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X.—*On the Effects produced by Small Quantities of Bismuth on the Ductility of Silver.*—*By* Surgeon-Major J. Scully, *Assay Master, Calcutta.*

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It is well known that alloys of silver and bismuth, in certain proportions, are brittle. In Dr. Percy's valuable work on Metallurgy (Silver and Gold—Part I), it is stated that alloys of silver with bismuth, in the proportion of 50 per cent. and 33 per cent. of the latter metal, are brittle ; while an ore of silver and bismuth, called Chilenite, in which bismuth occurs only to the extent of 14·4 to 15·3 per cent., is said to be malleable. The least amount of bismuth, however, which will injuriously affect the ductility of silver, for example, in such an operation as the lamination of silver bars for coinage, does not, so far as I am aware, appear to have been experimentally investigated. It may here be mentioned at the outset that an alloy of silver and bismuth may, by careful hammering, be extended considerably, so as to pass muster as malleable ; although, if subjected to lamination by means of steel rolls, the same alloy will crack at the edges and thus show a deficient ductility, as compared with pure silver or some silver-copper alloys. It is to the deficiency in ductility, as tested by rolling, of silver containing only very small proportions of bismuth that I here wish to call attention.

My attention was first prominently directed, about two years ago, to the injurious effects caused by small quantities of bismuth in silver by

the circumstance that some silver bullion, in the shape of English refined bars of as high a fineness as 990 per mille, proved so brittle as to be unfit for mintage. Attention was first attracted to this matter by the peculiar behaviour under assay of the granulated samples taken from this silver after melting. The appearances noticed under assay will be referred to presently, but they led to the bullion being at once tested for brittleness. A bar, about 21 inches long, 2·25 broad, and 1 inch thick, was hammered out at one end without cracking, but on being passed through the rolls it cracked badly at the edges and was pronounced to be "brittle," in the Mint sense of the term. The bullion was then remelted in five plumbago pots, and a partial refinement of it attempted in the ordinary way with nitre, about eight to ten pounds of this salt being used for each pot. The resulting silver bars were not appreciably improved by this treatment; hammering again proved an inconclusive test, but a bar of the size I have mentioned broke in two by merely dropping on the floor of the melting room.

In the meantime the assay had shown that the brittle bullion contained bismuth, and that this was the only substance present likely to be the cause of brittleness. The Indian process of assaying silver has been described by Dr. Busteed in the Journal of the Asiatic Society of Bengal (1870, Part II. p. 377); and a brief abstract of this paper is given on p. 292 of Dr. Percy's work before mentioned. The main features of the process may here be briefly recapitulated for the purpose I have in view. A fixed weight of the silver bullion to be assayed is dissolved in an assay bottle, by means of nitric acid aided by heat; the solution is diluted with water and an *excess* of hydrochloric acid is added, to precipitate all the silver present as chloride. The silver chloride having been caused to aggregate and settle by vigorous shaking, the bottle is filled up with water and the supernatant fluid is subsequently syphoned off, to remove all the now dissolved matter which may have been contained in the bullion. Under these conditions of solution, precipitation and dilution with water, chemists will readily understand that even a small trace of bismuth, if it be in the silver, will reveal its presence by the partial formation of insoluble oxychloride of bismuth. Now, in the assay of the brittle bullion under consideration, solution in nitric acid had been readily and completely effected by the aid of heat: antimony and tin were consequently absent. After the addition of water and hydrochloric acid, however, the solution in the assay bottles could not be cleared by shaking; the bulk of the silver chloride collected at the bottom of the bottles, but the supernatant fluid remained turbid. Tin and antimony being excluded, only two metals could produce this result in the wet assay of silver, namely, mercury and bismuth. To

determine which of these is the interfering metal it is only necessary to note the effect of solar light on the silver chloride formed; when mercury is present the silver chloride maintains its pure white colour unaltered, while in the presence of bismuth the chloride immediately acquires the well known purple colour under the influence of daylight. Our assays, then, being turbid after precipitation and yet the silver chloride blackening readily under the influence of daylight, it was evident that bismuth was present. The turbidity produced was due to the partial formation of bismuth oxychloride; and this compound diffusing itself in its characteristic manner through the solution had broken up part of the silver salt into very fine powder, so that some hours had to elapse before the supernatant fluid cleared by the gradual subsidence of both bismuth oxychloride and the finely divided silver chloride. The assay was of course thus rendered unreliable, since the silver chloride to be weighed, and on which the calculation of the fineness rested, was contaminated with bismuth oxychloride. A cupellation assay of this bullion was at once had recourse to for ascertaining its fineness.

