XLII.—*On Silver containing Bismuth.*

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THE experiments recorded in this paper were made with the object of determining the effects produced by the presence of small quantities of bismuth on the ductility of silver, and on the uniformity of composition of silver bullion.

The silver bullion received in the Imperial Mint from certain Japanese mines and refineries, is occasionally found to be possessed of extraordinary brittleness. On melting this silver with its surface uncovered, and removing the slag formed from time to time, the brittleness disappears, a more or less prolonged exposure of the molten metal to the oxidising action of the air being required, according to the extent of the brittleness. On examining the slags formed during the early stages of the melting, they are found to consist chiefly of litharge, bismuthous oxide being present in but small amounts. As the oxidation proceeds the bismuthous oxide increases in quantity, until at the end of the process, when the silver has become tough, the slags are richly bismuthiferous. Every lot of brittle silver of high fineness which has been received during many years has been so melted and toughened, in some cases potassium nitrate being used to hasten the operation. The slags have been for some time frequently examined, and have always been found to contain bismuth but no other metals in proportions likely to cause brittleness. Arsenic and antimony have been repeatedly sought for, but have never been found in appreciable quantities.

An ingot weighing 651·24 troy oz. (20·2558 kilos.), which was brittle to an extraordinary degree—so much so that it broke into halves whilst a small cutting was being taken for assay from one edge of its base—was analysed, and found to be of the following composition :—

Silver	98·100
Gold	0·015
Bismuth	0·756
Lead	0·857
Copper	0·058
Iron	0·022
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	99·808

The amount of lead present in this example might perhaps have been partially the cause of the brittleness, hence in order to demonstrate that bismuth alone is capable of inducing this property in silver, the following synthetical experiments were made.

Pure silver was melted with bismuth in the following proportions:—

	I.	II.
Silver....	6.41 grams = 99 p. c.	6.45 grams = 99.5 p. c.
Bismuth .	0.06 „ = 1 „	0.03 „ = 0.5 „

The melting was carefully performed under charcoal in small clay crucibles, and well melted buttons were obtained. The buttons in both cases were brittle, and were broken easily in a vice, without being first cut or nicked with a chisel. Their fractures were similar, dull, and minutely crystalline. When hammered or rolled, both alloys behaved in the same way. On hammering a piece, it cracked much at the edges, but on rolling, although at first the edges cracked, yet on cutting off the cracked portions and rolling further, the metal became slightly ductile.

On obtaining these results, another alloy was prepared. 194.4 grams of pure silver were melted with 2.98 grams of bismuth, giving a millesimal composition of silver, 984.89, bismuth 15.11, the silver being first melted under charcoal, and the bismuth added to the molten silver. After careful stirring the metal was poured into a small iron bar mould, yielding a bar measuring 82 mm. long, 44.5 mm. broad, and 6.3 mm. thick.

The bar was nicked slightly on the line AB (Fig. *a*), and broken in a vice. It broke easily, with a short, dull, minutely crystalline fracture.

FIG. *a*.

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The longer portion was then rolled to a thickness of 2.5 mm., when it cracked too much for further rolling, the chief cracks extending very nearly to the middle of the strip, and minute cracks covering its entire surface. Assays were made of cuttings from several points in the rolled strip, in order to ascertain whether the bismuth had concentrated in any part during solidification. The results of the assays are given in Fig. *b*. From these it will be seen that there is slight concentration of silver in the middle of the bar.

FIG. *b*.

984.5	9850 984.7	984.3
984.9	984.8 985.1	985.2
984.3	984.6 984.7	984.2

But as in such a small bar solidification must have taken place with great rapidity, and as different results may follow with larger masses under conditions of slower cooling, it was deemed advisable to operate on a larger scale, and to determine the effect exercised by the presence of small quantities of bismuth on the uniformity of the composition of silver bullion when in ingots of the size and form ordinarily met with in commerce. Also at the same time to ascertain from which part of an ingot an assay cutting should be taken so as to most accurately represent its mass.

To this end 1030.01 troy oz. (32.0369 kilos.) of silver were melted with 15.50 troy oz. (0.4821 kilo.) of bismuth, under the conditions and in the manner described below.

The silver consisted of two ingots, which assayed respectively 999.1 and 999.2 millesimal fineness.

