong dependence of the onset of liquid-metal embrittlement on the composition of the alloys of this system.

EXPERIMENTAL METHOD

The impurity level in the metals studied was less than 0.01%. The alloys were melted in quartz test tubes under dibutyl phthalate. After the melt was carefully mixed, the test tubes were lowered into water; the result was rapid crystallization of ingots without any appreciable development of shrinkage cavities. Then the ingots were rolled into bands 1.4 mm thick, from which samples 8 × 25 mm in area were cut.

The content of the second component in the samples was varied at 10% intervals up to 100%. In an effort to determine more accurately the concentration boundaries between the regions of brittle and plastic deformation during contact melting with various metals, we prepared alloys having other concentrations, varying by 5%, 1%, and even 0.1%, where necessary.

The samples were annealed to remove cold working. The samples were subjected to bending deformation at the specified temperature while held under contact-melting conditions with the selected metal in a protective medium (glycerine or dibutyl phthalate). Each sample was loaded at approximately the
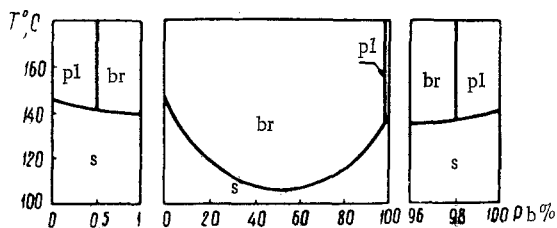
Fig. 1. Regions of the brittle destruction of tin—lead alloys during contact melting with bismuth.

same rate by means of micrometer screws. The deformation was begun when contact melting became visually apparent on the sample under a small piece of the pure metal. Depending on the experimental temperature, the alloy composition, and the nature of the metal in contact, the material displayed either plastic bending or brittle destruction. To show that the impurity by itself does not cause embrittlement, we subjected all the alloys to tests in controlled experiments under the same conditions, but without contact with a melt. From the data we constructed diagrams, plotted as the alloy composition versus the experimental temperature, showing the regions of brittle and plastic behavior of the materials deformed during contact melting with pure metals.

RESULTS AND DISCUSSION

The experimental results are shown in Figs. 1-3. The "br" regions correspond to the temperature regions in which the alloys of a given composition undergo brittle destruction under the influence of the melt formed at the contact with the test material. The "pl" regions correspond to plastic deformation. The low—temperature region in which an observable amount of liquid phase does not form at the metal—alloy contact is denoted "s" for solid phase.

Figure 1 shows that the tin—lead alloys are embrittled by bismuth at all temperatures and at essentially all compositions; the only exceptions are compositions in two narrow regions adjacent to the pure metals. The addition of 0.5 wt. % lead to tin thus causes a rapid change in the sensitivity of tin to liquid-metal embrittlement during contact melting with bismuth. In a melt, bismuth does not nucleate cracks in pure tin during bending [3], but it does lead to the catastrophic destruction of tin containing lead. On the other hand, although pure lead is not embrittled by bismuth [3], alloys of lead with more than 2 wt. % tin suffer a reduction of plasticity when exposed to a melt containing bismuth.

Similar behavior is observed when tin—lead alloys are deformed during contact melting with cadmium (Fig. 2). With 0.2 wt. % lead or more in the tin, liquid-metal embrittlement of the alloys occurs in this case, although cadmium is inert with respect to both tin and lead [3].

Deformation of tin—lead alloys under contact-melting conditions with indium, or when molten indium is present on the sample surface, is characterized by two regions of brittle destruction (Fig. 3). In contrast with the embrittlement diagrams described above for the cases of bismuth and cadmium, in this case a narrow concentration range appears in the brittle-destruction region in which the embrittlement disappears. This range corresponds approximately to the eutectic composition of the tin—lead system. Alloys of other compositions, except for the compositions near the pure metals, were subjected to molten indium or indium in a contact melt. Indium is very soluble in tin and lead and thus cannot cause liquid-metal embrittlement of these metals.
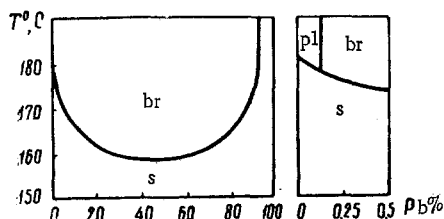

Fig. 2

Fig. 3

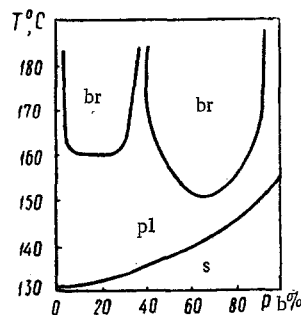Fig. 2. Regions of brittle destruction of tin—lead alloys during contact melting with cadmium.