So far, then, this tender of silver bullion seemed to establish the following points:—

1. Silver bullion of as high fineness as 990 per mille is rendered unfit for coinage purposes by an amount of bismuth which, in this particular case, could not possibly have exceeded 1 *per cent.*, and was probably less than that proportion.

2. Hammering a bar of silver bullion is not a good test for detecting brittleness, as far as mint purposes are concerned.

3. The toughening of silver bullion 990 fine, and containing only a small amount of bismuth, by the aid of nitre in plumbago melting pots, is not readily effected.

4. The presence of a trace of bismuth in silver of high fineness is immediately detected in the ordinary course of assay by the Indian method, but this bismuth interferes with the perfect accuracy of the results obtained by that process.

A comprehensive research seemed therefore called for to elucidate the whole subject, and the necessity for this investigation has since been emphasized by the fact that silver bullion contaminated with bismuth has frequently found its way to the Mint since its first discovery here. The points to be investigated seemed naturally to group themselves under the following heads:—

I. Is our ordinary wet assay of silver susceptible of such easy modification as will enable us to obtain perfectly accurate results by it, in presence of bismuth, without having recourse to the confessedly less accurate assay by cupellation? And, how may small quantities of bis-

muth in silver be readily estimated with the despatch indispensable for mint operations ?

II. What is the smallest amount of bismuth in silver that will render it unfit for coinage, when present in bars of the Indian standard fineness of 916·6 ? And, what is the amount of bismuth that may be tolerated in such bars without materially injuring their ductility ?

III. How is silver bullion containing bismuth which may be tendered to the Mint, to be dealt with, supposing that establishment accepts any metal that is brittle ; and how is the presence of bismuth in refined bars to be accounted for ?

I. As the purity of the bismuth to be used in the experiments now to be detailed was a matter of first importance, I may briefly mention the steps taken to ensure the purity of the metal. Refined bismuth was dissolved in nitric acid, precipitated as basic nitrate by diluting largely with distilled water, the nitrate digested in solution of caustic potash, and then well washed, dried, and reduced by heating with charcoal in a clay crucible. A series of synthetical assays, made by dissolving together pure silver and pure bismuth, the latter in the proportion of from 1 to 5 millièmes, showed that our ordinary process of assay, under such conditions, gave unreliable results, there being a surcharge, or higher report than should have been obtained, which varied from 0·7 to 2·7 mill. when the proportion of bismuth was from 3 to 5 millièmes. A modification in our process of assay was evidently required if it were to be used for determining the fineness of silver bullion containing bismuth ; and the necessary steps to this end were, after repeated experiment, found to consist in adding the smallest possible amount of hydrochloric acid for the precipitation of the silver, and increasing the amount of nitric acid in which it was first dissolved. We use ordinarily for the precipitation of an assay pound of silver 5·4 cc. of hydrochloric acid of sp. gr. 1075, but 2·5 cc. of acid of this strength suffices for the complete precipitation of an assay pound of even fine silver ; so that we have here at once a means of diminishing the tendency of any bismuth in the silver to form insoluble oxychloride. If in addition to diminishing the amount of hydrochloric acid we added a considerable excess of nitric acid to the solution (which acid would not in any way interfere with the silver chloride formed), all risk of the partial formation of insoluble bismuth salts seemed removed. This in fact has proved to be the case, and the successful modified process for the assay of silver containing bismuth is as follows :—

The assay pound of silver bullion containing bismuth is dissolved in 5·5 cc. of nitric acid, sp. gr. 1200, with the aid of heat, about 5 ounces of water are added and then 10 cc. of nitric acid sp. gr. 1320. The silver

is now precipitated by the addition of 2·5 cc. of hydrochloric acid, and after vigorous shaking the supernatant fluid will be found perfectly clear; and it will remain so when the bottle is filled up with water, all the bismuth present being in solution. Whenever samples of silver now show the presence of bismuth during the assay, a fresh set is taken up and worked by the modified process, the delay thus caused not amounting to more than a few minutes. It may be mentioned here that all our assays are reported to one-tenth of a millième (0·1 per mille).