The bismuth was the pure refined metal of commerce. It was found to contain only traces of gold, copper, nickel, and lead, and 1.8 per mille of silver.

The plumbago crucibles, covers, and stirrers were new.

The weight and composition of the charge were as follow:—

Ingot of silver	418.83 troy oz. (13.02707 kilos.),	999.1 fineness.
" "	611.18 " (19.00983 "),	999.2 "
Bismuth	15.50 " (0.4821 ")	containing 1.1 per mille of silver.

INGOT OF SILVER CONTAINING BISMUTH.

WEIGHT 1037.4 TROY Oz.=32.2668 KILOGRAMS.

SCALE $\frac{1}{4}$.

FIG. 1.

FIG. 2. SECTION A. B. C. D.

FIG. 3. SECTION E. F. G. H.

COMPOSITION OF GRANULATED DIP 985.5.

The theoretical millesimal composition being—

Silver	984.37
Bismuth	14.80

The ingots of silver were melted under charcoal in a plumbago crucible, the bismuth, in small pieces, was added as soon as the silver was fluid, and thoroughly mixed with it by vigorous stirring with a plumbago stirrer. The crucible was then removed from the furnace, and its contents poured into an ordinary open iron ingot mould of rather more than 1000 oz. (31.103 kilos.) capacity. The ingot obtained measured 30.47 cm. long, 11.3 cm. broad at the top, 10.6 cm. at the bottom, and 10.1 cm. thick. Its upper surface was marked with transverse furrows, resembling in this respect the surface of ingots of refined copper. A narrow depression, about 17 mm. deep at its deepest part, extended along the middle portion of its median line. The ingot, after being cooled in water, was placed with its ends only resting on two iron blocks. On being then struck with a sledge-hammer, it broke after a few blows into two nearly equal pieces. The fractured surfaces showed a coarse crystallo-granular structure near their central parts, gradually becoming more and more largely crystalline towards the outer sides, where elongated columnar crystals extended inwards to a depth of 16 mm. from and at right angles to the cooling surfaces. There was a small cavity near the middle of the top of the ingot, just below the central depression, with crystals of the form of a four-sided pyramid with isosceles faces, the upper halves of distorted octahedra, projecting from its sides.

To ensure thorough admixture of the bismuth with the silver, the metal was again carefully melted and stirred, a new crucible and stirrer being used. A small quantity was dipped out and granulated in water for assay, and the metal was poured as before into the same mould.

The ingot weighed 1037.40 troy oz. (32.2667 kilos.). Portions of metal were taken from several parts, viz., one from each corner and three from each long edge of its base, and one from each corner and from each long edge of its top. On account of its great brittleness these could not be cut off in the usual way, as a single blow of the hammer caused the chisel to break off large and irregular lumps. Pieces of approximately equal size were obtained after some difficulty, and were assayed with the results shown in Fig. 1* in the plate. The numbers there given are the means of duplicate or triplicate assays made by a modification of the Gay-Lussac volumetric process.

* In this plate the figures 98 are usually omitted in stating the fineness; 5.3, for instance, meaning 985.3.

The granules taken as previously mentioned, and which hence represent the mass in composition, assayed 985.5 silver per mille. None of the parts assayed in Fig. 1 reach this fineness, yet from one or other of these it is customary to find assay pieces cut from ingots of bullion for their valuation. The mass is thus slightly richer in silver than an assay made from an ordinary cutting would indicate.

Hence, in silver—even of comparatively high fineness—suspected to contain bismuth, the portion required for assay should be taken from the metal whilst melted, and be granulated in water. Should it be impossible to melt the bullion, an assay piece cut from the middle of one of the long edges of the bottom of the ingot will give results approximating to its average composition. A bright brown resinous-like coating—bismuthiferous litharge—on cakes of silver from Japanese cupellation hearths, quite distinct in appearance from ordinary litharge, is an almost invariable indication of the presence of bismuth in injurious quantities.

A plate, A, B, C, D, Figs. 1 and 2, about 8 mm. in thickness, was then cut out transversely through the middle of the ingot by a slotting machine, and a similar plate, E, F, G, H, Figs. 1 and 3, longitudinally from the middle of one of the halves. Portions approximately in the form of cubes were taken from the points in these plates, shown in Figs. 2 and 3, and were assayed with the results there given.

