

CHAPTER X.
GERMAN SILVER, AND MISCELLANEOUS COPPER
ALLOYS.

GERMAN silver probably exists under a greater number of names than any other alloy. Nickel silver, argentan, packfong, white copper, silveroid, silverite, Nevada silver, Potosi silver, Virginia silver, and electrum are some of the names which have been used to describe it in this country; while on the Continent it is known as *maillechort* (after Maillet, who introduced it into France in 1719), *alfénide argiroide*, *neu-silver*, and *weiss-kupfer*. The alloy consists of copper, nickel, and zinc, but the quantities vary considerably in different samples. Before dealing with the ternary alloy it may be well to briefly consider the binary alloys of copper and nickel, as they have (to a limited extent) their own industrial applications. Unfortunately, very little work appears to have been done in connection with either series of alloys, and the information concerning them is incomplete and unsatisfactory.

From the freezing-point curve of the copper-nickel series, as determined by Gautier, it would seem that a compound corresponding to the formula $CuNi$ is formed, which is soluble in copper and nickel. The micro-structure of the alloys confirms the view that they are solid solutions, but does not indicate the existence of a compound. The electrical conductivity of the series, however, shows a minimum in the alloy containing 40 per cent. of nickel, which is not far removed from the composition of the supposed compound.

Apart from the alloy containing 50 per cent. of nickel, which is used in the manufacture of German silver, the alloys generally used contain quantities of nickel not exceeding 25 per cent.

These alloys, when cast, exhibit the characteristic structure of quickly-cooled solid solutions, but, on annealing, the crystallites undergo gradual absorption and are replaced by the regular crystalline structure of simple metals and homogeneous solid solutions. This change of structure with annealing has been considered in some detail in the case of the copper-zinc alloys containing 30 per cent. of zinc.

An alloy containing 25 per cent. of nickel has been largely used as a coinage alloy, but at the present time there appears to be a tendency to substitute nickel coins for those of the alloy. A 25 per cent. alloy has also been used for locomotive firebox plates with satisfactory results; while an alloy containing only 5 per cent. of nickel has been adopted by the British Government for the driving bands of projectiles. Copper containing 3 per cent. of nickel has also been found to give excellent results for locomotive boiler tubes. In this connection an instructive experiment was made by Mr Webb of the London and North-Western Railway Works at Crewe. A four-wheels-coupled passenger engine was fitted with 198 tubes by ten different makers and a record kept of the tubes requiring renewal. The first tube failed after the engine had run 34,067 miles, and the second tube (of the same make) after 40,612 miles. The first and only failure of the make which stood best did not occur until the engine had run 123,896 miles. The failure of the tubes, which was due to wear from the inside by the corrosion of furnace gases and abrasion of cinders, invariably occurred at a point within 6 inches of the firebox and at the bottom of the tube. Analyses of all the tubes showed that those giving the best service contained about 3 per cent. of nickel, and excellent results were obtained from those containing not less than 0.5 per cent. of arsenic.

An alloy containing 60 per cent. of copper and 40 per cent. of nickel is known under the name of *constantan*, and is used in the form of wire for electric resistances, and also in conjunction with a copper wire as a thermoelectric junction suitable for the measurement of temperatures which are not sufficiently high to necessitate the use of a platinum couple.

The addition of zinc to the copper-nickel alloys is not attended with the formation of compounds, and the resulting alloys (the

German silvers) consist of a single homogeneous solid solution. Photograph 34 shows the structure of a rolled German silver. They may be regarded either as brasses containing nickel in solution, or as copper-nickel alloys containing zinc in solution. They are very ductile, and can be rolled, hammered, stamped, and drawn. At the same time they are hard, tough, not easily corroded, and, above all, possess the valuable property of being white. As in the case of most solid solutions, the alloys are softened by annealing.