Having thus ascertained the presence of bismuth in silver bullion and put in practice a modification of the assay process which renders us indifferent to its presence, it is still of importance to ascertain the exact proportion of bismuth which is present in the bullion; and, to be of practical use for mint work, this determination must be effected rapidly and as simply as possible. The ordinary directions given for the separation of bismuth in the presence of silver, by first removing the latter as chloride and then precipitating the bismuth as carbonate, do not, I find, give accurate results when silver is present in such overwhelming proportions as obtain in the cases under consideration.

I have therefore adopted the following plan, which a number of synthetically prepared solutions have proved to give quick and good results, though sometimes the amount of bismuth present is very slightly under-estimated. The ordinary silver assay having given a rough visual estimate of the amount of bismuth likely to be present, enough of the bullion is taken to yield a fairly weighable amount of bismuth oxide in the final result. The bullion is dissolved in a small amount of nitric acid, the solution carefully diluted, and an excess of ammonium carbonate at once added, the precipitation being aided by heating. The carbonates of silver and copper at first formed are re-dissolved, and the carbonate of bismuth after a time settles completely at the bottom of the beaker. The contents of the beaker are then passed through a filter, of which the weight of ash yielded by incineration is known, and the carbonate of bismuth on the filter washed quite free of all traces of silver. The filter is then dried, its contents transferred to a porcelain crucible for ignition, the filter paper being ignited separately, treated with a drop or two of nitric acid to re-oxidise any bismuth oxide reduced by contact with the carbon of the filter, and the ash added to the crucible. From the weight of bismuth oxide thus found, after deducting the weight of the filter ash, the amount of metallic bismuth present in the sample of bullion taken for analysis can be at once found.

There are only two metals likely to interfere with accuracy of the process here described, namely, cadmium and lead; the carbonates of both these metals being as insoluble in excess of the precipitant employed as

bismuth carbonate. Cadmium is very unlikely to be found in silver bullion and its consideration may be neglected, but if the presence of lead is suspected the carbonate filtered from the silver solution is dissolved in nitric acid, evaporated down with the addition of sulphuric acid, and the lead sulphate formed (if any) collected and weighed in the usual way. The bismuth is again precipitated as carbonate and treated as before directed. Many experiments have been made with synthetically prepared mixtures of silver, copper, lead, and bismuth, the latter two metals being in very small proportion to the silver, so as to imitate the composition of some refined bars. Ullgreen's plan for the separation of the carbonates of lead and bismuth, by dissolving them in acetic acid and then precipitating the bismuth by means of a lead rod, does not work satisfactorily and requires too long a time for the precipitation.

II. As it seemed likely that a large number of experiments would be required to determine accurately the smallest amount of bismuth that would injure the ductility of our coinage alloy, and the still smaller proportion that would not sensibly affect this ductility, it was determined to begin the enquiry by a number of laboratory experiments on small bars of silver; before trying the effects of bismuth on ordinary coinage bars and with the procedure for lamination carried out in the Mint. These laboratory experiments were made in the following way: Pure silver prepared for assay check purposes, or an alloy of silver and copper of which the exact composition had been determined by assay, was melted in a clean plumbago crucible under charcoal. When the metal was in fusion the necessary amount of bismuth was rolled in a piece of paper, carried down at once to the bottom of the silver bath, and then thoroughly mixed with the silver by stirring. The calculated composition was confirmed by assay of the silver. When this mixture had been accomplished, the contents of the crucible were poured into an open iron ingot mould, and after cooling, either quickly by plunging the casting into water or slowly in contact with the mould, the bar so cast was tested for brittleness by hammering and rolling. The bars cast were of two sizes, one set being 3·75 inches long, 1·125 broad, 0·375 thick and weighing about 6·2 troy oz.; and another set 2·69 inches long, 1·125 broad, 0·25 thick and weighing about 4·1 troy oz. When reduced to the fullest extent by rolling, these bars were converted into straps about 0·015 in thickness. In laminating them they were twice annealed, first after having undergone four pinches in the rollers, and again after the tenth pinch from the beginning Similarly shaped bars of silver, without bismuth, were occasionally laminated in the same way to obtain a sure means of comparison. Before any result was accepted as to brittleness or its absence, the bar under