All the pieces were brittle. Those from the sides and upper surfaces appeared to consist of an interlacing mass of loosely agglomerating columnar crystals which singly were ductile when hammered.

At the point F, Figs. 1 and 3 of the upper surface, just above a cavity containing crystals, the composition is extremely irregular. Disregarding this part, the difference between the two points of highest and lowest fineness, viz., 988.3 and 984.6, amounts to 3.7 per mille.

It will be seen from Figs. 1 and 2 that concentration of silver occurs generally throughout the internal portions of the upper two-thirds of the ingot, that is, in those parts which remained longest fluid, and notably along the median line of the upper surface. The ductility of the metal when rolled was tested in the following manner:—

A plate, measuring 90 mm. long, 33 mm. broad, and 8 mm. thick, was cut from one of the remaining parts of section E, F, G, H, Fig. 3; this was annealed at a dull red heat in an assay muffle, and then rolled. Soon after the commencement of the rolling, the edges became deeply jagged with cracks, but on continuing to roll these extended but little further inwards, and the metal was rolled down to a thickness of 0.5 mm. without destroying the continuity of the central portion.

This portion had in fact become ductile through the mechanical treatment, and could be bent almost completely over without fracture. It would thus appear that when the crystalline structure is once broken down ductility ensues. Hence the brittleness of silver containing bismuth is probably due to the crystalline structure which the presence of that metal induces in it.

Experiments were also made to ascertain the effect of bismuth on the ductility of silver coinage bars of 900 standard. A portion of the metal from the preceding experiments, weighing 370.72 oz. (11.5307 kilos.) was melted with the necessary quantity of electrottype copper, and cast into four bars, each measuring 58 cm. long, 4.35 cm. broad, and 1.25 cm. thick.

A portion taken from the molten metal, and granulated in water, assayed 899.6 silver per mille. One of the bars was slightly nicked with a chisel on one of its surfaces transversely 13 cm. from its upper and similarly 9 cm. from its lower extremity. At both points the bar broke at once on being struck with a heavy hammer. The fractured surfaces of both parts were somewhat conchoidal, dull, and non-crystalline. A bar of the same size and fineness prepared with refined silver, was similarly treated for comparison; it was broken with great difficulty, and bent to an angle of 30° before fracture. Its fractured surfaces were hackly. They were notably different in colour from those of the alloy containing bismuth, being white with only a faint fawn-coloured tinge, whilst in the latter they were distinctly reddish-fawn-coloured.

An attempt was made to roll the middle portion of the bismuthiferous bar, 31 cm. long, but it split before it was reduced to 9.5 mm. Two of the other bars split similarly, and could not be rolled. The fourth bar was then previously annealed, and after this treatment it was successfully rolled to 4.5 mm., again annealed, and then rolled to a thickness of 2.26 mm. without showing the slightest trace of cracks even at the edges. Three additional bars were prepared, and annealed, and rolled as the last, two rolled well and one broke; but the metal in all cases was hard and unsuitable for mintage.

The bismuthiferous silver which reaches the mint has been traced to three localities, viz.: Ikuno, in the province of Tajima; Odomi, in Hida; and Ani, in Ugo; at all of which it is obtained from argentiferous copper. At the Ikuno mine, according to Professor Milne, native bismuth has been found occasionally. At the others, no species of bismuth mineral has yet been identified. The copper produced at these mines contains small quantities of silver, generally sufficient to be worth extracting by liquation with lead. Any bismuth which may be present in the copper subjected to the liquation process is removed from it, together with the silver, by the lead. When the argentiferous

lead is subsequently treated on cupellation hearths for the separation of the silver, part of the bismuth remains in the silver obtained.

A similar occurrence of bismuth in silver is mentioned by Dr. Percy (*Metallurgy of Lead*, pp. 201 and 202).

Summary.

α. When silver is obtained from copper containing bismuth by the liquation process with subsequent cupellation of the argentiferous lead, it contains part of the bismuth which was present in the copper.

β. This silver is brittle even when containing only small amounts of bismuth.

γ. Ingots of such silver are not uniform in composition throughout their mass, the parts which have remained longest fluid being richer in silver than the others.

δ. When coinage bars of 900 millesimal fineness are prepared with it, they cannot be rolled without special treatment, and even then are hard and unsuitable for mintage.

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