The following table gives the results of a number of analyses of German silvers (collected by Hiorns) with the names of the authorities:—

Authority.	Composition per cent.					
	Copper.	Nickel.	Cobalt.	Zinc.	Iron.	Lead.
1. Fyle	40.4	31.6	...	25.4	2.6	...
2. Fricke	50.0	31.2	...	18.8
3. Guettier	53.3	26.6	...	20.1
4. "	51.6	26.0	...	22.4
5. Krupp	51.6	25.8	...	22.6
6. "	48.5	24.3	...	24.3	...	2.9
7. Hiorns	57.0	24.3	...	18.7
8. Guettier	59.0	22.2	...	18.5	...	0.3
9. "	55.2	21.4	...	23.4
10. Hiorns	59.1	20.2	...	20.4	0.3	...
11. "	56.5	20.3	...	23.2
12. Henry	67.0	19.3	...	13.6
13. Lonyet	63.3	19.1	...	17.4
14. D'Arcet	50.0	18.7	...	31.2
15. Hiorns	58.0	18.5	...	23.5
16. Smith	60.0	18.8	3.4	17.8
17. Krupp	58.3	19.4	...	19.4	...	2.9
18. Hiorns	53.1	16.2	...	30.0	0.67	...
19. "	55.6	15.7	...	28.7
20. "	56.8	15.6	...	27.2	0.3	...
21. Lonyet	62.4	15.0	...	22.1
22. Krupp	57.8	14.3	...	27.1	...	0.8
23. Hiorns	58.7	13.8	...	26.4	1.0	...
24. "	57.0	13.4	...	27.6	2.0	...
25. Elsner	57.4	13.0	...	26.6	3.0	...
26. Hiorns	55.4	11.6	...	31.4	1.6	...
27. Lonyet	62.6	10.8	...	26.5
28. Rochet	59.1	9.7	...	31.2
29. Hiorns	66.0	8.2	...	25.3	0.5	...
30. Krupp	63.0	6.0	...	31.0

The same authority gives the composition of the various qualities of German silver made by the best makers in Birmingham, together with the trade names under which they are known:—

Name.	Composition per cent.		
	Copper.	Nickel.	Zinc.
Extra white metal	50	30	20
White metal	54	24	22
Arguzoid	48½	20½	31
Best Best	50	21	29
Firsts or best	56	16	28
Special firsts	56	17	27
Seconds	62	14	24
Thirds	56	12	32
Special thirds	56½	11	32½
Fourths	55	10	35
Fifths, for plated goods	57	7	36

The best of these alloys are somewhat costly; and for most purposes the quantity of nickel does not exceed 20 per cent.

As the result of a number of experiments on the relative composition of German silver, Hiorns concludes that, for alloys containing less than 16 per cent. of nickel the quantity of zinc should be 30 per cent. in order to give the best results; while with alloys containing more than 16 per cent. of nickel the quantity of zinc should be less than 30 per cent.

As regards the impurities found in German silver, those most often met with are iron, lead and tin. Iron forms a solid solution with the alloy, with the result that it increases the strength, hardness, and elasticity of the alloy, and at the same time makes it slightly whiter. It follows that for some purposes the addition of one or two per cent. of iron may be an advantage. Tin, on the other hand, does not enter into solid solution in the alloy, but forms a eutectic which renders the metal brittle and unfit for rolling. It also makes the alloy decidedly yellow in colour when present even in small quantities. Lead does not alloy with German silver, but separates out as metallic lead, in the same way as already described in the case of brass. This metal is, therefore, purposely added to the extent of two or three per cent. when the

metal is to be cast and subsequently worked, but is not permissible in metal that is intended for rolling. The remarks which have been made with regard to lead in brass apply equally to the case of German silver. Cobalt is occasionally found in small quantities, owing to its presence in the nickel, and has sometimes been purposely added; but it is an expensive metal and does not appear to confer any properties upon the alloy to justify its presence.

German silver is made by melting the metals in the usual way in graphite crucibles. The separate metals, however, are not melted together; but are used in the form of alloys of copper and nickel and copper and zinc. This method answers the double purpose of more readily producing a homogeneous alloy and lessening the oxidation of the zinc. Shortly before pouring the metal a further small quantity of zinc may be added, to compensate for volatilisation and ensure thorough deoxidation of the alloy.

The metal is cast in iron moulds similar to those used in brass casting, but of different sizes. For ingots which are intended to be rolled into sheets the moulds are from 16 to 18 ins. in length, 1 to $1\frac{1}{4}$ ins. thick, and from 4 to 5 ins. wide; while for ingots for wire drawing the sizes are from $4\frac{1}{2}$ to 5 ft. long, $1\frac{1}{4}$ ins. thick, and $3\frac{1}{4}$ ins. wide. The method of casting is exactly the same as in the case of brass; but the melting-point of German silver being higher than that of brass, the casting has to be performed rapidly, or the crucible has to be returned to the furnace to be reheated.

From time to time various metals have been added to German silver for special purposes, and a great number of complex alloys have been patented; but very few of them appear to have met with any success. There are, however, a few exceptions which may be mentioned.