experiment was always remelted and tried at least a second time. The number of experiments in this series amounted to *fifty-three*, and the following is a summary of the results obtained.

Fine silver when alloyed with only 1 per mille (one thousandth part of its weight) of bismuth, and the casting rapidly cooled by plunging it into water as soon as it has set, has its ductility, as tested by lamination, sensibly but slightly impaired, the straps resulting from rolling having slightly jagged edges. When the proportion of bismuth is increased to 2, 3, 4 and 5 per mille, the plan of cooling remaining the same, the raggedness of the edges of the straps was somewhat increased but not very markedly. If, however, the casting was allowed to cool down completely, but very slowly, in contact either with the mould or a stone floor, the results were very different. Under this condition of cooling, a bar composed of fine silver with 4 per mille of bismuth was completely brittle; it was readily broken and its fracture was strongly crystalline. On laminating it, small cracks appeared all over the surface on the second pinch, the bar emitting a crackling sound under the rolls, much like the " cry " of tin, and on the 4th pinch the bar cracked deeply at the edges. This remarkable effect on the molecular structure of this alloy of silver and bismuth, as due solely to the mode of cooling the casting, was repeatedly verified on the same metal by remelting and cooling rapidly and slowly alternately. The case seems analogous to that of bronze, where slow cooling of the alloy after casting is said to make it hard and brittle.

Fine silver with 6 per mille of bismuth, rapidly cooled, was distinctly cold-short and crystalline on fracture; the bar cracked on the surface at the 4th pinch. With 7 per mille of bismuth these evidences of diminished ductility were slightly more pronounced. With 8 per mille of bismuth the silver was still more brittle, the bar broke readily when hammered, and cracked all over the surface on the 4th pinch from the rolls. With 9, 10 and 11 per mille of bismuth, the bar of silver could be readily broken in two by merely striking it against the edge of an anvil, the fracture was coarsely crystalline, and the bar, in one case, proved to be very red-short, a mere tap from the tongs sufficing to break it in two when heated for the purpose of annealing. Although these bars were so very brittle, it was still possible to roll them into thin straps after careful annealing; but the edges of the straps so produced were deeply jagged and indented by cracks. These bars also all emitted the peculiar crackling noise under the rolls which has before been mentioned.

An alloy containing 990 parts of silver and 10 of copper then had added to it successively 1, 2, 3, 4, and 5 per mille of bismuth, the cast-

ings being rapidly cooled. The remarks already made with reference to fine silver alloyed with the same proportions of bismuth would apply here almost exactly, that is to say, the bars were rolled out to a thickness of 0·015 with somewhat ragged edges, so that, although ductility, as thus tested, was impaired, it was only slightly so. With 6 per mille of bismuth (fineness of metal on assay 983·9) the edges cracked a little, and, after annealing and rolling out, the strap had decidedly jagged edges and was split for some distance at one end. The bars containing 4, 5 and 6 per mille of bismuth were now remelted and allowed to cool slowly and completely in the mould. They were all found to be highly brittle, broke easily under the hammer—the fracture being granular and not crystalline—and on being rolled they cracked badly, all over the surface and at the edges, on the 1st or 2nd pinch; in one case the bar broke in two on the 2nd pinch. That these very different results were again solely due to the manner of cooling was proved by remelting and rapidly cooling the castings, when the same metal proved comparatively ductile, as first stated.

