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USE OF BISMUTH IN FUSIBLE ALLOYS

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USE OF BISMUTH IN FUSIBLE ALLOYS

ABSTRACT

Bismuth is an essential constituent of most of the readily fusible alloys. Consequently a study of these alloys was undertaken as part of an investigation seeking to develop and extend the uses of metallic bismuth.

The literature and uses of fusible alloys are reviewed in this paper. Two, three, and four component fusible metals are discussed. Tables of fusible alloys are given, and the question of volume changes in the alloys during and after solidification is discussed.

CONTENTS

I. INTRODUCTION

This publication is a continuation of the compilation of existing information on the uses of bismuth, carried out in connection with a research project on the properties and uses of that metal. A general review of the entire field is contained in Circular No. 382, Bismuth. The present paper is concerned with a more detailed study of one important section of the field of usefulness of metallic bismuth. This material was prepared by J. G. Thompson, research associate for the Cerro de Pasco Copper Corporation.

Metallic alloys which are completely molten at temperatures appreciably below the melting points of the component pure metals have been known approximately as long as the study of metallurgy has existed. In fact, the early study of metallurgy may be considered as a study of low-melting alloys, since the first specimens of metals almost invariably were impure, and one of the notable effects of the presence of impurities in a metal usually is a lowering of the melting point. This lowering of the melting point in proportion to the amount of impurities present frequently persists beyond the point where the foreign ingredients are present as "impurities" and enters the field of "alloys," where definite amounts of foreign ingredients purposely have been added to alter the properties of the original pure metal. The presence of "impurities" may lower the melting point of a metal 1° or 2°, whereas the conversion of the pure metal into an alloy may be accompanied by a lowering of the melting point of 100° or more. In the case of alloys of lead and tin (42),[1] the pure metals melt at 327°

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[1] The figures given in parentheses here and throughout the text relate to the reference numbers in the bibliography given at the end of this paper.

and 232° C., respectively, and the eutectic alloy, which contains 63 per cent tin, melts at 181° C. This is 51° below the melting point of pure tin and 146° below that of pure lead. An even more striking illustration is found in the alloys of lead and bismuth (43). In this case the eutectic alloy, which contains 42 per cent lead, melts at 125° C. This is 202° below the melting point of pure lead. The metals lead and tin form the basis for most of the low-melting alloys. If still lower melting points are desired, bismuth or bismuth and cadmium are added to the lead-tin mixture. For extremely low melting points, or for metallic alloys which will remain liquid at room temperature, mercury is a necessary constituent.

Bismuth and cadmium possess to an unusual degree the property of lowering the melting points of metallic alloys. Rosenhain (30) has suggested that variations in the melting point and other properties of alloys, with varying composition, are related to the distortion of the crystal lattice of the solvent metal caused by the intrusion of the solute atom. Expansion of the crystal lattice is accompanied by lowering of the melting point, whereas contraction of the lattice raises the melting point. In either case the extent of the change in properties is dependent upon the amount of distortion of the lattice. The theory presents interesting possibilities and is confirmed in some respects by experimental evidence. If bismuth and cadmium distort other lattices, and are distorted by other metals, to an unusual degree it would account for the low melting points of the bismuth and cadmium alloys. However, an explanation has not appeared as to why these two lattices are unusually susceptible to distortion and are able to cause unusual distortion in the lattices of other metals.

II. USES FOR FUSIBLE ALLOYS

A wide variety of uses has been found for fusible alloys based on their low melting points. The principal use is in soldering operations, the selection of a particular alloy depending upon the conditions of that particular operation. A special soldering application arises from the fact that several of the fusible alloys wet glass and melt at such low temperatures that they can be safely applied to glass. They are used, therefore, in making seals and gas-tight joints in glass apparatus (28). Another important use has been in safety devices, particularly in protection from fire. The melting of the fusible metal releases water pressure into a sprinkler system, operates an alarm, releases automatic fire doors, gives warning of excessive temperature and pressure in steam systems, etc. The temperature at which the device operates depends upon the melting point of the alloy chosen.