Platinoid is a German silver containing tungsten. It consists of 60 per cent. copper, 14 per cent. nickel, 24 per cent. zinc, and 1 to 2 per cent. tungsten. This alloy possesses a low electrical conductivity, and has therefore been largely used in the manufacture of electrical resistances.

German silvers containing silver were introduced long ago by Ruolz, and were used for making jewellery. The composition of the alloys varied, but they contained from 20 to 30 per cent. of

silver, 25 to 30 per cent. of nickel, and 35 to 50 per cent. of copper. Similar alloys, but containing less silver, have been used for the subsidiary coinage of Switzerland. The percentage composition of these alloys was as follows:—

	20 Centimes.	10 Centimes.	5 Centimes.
Silver	15	10	5
Copper	50	55	60
Nickel	25	25	25
Zinc	10	10	10

Several German silvers containing aluminium have been suggested, the aluminium acting as a deoxidiser. An alloy of this description containing 57 per cent. copper, 20 per cent. nickel, 20 per cent. zinc, and 3 per cent. aluminium, is largely used for typewriter parts. Magnesium is sometimes used for the same purpose, and an alloy containing 75 to 90 per cent. of copper, 10 to 25 per cent. of nickel, and 1 to 2 per cent. of magnesium, is said to be largely used in Germany. The high cost of these alloys, however, is a serious drawback.

German silver can be readily soldered, the alloy used for this purpose being made more fusible than the German silver by having a larger proportion of zinc. The usual composition of German silver solder is: Copper 47 per cent., nickel 11 per cent., and zinc 42 per cent.

Phosphor-copper.

Copper and phosphorus combine very readily with the formation of a definite chemical compound corresponding to the formula Cu_3P . It has a bluish-grey metallic lustre, is very hard, and brittle enough to be easily reduced to powder. It forms with copper a simple series of alloys with a eutectic containing 10 per cent. of copper and melting at 704°C . Commercial phosphor-copper occurs in two varieties—one containing 15 per cent. of phosphorus, which is practically the compound Cu_3P ; and the other containing 10 per cent. of phosphorus, corresponding to the eutectic. Both these phosphor coppers are exceedingly brittle;

this is a great advantage, as their sole use is that of a deoxidiser to be added to copper and copper alloys. A brittle substance which can be broken into small lumps or powdered, possesses obvious advantages when exact quantities have to be weighed out.

Phosphor-copper is made either by passing the vapour of phosphorus over heated copper, or, more readily, by adding phosphorus to molten copper. A convenient device for effecting the combination is shown on p. 151.

Cupro-silicon.

The alloys of copper and silicon, like those of copper and phosphorus, are used purely as deoxidisers in the manufacture of copper alloys. Commercial cupro-silicon is made in the electric furnace, and contains as much as 50 per cent. of silicon; but the alloys most generally used do not contain more than 35 per cent. These alloys are extremely brittle.

According to Guillet the alloys containing less than 7 per cent. of silicon consist of solid solutions; but beyond this point there is a eutectic which melts at about 800°.

Copper containing a small quantity of silicon, not exceeding 0.1 per cent., is much stronger than pure copper, and has been largely used for the manufacture of telegraph and telephone wires. For this purpose silicon is much better than phosphorus as a hardening agent for copper, the conductivity of the wire being considerably higher. The addition of phosphorus to copper is accompanied by a very marked increase in its electrical resistance.

Copper containing a small percentage of silicon has also been successfully used as a material for firebox plates.

Cupro-manganese.

Reference has already been made to the alloys of copper and manganese in connection with the manufacture of manganese-bronzes and brasses. The commercial alloys contain about 30 per cent. of manganese and sometimes from 2 to 4 per cent. of iron, and they appear to be homogeneous solid solutions of manganese in copper. They are principally used in the manufacture of the