Silver of the Indian standard of 916·6 per mille (the rest being copper) to which 2 per mille of bismuth was added, gave on lamination straps with slightly jagged edges and proved to be red-short. With 4 per mille of bismuth the bars showed a few surface cracks on being rolled, and the resulting straps had decidedly jagged edges. Slow cooling of these castings did not affect their ductility, thus showing a marked contrast to what had been observed in the case of fine silver and the alloy containing only 10 per mille of copper. When the amount of bismuth was increased to 5 per mille, the copper present remaining at 83·4 per mille, the bars were decidedly brittle and cracked readily on hammering—the fracture being again granular, and not crystalline as in the case of fine silver. On lamination both surface and edge cracks developed after four pinches from the rolls, and in annealing one of these bars the whole surface blistered considerably, no doubt owing to the temperature having been carried a little too high. Standard silver with 10 per mille of bismuth, reducing the fineness as ascertained by assay to 906·6, was very brittle, the bars breaking easily under the hammer, and on the 4th pinch from the rolls splitting and cracking all over the surface. In the course of these latter experiments it was ascertained that with from 83·5 to 70 per mille of copper present slow or rapid cooling of silver alloys containing bismuth made no appreciable difference in their ductility.

The foregoing experiments having furnished some information as to the amount of bismuth that might be expected to injure our coinage alloy, it was now decided to test that point practically, by operating on

coinage bars subjected to the regular procedure for the manufacture of rupees in the Calcutta Mint. The experiments made in this connection were *fourteen* in number. The bars used here for coinage weigh about 253 troy ozs. and are about 20 inches long, 2·25 broad, and 1 inch thick; they are cast in vertical iron moulds. In lamination they are first reduced by 11 pinches to a thickness of 0·23 in.; they are then annealed and finally reduced by 12 additional pinches to a thickness of 0·06 inch. A number of bars, poured from a pot of which the contents had proved on assay of a granulated sample to be 916·6 fine, were selected for the experiments, and as a preliminary step one of the bars was laminated to test its ductility. It rolled out with smooth " wire " edges, and indeed its ductility was beyond suspicion as it resulted from a melting of good coins. Another bar of the same batch was now melted and 1 per mille of bismuth added to it, the result of the addition being checked, in this and all following cases, by the assay of a granulated sample of the metal, taken after thorough stirring. At the 8th pinch both edges of the lower half of this bar began to crack, and at the 11th pinch these cracks extended towards the middle line of the strap for about a quarter of an inch, and occurred at about every half inch of the edge. After annealing, and in the subsequent lamination to a thickness of 0·065 inch, these cracks increased considerably in number, but did not become sensibly deeper. The strap as finished was pronounced unfit for coinage purposes; for although two blanks could have been cut from its width, the edges were too jagged to admit of the blanks being obtained exactly along the line from which it was desired to cut them—this position being attained by means of a fixed lateral guide against which the edge of the strap had to be maintained in cutting. With 2 per mille of bismuth the results obtained on rolling were not much worse than with 1 per mille. But the side cracks opened out more, and here again it was noticed that the lower portion of the bar (upper and lower here having reference to the casting in upright moulds) was somewhat less ductile than the upper part.

With 3 per mille of bismuth (fineness on assay 913·8) the bar began to crack on both edges at the 9th pinch; at the 11th pinch there were many cracks quite a quarter of an inch deep, aud after annealing the bar these cracks increased at every pinch, so that at the 21st pinch the strap was cracked all along both edges very badly. It would only have been possible to obtain one blank from the width of this strap.

As it was perfectly clear that no further experiments were required with larger proportions of bismuth, the subsequent trials were made on coinage bars containing 0·5 per mille, 0·25 per mille, and, by dilution of the latter bars with standard silver, to even half and a quarter

of the lesser proportion just stated. Here the results were rather discordant; they appear to have been somewhat influenced by the state of different rolls, and by quick or slow annealing. The general outcome of the tests, however, was that although some of the straps, containing the proportions given of bismuth, were jagged at the edges, and so would have yielded a diminished percentage in outturn of good blanks, others were not materially worse than the average of straps without any bismuth at all. As a result of this part of the enquiry, it may, I think, be fairly concluded that if our coinage bars contain less than 0·5 per mille of bismuth their ductility will not be materially affected. It must be borne in mind that these results only apply to bars of the size and shape of those experimented on, and with the particular treatment in lamination above detailed. With thinner bars and a different method of rolling, different results may be expected. The system of cutting out blanks has also to be considered, for in some mints straps with saw edges are not so prejudicial as in others.