Baths of readily fusible metals have been used in a variety of quenching and drawing operations for the treatment of small tools and the like. A constant temperature bath can be obtained by choosing the proper alloy and maintaining the temperature within its melting range. The use of low-melting alloys in machine shop and in testing operations is growing in importance. Grips of low melting alloys can be cast on pieces of irregular cross section and can be removed after the machining or testing operation is complete. The casting and subsequent removal of the fusible alloys can be carried out at temperatures below 100° C., low enough to avoid any possibility of injuring the specimen. A modified fusible alloy which melts somewhat above 100° C., and which is stronger and more resistant to compression than are the extremely fusible alloys, has been described recently (45). This "matrix" alloy is being used in the alignment, setting, and repair of punch press dies. A die can be set in position by means of this alloy more quickly and easily than by means of screws, wedges, and other mechanical means, and the alloy setting is more permanent and requires less attention. The alloy can be melted with a small torch, to free the die, at temperatures so low that the temper of the die is not affected.

Many of these low-melting alloys possess excellent casting properties. Pure bismuth expands about 3 per cent of its volume during solidification and it possesses a coefficient of thermal expansion of 0.00001316 for the range from 0° to 100° C. This coefficient is approximately half that for aluminum or lead. Alloys which contain appreciable amounts of bismuth do not shrink as much as do many metals during solidification nor on further cooling of the solid metal. Both of these factors are desirable in pattern making. It is possible to prepare alloys high in bismuth which do not change in volume during solidification, or which expand during solidification, but this is possible only when the bismuth content is over 50 per cent (see discussion of fig. 2). All of these alloys exhibit shrinkage of the solid metal as it cools from temperatures near the melting point to room temperature, but this coefficient of expansion of the solid metal usually is low. Low-melting alloys have been used to repair defects in castings and to reproduce delicate patterns. Castings can be made in wooden molds or from wooden patterns. By adding mercury to the alloys the melting point can be lowered to such an extent that castings of anatomical specimens or of delicate objects, such as leaves or flowers, can be made without injuring the specimen.

Gasoline tanks for airplanes have been made seamless and jointless by electrodeposition of copper on a fusible casting, which is subsequently melted with hot water, leaving the copper shell (29). Fusible alloys also have been used to provide a gas-tight, noninflammable liquid seal for apparatus, such as large nitriding ovens (41).

Minor applications of fusible alloys include their use for fuse rods and indicator blocks for bearings (23), for silvering mirrors, and for the preparation of toys, such as the fusible teaspoons which melt in hot water. Mackenzie's amalgam is an interesting curiosity. The amalgam is prepared in two portions: (*a*) An alloy of bismuth and mercury in the approximate proportions of 2:1, and (*b*) an alloy of lead and mercury in the approximate proportions of 4:3. Both (*a*) and (*b*) are metallic solids, but when rubbed together in a mortar at room temperature, or in the palm of the hand, a liquid results.

These uses of fusible alloys almost without exception are based solely upon the melting point of a particular alloy or alloys. Little information is available regarding properties of these alloys other than melting points, but it may be expected that increased knowledge of mechanical properties would suggest new and wider use for the alloys. A few mechanical data are presented in a recent publication (44).

III. SOLDERS

Lead-tin alloys, 50:50 or 60:40 in composition, constitute the bulk of the soft solders ordinarily employed. However, such large proportions of tin make the cost of the alloy rather high and there are grounds for improvements in regard to porosity and in resistance to corrosion.

An improved solder is reported (36) to result from the replacement of part of the tin by a small amount of cadmium. Preliminary experiments on similar replacement of part of the tin by small amounts of bismuth produced solders which wet copper and brass satisfactorily and which appeared to compare favorably with the standard solders in regard to mechanical properties and cost. These preliminary experiments indicate a possible use for bismuth in the field of soft solders.

The minimum melting point of the lead-tin system is 181° C. If lower-melting alloys are desired, there are other binary systems available, such as the bismuth-tin system with a minimum melting point of 135° C., or the bismuth-lead system with a minimum melting point of 125° C. However, the low cost of lead and the desirable features contributed by the presence of tin make it customary to start with lead-tin alloys and to obtain lower melting points by the addition of bismuth or cadmium or both. Charpy's diagram, (12) published in 1898, showed the melting points of the different possible alloys in the ternary system—lead, tin, and bismuth. He found that the ternary eutectic composition was 32 per cent lead, 16 per cent tin, and 52 per cent bismuth, and that this eutectic alloy melted at 96° C. Minor deviations from eutectic composition can be made without raising the melting point above 100° C. (See fig. 1.) Consequently, a number of ternary alloys which are molten at the temperature of boiling water are recorded in the literature. Rose's metal is the most common designation for these alloys but Onion's, Dobereiner's, Lichtenberg's, and D'Arcet's alloys also are encountered. Compositions all approximate the eutectic composition given above,