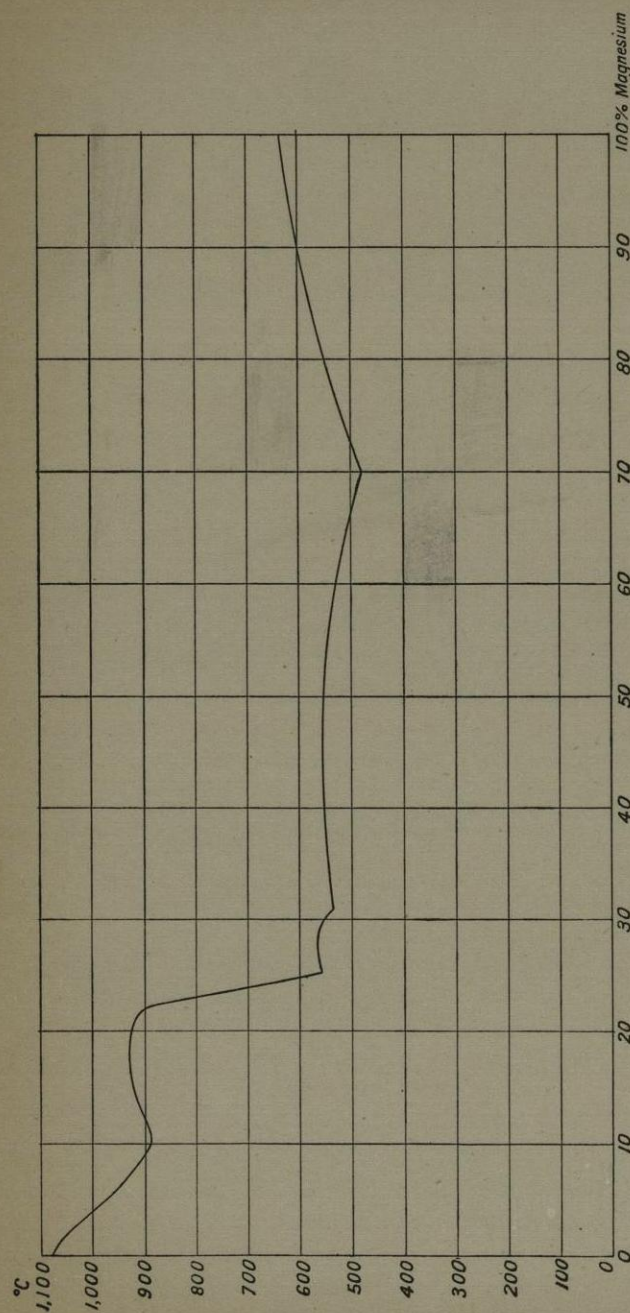


FIG. 40.—Freezing-point Curve of Copper-magnesium Alloys.

CHAPTER XI.

WHITE METAL ALLOYS—LEAD, TIN, AND ANTIMONY.

THE alloys of these metals are very largely employed in the industrial world, and are usually met with under the name of "white-metal." The term is applied indiscriminately to any of the alloys, whether composed of only two of the metals or all three together; but, as each series of alloys has its distinct uses, it will simplify matters to deal first with the three possible series of binary alloys—viz. lead-tin, lead-antimony, and tin-antimony—and then with the triple alloys.

Alloys of Lead and Tin.—These metals do not form compounds or solid solutions, but mix in all proportions, thus forming the simplest series of binary alloys. The freezing-point curve of the series has already been referred to, and it is only necessary to repeat that the eutectic contains 37 per cent. of lead, and melts at 180°. On either side of this point the alloys consist of one or other of the metals surrounded by the eutectic. The percentage of tin in the cast alloys can be roughly estimated by the appearance of the surface. Those rich in lead possess the dull bluish colour characteristic of that metal; while the alloys rich in tin have a white surface, which has a slight yellow superficial deposit of oxide of tin. The alloys containing more than 25 per cent. of lead will leave a mark when drawn across paper.

The alloys of lead and tin are used principally in the manufacture of solders, toys and cheap jewellery, and pewter.

Solders are very variable in composition according to the quality of the metal to be soldered. Those rich in tin are, of course, the most valuable, and the alloys are known, according to the amount of tin they contain, as "common," "medium," and "best."

For soldering tin and alloys rich in tin a solder rich in tin must be employed; while for lead and alloys rich in lead a solder rich in lead is used. Probably the alloy most commonly employed is that containing 66 per cent. of lead and 34 per cent. of tin, or two parts lead to one of tin.

The suitability of the alloys of lead and tin for soldering is dependent on the fact that these metals do not form compounds or solid solutions, and, in consequence, almost the entire series of alloys is composed of a metal and a eutectic mixture: at temperatures lying between the melting-points of these two the alloy is only partly solid, or in the pasty condition which enables it to be easily applied in soldering. Thus, in the case of the alloy referred to above containing 66 per cent. of lead, there is a range of temperature of 60° during which the alloy is in a pasty condition. The eutectic itself and the alloys in its immediate neighbourhood are not suitable for solders; but they solidify with an exceedingly bright surface, and have been used for making imitation jewels, sometimes known as Fahlum brilliants, for stage purposes. The eutectic alloy is cast in moulds with facets resembling the cutting of diamonds. Alloys rich in lead are used for making toys such as lead soldiers, etc. These, however, contain very little tin—seldom more than 4 or 5 per cent.