III. We have now to consider the best way of dealing with silver tendered for coinage which is proved to contain bismuth; and a few remaining points.

The only experiment on a large scale for refining such silver here, as far as I know, has already been described. The want of success which attended it seemed to be due to the very small amount of base metal in the bullion, for the formation of a slag in which the bismuth oxide could be entangled and removed by skimming; and possibly the reducing action of the plumbago pots used may have added to the difficulty. As it seemed certain, however, that nitre would effect the desired oxidation of the bismuth, some experiments were tried in this direction on a small scale. About 20 troy ozs. of silver containing 2·5 per mille of bismuth, and no other metal in appreciable quantity, was melted in a *clay* pot and repeatedly treated with nitre and borax, the bath being skimmed from time to time. After prolonged treatment in this way, the fineness of the silver being three times tested by a dip assay, the report on the silver was raised from 997·5 to 999·2; so there can be no doubt that bismuth may be removed in this way. But the process, as several experiments showed, is tedious; and of course is attended with a loss of silver which in large operations would be of notable amount. Considering therefore that silver containing bismuth has hitherto only been met with at the Mint in bars of high fineness, and that these are not readily refinable by the ordinary process, it would seem as well, if such silver be accepted at all, to deal with the bismuth in it by the plan of *dilution*. The proportion of bismuth any silver contains being ascertained, it may, if convenient, be mixed by melting with sufficient silver free from bismuth,

and with copper, so as to reduce the proportion of bismuth in the coinage bars to less than 0·5 per mille; and thus neutralize its injurious effects on the ductility of the bars.

The explanation of small quantities of bismuth being found in refined silver, *i. e.*, silver which has undergone parting for the extraction of the gold which was contained in it, seems sufficiently indicated in the following extract from Dr. Percy's work (Silver and Gold, Part I, p. 474), where that author is referring to the experience of Dr. Rössler in parting silver: "Bismuth has been found in nearly all kinds of silver; but in parting by sulphuric acid it is lost *partly in the fine silver* and partly in the slags." The italics are mine. That small quantities of bismuth adhere very tenaciously to silver, when once mixed with that metal by melting, is shown by the following experience. A quantity of silver containing bismuth, which had accumulated from the laboratory experiments before detailed, was melted, granulated, dissolved in nitric acid, and the silver precipitated as chloride. The silver chloride, after repeated washings, was reduced by heating in a plumbago pot with chalk and charcoal. The resulting ingots, on assay, showed at once that bismuth was still present in them in very appreciable quantity.

It may here be of interest to mention that I have found about 0·7 per mille of bismuth in some old Hindu punched coins, forming part of of a treasure trove which was found at Chaibassa, in the Singhbhum District.

The following is a summary of the main results detailed in this paper:—

1. The Indian assay process for silver bullion is, incidentally, a delicate qualitative test for the presence of bismuth in such bullion.

2. The assay process can be readily modified so as to give accurate results in the presence of such proportions of bismuth as are likely to be encountered in practice.

3. Fine silver when alloyed with only 1 per mille of bismuth has its ductility sensibly impaired thereby; and 1 per cent. of bismuth is snfficient to render fine silver, or alloys of it with copper down to 906 fine, extremely brittle.

4. Fine silver alloyed with small quantities of bismuth, and silver-copper alloys down to 980 fine when containing small proportions of bismuth, have the remarkable property of being more ductile when rapidly cooled in water after casting than if allowed to cool very slowly, thus resembling bronze in this respect.