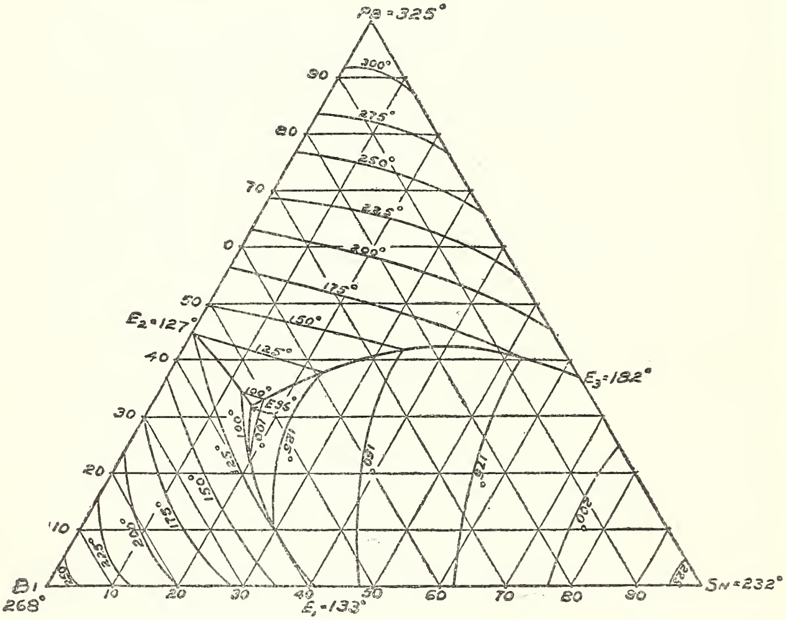

FIGURE 1.—*Melting point diagram for the system bismuth-lead-tin (12)*

IV. THREE-COMPONENT ALLOYS

but are usually rounded off for convenience to figures such as 30 lead, 20 tin, and 50 bismuth.

Alloys of lead, tin, and bismuth melting above 100° C. have been studied rather extensively. The principal interest in these alloys has been in connection with their use in automatic sprinklers, alarms, releases for fire doors or in other safety devices. Variations in composition produce alloys melting at any desired temperature, and tables of such alloys arranged in order of their melting points are found in many textbooks. Table 1 represents such a list of "alloys which are useful for steel-tempering baths, constant-temperature baths, and the like" (1). Practically all of the subsequent lists appear to be copies of this list of Thurston's, published in 1890, and it is not clear that the list originated with Thurston. The lists should be revised and the melting points, or melting ranges, redetermined. Sharp melting points are attributed to all of the alloys in the table, whereas it is now recognized that a sharp melting point exists only for pure metals, eutectic alloys and intermetallic compounds, and that other alloys soften and gradually liquefy over a melting range which may be appreciable in extent.

TABLE 1.—*Fusible alloys of bismuth, lead, and tin* (*1, p. 195*)

Parts by weight			Reported melting point		Parts by weight			Reported melting point	
Bismuth	Lead	Tin	° C.	° F.	Bismuth	Lead	Tin	° C.	° F.
8	5	3	94.5	202	8	16	24	158	316
8	6	3	98	208	8	18	24	155	312
8	8	3	108	226	8	20	24	154	310
8	8	4	113	236	8	22	24	153	308
8	8	6	117	243	8	24	24	154.5	310
8	8	8	124	254	8	26	24	160	320
8	10	8	130	266	8	28	24	166	330
8	12	8	132	270	8	30	24	172	342
8	16	8	148	300	8	32	24	178	352
8	16	10	152	304	8	32	28	166.5	332
8	16	12	146	294	8	32	30	164.5	328
8	16	14	143	290	8	32	32	160	320
8	16	16	144	292	8	32	34	159	318
8	16	18	148	298	8	32	36	160	320
8	16	20	151	304	8	32	38	161	322
8	16	22	155	312	8	32	40	162	324

Other ternary systems of interest in connection with fusible alloys are lead-tin-cadmium, lead-bismuth-cadmium, and tin-bismuth-cadmium. The eutectic compositions and their freezing points, according to Budgen (29), are shown in Table 2.