The best known of the lead-tin alloys is that commonly known as pewter. This alloy is largely used, and its composition varies considerably. When intended for the manufacture of drinking-vessels it is essential that the alloy should be rich in tin. This is evident from the consideration of the constitution of these alloys, for those containing more than 37 per cent. of lead (that is to say, more lead than is sufficient to form the eutectic of the series) will contain free lead in a form readily corroded and dissolved by acid liquids. In order to avoid risk of lead-poisoning, therefore, pewter should contain at least 63 per cent. of tin, and in France the law prohibits the use of pewter containing more than 18 per cent. of lead for drinking-vessels.

A large quantity of pewter is used in the arts. For this purpose the composition may be altered to suit the requirements of the work. Copper in small quantities is a frequent constituent of pewter. It produces a harder alloy, but, if present in more than

small quantities, has an injurious effect upon the colour of the pewter.

Lead and Antimony.—As in the case of the lead-tin alloys, these metals do not form compounds or solid solutions, but produce a simple series of alloys with a eutectic containing 13 per cent. of antimony and melting at 228°. On one side of this point the alloys consist of lead embedded in eutectic, and, on the other side, antimony embedded in eutectic. The useful alloys of lead and antimony are somewhat limited; those consisting principally of lead with small amounts of antimony, introduced as a hardening agent, being the most useful. An alloy, however, containing 67 per cent. of lead and 33 per cent. of antimony is occasionally met with, and is used in making the keys of wooden wind instruments. Antifriction metals consisting of lead and antimony are still sometimes met with, but these have been superseded by the more efficient triple alloys.

Lead containing antimony up to about 4 per cent. is largely used in the manufacture of the framework of accumulator plates, as the alloy is stronger than pure lead, less liable to buckle, and cheaper. Antimonial lead is also used in the manufacture of shot and bullets.

With the addition of small quantities of other metals the alloys of lead and antimony are extensively used as type-metal. The essential requirements of a good type-metal are: (1) that it shall give good, sharp castings; and (2) that it shall be sufficiently strong to withstand the necessary wear and pressure without losing its form. The first of these requirements is fulfilled by the alloys containing not more than 15 per cent. of antimony, which possess the property of expanding on cooling; but they are not strong enough to stand hard wear. In order to increase the strength of these alloys a certain quantity of tin is added, which forms a hard compound corresponding to the formula SnSb; and this compound crystallising out in the soft alloy has the effect of considerably increasing the compressive strength of the mass, without otherwise altering the character of the alloy. The composition of type-metal varies considerably. An alloy containing lead 50, tin 25, and antimony 25 is said to give the best results for high-class work; but the price of such an alloy is too high on account of the tin it contains, and a more usual

composition is approximately lead 60, antimony 30, and tin 10 or even less. Plates for music engraving of somewhat similar composition are used abroad, but in this country the best music printing is done on pewter plates.

Alloys of lead and antimony are frequently used in the construction of pumps required for dealing with corrosive liquids, and, as it is important to know the strength of these alloys, Prof. Goodman has made a number of very complete determinations. The alloys selected had the following compositions:—

Number.	Antimony.	Lead.	Tin.
1	10	90	...
2	13	87	...
3	15	85	...
4	15	80	5

and the tests were carried out with the object of determining—

- (1) The tensile strength and elasticity.
- (2) The compressive strength and elasticity.
- (3) The crushing strength.
- (4) The bending strength.
- (5) The shearing strength.

The results of these tests are given in the tables on p. 186.