Fig. 3. Regions of brittle destruction of tin—lead alloys during contact melting with indium.

Accordingly, in all these cases of the deformation of tin—lead alloys in contact with inert metals, we find a rapid decrease in plasticity at certain compositions.

These results can be explained on the basis of the mechanism described in [3] for the embrittlement of solid metals by liquid metals. According to this mechanism, a crack grows in the presence of the liquid metal because atoms diffuse from the liquid into grain boundaries, forming a melt there. The penetration of this melt into the interior of the metal is equivalent to the growth of a crack filled with a liquid metal. The stress serves to accelerate grain-boundary diffusion [4].

The basic difficulty involved in this explanation of liquid-metal embrittlement is in explaining the high crack growth rate on the basis of arguments about diffusion processes. An estimate in [5] shows, however, that the diffusion mechanism is quite capable of explaining the experimental crack growth rate.

In this case we would expect that if the alloy contained an active component it would lose its plasticity during contact melting with an inert metal because of the melting of the active component. This explanation is not correct, however, because the concentration of the active component in a melt which forms during contact melting of an alloy containing a slight amount of this component is much smaller than the concentration required for an appreciable affect on the plasticity of the pure metal. For example, it was shown in [6] that cadmium—lead alloys cause liquid-metal embrittlement of pure tin during contact melting only if the lead concentration is at least 40%. Clearly, the concentration of the active component in the melt which forms during the contact melting of cadmium with tin containing lead on the order of tenths of 1% is much lower than the concentration capable of causing liquid-metal embrittlement.

An even stronger argument against this explanation of the results is that lead alloys are affected by melts which contain no component which interacts with lead, since none of the metals which have been used reduce the plasticity of lead during contact melting [3]. Binary alloys of inert components are also inert [6], so the reason for an alloy's loss of plasticity in the presence of an apparently inert melt should be sought in a change in the properties of the deformed metal, rather than the composition of the liquid phase.

The alloying of a metal to improve its strength is a possible cause of the change in its sensitivity to liquid melts. Higher stresses can be applied to a strengthened material, so it is easier for atoms to penetrate from the melt by diffusion along grain boundaries.

Another reason why alloys are more sensitive to embrittlement than pure metals is, as mentioned above, the change in the chemical composition of the grain boundaries during alloying. Even very soluble impurities form so-called equilibrium segregations along grain boundaries [7]. The tin—lead system is a eutectic system, so, except for alloys having slight amounts of the second component and for the eutectic alloys, all the alloys of the system have a sharply defined structural inhomogeneity: grains of the primary solid-solution crystals are surrounded by eutectic alloy. With this alloy structure, contact melting with a third metal readily produces a liquid phase, a ternary eutectic system, along grain boundaries where there is a binary eutectic system. This circumstance leads to the selective formation of liquid phase along grain boundaries and to the catastrophic loss of plasticity under external loads.

Although there is no ternary eutectic composition in the Sn—Pb—In system, lead along the boundaries of tin grains should facilitate the formation of liquid phase there, since there is a minimum on the liquidus curve of the binary Pb—In system [8, 9].

The high plasticity, low mechanical strength, and quite pronounced structural homogeneity of the eutectic alloy (due to its highly dispersed structure) are apparently responsible for the inability of liquid indium to sharply reduce the plasticity of this alloy.

LITERATURE CITED

1. R. Rozenberg and I. Kadof, in: Destruction of Solids [in Russian], Metallurgizdat (1968).
2. N. M. Parikh, Environment-Sensitive Mechanical Behavior, Part 2, New York (1965), p. 563.
3. A. P. Savitskii and L. K. Savitskaya, Surface Phenomena in Melts and in the Solid Phases Arising from Them [in Russian], Nal'chik (1965), p. 449.
4. M. I. Chaevskii, I. N. Toropovskaya, V. V. Popovich, and A. M. Datsishin, FKhMM, 5, No. 6 (1969).
5. W. M. Robertson, Trans. AIME, 236, No. 10, 1478 (1966).
6. N. V. Cherkasova, I. N. Anokhina, V. N. Zhdanova, L. K. Savitskaya, and A. P. Savitskii, Izv. VUZ, Fizika, No. 6, 59 (1968).

7. D. McLean, Grain Boundaries in Metals, Clarendon Press, Oxford (1957).
8. H. M. Davis, Trans. ASM, 39, 712 (1947).
9. A. N. Campbell, R. M. Screaton, T. P. Schaefer, and C. M. Hovey, Can. J. Chem., 33, No. 3, 511 (1955).