TABLE 2.—*Low melting ternary eutectics* (*29*)

Per cent, by weight				Freezing point
Bi	Pb	Sn	Cd	
				° *C.*
51.65	40.2	----------	8.15	91.5
52	32	16	----------	96
40.7	----------	27.9	31.4	103
----------	32	49.8	18.2	145

The bismuth-lead-cadmium eutectic melts at a slightly lower temperature than the bismuth-lead-tin alloy, but the latter possesses better mechanical properties. Other ternary alloys—for instance, those which contain zinc—have been studied but the alloys of bismuth, lead, tin, and cadmium constitute practically all of the ternary and quaternary fusible alloys which are at all commonly used.

V. FOUR-COMPONENT ALLOYS

The best known of all the really low-melting alloys are the quaternary alloys of bismuth, lead, tin, and cadmium. When the composition approximates that of the quaternary eutectic the alloy usually is called Wood's metal, or less commonly Lipowitz metal. Both names are applied loosely to any metallic alloy which is completely molten at temperatures appreciably below 100° C., or more specifically to alloys which melt not far above 70° C. Parravano and Sirovich's (20) study of the bismuth-lead-tin-cadmium system showed that the eutectic composition was 49.5 per cent bismuth, 27.27 per cent lead, 13.13 per cent tin, and 10.10 per cent cadmium. The melting point of this eutectic composition was given as 70° C. Hommel (24) reported the eutectic composition to be 50 Bi:27 Pb:13 Sn:10 Cd confirming Parravano's results, but Hommel found the eutectic arrest to occur at 66° C. Considerable confusion still exists in the literature. The data in Table 3 illustrate the variety of compositions known as Wood's metal or Lipowitz metal, the similarity in composition of the two groups, and the wide variation in melting points ascribed by different authors. Lassieur (26) in 1922 showed that many of these fusible alloys are molten only at temperatures decidedly above their reported melting points. The fallacy of a 60° C. melting point in the absence of mercury still persists in recent articles (40). In one case (29) the statement that Parravano and Sirovich's eutectic melts at 70° C. is followed by the statement that Wood's metal (50:25:12.5:12.5) melts at 60° C.

TABLE 3.—*Reported composition and melting points of quaternary fusible alloys*

No.	Name	Bi	Pb	Sn	Cd	Melting point	Reported by—
		Per cent	*Per cent*	*Per cent*	*Per cent*	*°C*	
1	Wood's metal	50	25	12. 5	12. 5	74	Threlfall (14).
2	do	50	25	12. 5	12. 5	60. 5	Gilbert (25).
3	do	52. 43	25. 85	14. 73	6. 99	75. 5	Do.
4	do	55. 74	13. 73	13. 73	16. 8	65–70	Do.
5	do	47	23. 5	17. 7	11. 8	65. 5	Do.
6	do	38. 4	30. 8	15. 4	15. 4	77–80	Lassieur (26).
7	do	50	25	12. 5	12. 5	60. 5	Budgen (29).
8	Lipowitz metal	49. 98	26. 88	12. 76	10. 38	80–85	Gilbert (25).
9	do	50	26. 7	13. 3	10	70	Budgen (29).
10	do	50	27	13	10	60	Ragatz (40).
11	Miscellaneous	50	26. 7	13. 3	10	75–76	Lassieur (26).
12	do	50	25	12. 5	12. 5	74–75	Do.
13	do	50	26. 7	13. 3	10	63	Goodrich (38).

Experimental data are presented in a recent publication (44) which confirm the results of Parravano and Sirovich. It appears that 70° C. is the lowest melting point obtainable in this quaternary system of bismuth-lead-tin-cadmium. However, mercury can be added to form 5-component alloys which will melt at lower temperatures than the quaternary eutectic. If enough mercury is present the 5-component alloy will remain liquid at room temperature.