Tin and Antimony.—These metals give rise to an extremely interesting but considerably more complex series of alloys than those just considered. The freezing-point curve, as determined by Reinders, indicates that the alloys containing antimony up to 10 per cent. consist of tin and a eutectic; but beyond 10 per cent. the characteristic cubical crystals of the compound SnSb make their appearance, and when 50 per cent. is reached the alloy becomes homogeneous and consists entirely of this compound. With more than 50 per cent. of antimony neither a eutectic nor a new constituent makes its appearance; but the crystals gradually change their form and become more and more like those of antimony. Evidently, then, this is a case of a compound being isomorphous with a pure metal; and this fact accounts for the abnormal freezing-point curve, which apparently fails to indicate the existence of a compound. The conductivity

Number.	Diameter in Inches.	Sectional Area in Sq. In.	Elastic Limit in Tons per Sq. In.		Maximum Stress in Tons per Sq. In.		Young's Modulus of Elasticity. Tons per Sq. In.		Reduction in Area per cent.	Extension per cent. on 10 in.
			Tension.	Compression.	Tension.	Compression.	Tension.	Compression.		
1	2.248	3.969	...	1.39	1740
	1.489	1.741	0.93	...	3.14	...	1700	...	1.3	0.4
	1.510	1.791	1	...	3.32	...	1690	...	1.7	1.1
	2	3.141	7.98
	2	3.141	7.20
2	2.246	3.962	...	1.0	1800
	1.490	1.744	0.95	...	3.28	...	1780	...	3.7	2.5
	1.503	1.774	0.90	...	3.10	...	1690	Broke in shoulder	...	1.3
	1.998	3.135	7.12
	1.999	3.138	7.31
3	2.245	3.958	...	1.07	1820
	1.510	1.790	0.92	...	2.71	...	1750	...	2.4	0.9
	1.508	1.786	0.92	...	3.07	...	1680	Broke in shoulder	...	1.4
	2	3.141	7.49
	2	3.141	7.49
4	2.245	3.958	...	1.01	1890
	1.497	1.760	0.80	...	2.27	...	1830	Broke in shoulder
	1.496	1.758	0.83	...	2.80	...	1660	Ditto	...	0.5
	2	3.141	7.00
	2	3.141	6.95

Number.	Breadth of Section in Inches.	Height of Section in Inches.	Breaking Load in Tons.	Modulus of Rupture in Tons per sq. in.	Final Deflection in Middle of Beam.	Shearing Strength in Tons per sq. in.	Ratio of Shearing Strength to Tensile Strength.
	b.	h.	W.	fm.	In.	fs.	
1	1.018	2.039	1.25	5.31	0.125	2.29	0.71
	1.025	2.030	1.25	5.33	0.143	2.28	
2	1.016	2.047	1.19	5.02	0.095	2.14	0.68
	1.005	2.042	1.18	5.07	0.134	2.18	
3	1.012	2.047	1.11	4.72	0.116	2.18	0.75
	1.025	2.047	1.09	4.58	0.117	2.16	
4	1.020	2.045	1.12	5.11	0.085	1.95	0.76
	1.025	2.045	1.09	4.59	0.075	1.92	

of the alloys (as determined by Matthiessen) and the electro-motive force of solution (as determined by Laurie) also fail to indicate the existence of a compound for the same reason.

The alloys of tin and antimony together with small quantities of other metals constitute the class of alloys known under the name of **Britannia metal**. The following table shows the composition of a number of these alloys:—

Alloy.	Tin.	Anti-mony.	Copper.	Zinc.	Bismuth.	Lead.	Other Metals.
Britannia metal (Eng.)	94	5	1
"	90	6	2	...	2
"	90	7	3
"	89.3	7	1.8	1.8	...
"	85.5	9.7	1.8	3.0
"	75.0	8.5	8.0	8.5	...
" (sheet)	90.6	7.8	1.5
" (cast)	90.6	9.2	0.2
Queen's metal	88.5	7.1	3.5	0.9
"	88.5	7.0	3.5	...	1
Ashberry metal	80	14	2	1	3
"	79	15	3	2	1
Minofor	68.5	18.2	3.3	10
German metal	72	24	4
"	84	9	2	5
"	20	64	10	6

The presence of copper in Britannia metal produces a harder and less ductile alloy and has an injurious effect upon the colour, if present in more than small quantities. Zinc and iron also increase the hardness and brittleness of the alloy, and are not desirable constituents. Lead, on the other hand, may be added with advantage where a very fluid metal is required for casting; but the amount added should be small, if the colour of Britannia metal is to be retained.

In all these alloys the antimony has the effect of hardening the tin, so that it is more easily worked and takes a finer polish. The best castings are obtained from brass moulds previously heated and coated with lamp-black. Britannia metal is extensively used in the manufacture of such articles as tea- and coffee-pots, mugs, etc., and also for taps.

The triple alloys of lead, tin, and antimony are largely used as antifricition alloys, and will be considered under that heading.