5. Coinage bars such as are used in the Calcutta Mint, and with the procedure there adopted for rolling, are quite unfit for coinage

owing to brittleness, if they contain only 3 per mille of bismuth; while if the latter metal forms less than 0·5 per mille of the whole mass the ductility of the bars is not much affected.

In conclusion, I have much pleasure in recording my appreciation of the services of Messrs. J. R. L. Durham and E. Hood, Head and Second Assistants in the Assay Office, in carrying out under my directions many details of the experiments recorded in this paper.

Calcutta, March, 1887.

P. S.—June 10th. The experiments detailed in the foregoing paper were completed early in November 1886 and it was proposed to embody the conclusions formed in an official report to be submitted this year. It was suggested to me, however, that the subject investigated might be of general interest, and I had determined to publish this paper when I noticed in the Chemical News of March 21st, 1887, (p. 137), a short abstract of a paper on "Silver containing Bismuth" by Messrs. Gowland and Koga of the Japan Mint. I have delayed presenting this paper until I had read the full text of the communication from Japan (Journal of the Chemical Society No. CCXCIV, May, 1887, p. 410), and I may now make a few remarks upon it in connection with what I have advanced.

Messrs. Gowland and Koga's very interesting paper to a great extent covers ground which I had not investigated, *viz.*, the want of uniformity in composition of silver bullion containing bismuth. This part of the subject was suggested to me for experiment, as some of my results seemed to show that bismuth mixed with silver by melting and careful stirring does not diffuse itself evenly throughout the solidified mass. But that fact, now proved by Messrs. Gowland and Koga, was of no practical importance to us in the assay and valuation of bullion, seeing that it is an invariable rule now in the Calcutta Mint to premelt and assay by a granulated sample *every* kind of bullion tendered to the Mint—from refined bars 999·5 fine to Mexican Dollars. The well-known want of homogeneity in solidified silver-copper alloys, and other contingencies to which silver bullion is subject, render this course imperative for purposes of valuation on any extended scale. The cutting of samples from silver bullion for assay, even if the spot where such samples should be cut has been determined after most laborious investigation, can at best give merely approximate results; as indeed our authors admit for the case of silver containing bismuth.

With regard to the toughening or refining of silver containing bismuth, Messrs. Gowland and Koga mention that this operation is successfully performed in the Japan Mint by prolonged exposure of the

molten metal to the oxidising action of the air, aided in some cases by the use of nitre. This may seem at variance with our experience here, but is probably not so after all. The brittle bullion treated in Japan evidently contained a considerable amount of base metal in addition to the bismuth; the slags formed in the early stages of the melting consisting chiefly of litharge, &c. What we had to deal with was refined silver 990 fine, and in this case of course it would be more difficult to free the bullion from bismuth than if lead and other base metals were present in sufficient quantity to form a copious slag. But in any case (without, however, venturing to give any authoritative opinion on the subject) I doubt whether the Indian Mints would willingly undertake any considerable refining operations on bullion. The conditions under which these Mints receive bullion are very different from those obtaining in the case of the American and Australian Mints, and the Imperial Mint of Japan. In those countries encouragement has to be given to native mining industries, and hence a good deal of work in the way of purification and separation of metals is undertaken by their mints. In India practically all the bullion is imported by banks and merchants, from Europe, America, and elsewhere, and tendered to the Mints for coinage at a fixed charge. The Indian Mints may therefore, as in the case of the Royal Mint in London, very properly require that all bullion tendered to them shall be free from taint of brittleness, and so far fit for coinage. It is for the importers to make sure that their purchases are satisfactory in this respect.

As to the amount of bismuth that will render silver brittle, my results seem to be substantially in accord with those of Messrs. Gowland and Koga. They found that pure silver alloyed with only 5 per mille of bismuth was very brittle; the casting, I suspect, was allowed to cool slowly. Coinage bars of 900 fine, containing nearly 14 per mille of bismuth, were brittle and altogether unfit for coinags, as I should have expected. But by special treatment in the way of repeated annealings, some of these bars were rolled down successfully without cracking, although they still could not be used for coinage.

In the other matters treated of in my paper the results obtained will supplement those of my *confrères* in Japan.