VI. VOLUME CHANGES OF FUSIBLE ALLOYS DURING AND AFTER SOLIDIFICATION

Discussion in the literature of the changes in volume, which occur during or after solidification of the alloys of bismuth and antimony, has included some of the fusible alloys. The statement that all alloys of bismuth or of antimony expand during solidification still is encountered, and this statement frequently is still used to explain why type metals containing 10 to 15 per cent antimony produce such good castings. Wiedemann (11) in 1883 showed that bismuth-lead alloys expanded or contracted during solidification, according to the proportions of the component elements. Endo (31) showed that the expansion or contraction during solidification of lead-antimony alloys is a regular function of the composition. His data (fig. 2) show that lead-antimony alloys exhibit smaller and smaller solidification contractions as the antimony content increases, until at about 72 per cent antimony an alloy is obtained which solidifies without change in volume. If the antimony is increased to more than 72 per cent, the alloy will expand during solidification, the extent of the expansion increasing as the composition approaches pure antimony. Matuyama (34) confirmed in general the work of Endo, although his constant volume alloy appears at about 78 per cent antimony, as his value for the expansion of pure antimony is lower than that used by

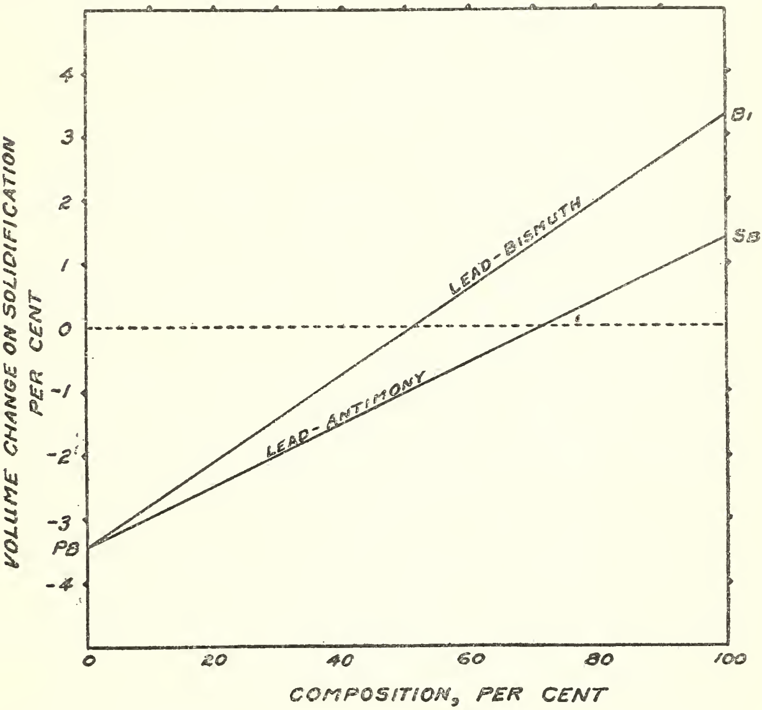

Figure 2.—*Expansion during solidification of lead-bismuth and lead-antimony alloys*

Endo. Matuyama states that lead-antimony alloys do not expand during solidification unless they contain more than 75 per cent antimony. He also presents experimental evidence to show that type metals contract about 2 per cent during solidification. Plotting the data for bismuth and lead, comparable to those for antimony and lead, it appears that only the alloys which contain more than 50 per cent bismuth expand. The alloy which solidifies without change in volume should be found at about 52 per cent bismuth.

This discussion of the volume changes in the lead-antimony and lead-bismuth systems applies only to the changes in volume during solidification of the molten metal. It is believed that all of these binary alloys exhibit normal solid contraction on cooling the solidified metal to room temperature, although the coefficient of thermal expansion or contraction of these metals in the solid state is low.

Volume changes and thermal effects during and after solidification of certain ternary and quaternary fusible alloys have been studied, but further information is needed. Shepherd (15) observed recalescence in several of the fusible alloys and associated this phenomenon with allotropic changes in the tin. Isihara (37) observed a volume change of bismuth-tin-lead alloys at about 76° C. and explained this on the assumption of the formation of a ternary compound, Bi_2SnPb, which is stable below 76° C., but which decomposes above 76° C. into three solid solutions. Gilbert (25), Goodrich (38), and Fleischmann (33) studied the volume changes of some of these alloys, but further data are needed.

In some of the experimental work performed at the bureau on alloys containing 50 per cent or less bismuth, it was noted qualitatively that the alloys studied, whether binary, ternary or quaternary, all showed unmistakable evidence of solidification shrinkage although this varied in extent. In the determination of the melting-point curve for Parravano's eutectic alloy, the metal could be allowed to solidify and cool to 50° C. and then be remelted several times without injury to the graphite crucible. However, if the crucible and metal were allowed to cool completely down to room temperature the crucible usually was broken. It is believed that this occurred because the graphite crucible contracted more than did the solid metal in cooling from the solidification point to room temperature.

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