Brittleness in copper

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SYNOPSIS

The paper deals with an extensive study to find out possible causes of brittleness in copper sheet obtained from The Indian Copper Corporation, who were from time to time getting a high percentage of brittle sheets in certain heats. As-cast samples from one such heat cast in the beginning, middle and end of casting, brittle sheets and ductile sheets were examined. Normally copper is cast in vertical water-cooled moulds with a 'flaming' dressing and phosphor-copper is used as a deoxidiser prior to casting. Reported brittleness was initially thought to occur when casting conditions were modified wherein mould dressing was changed to bone-ash and phosphor-copper deoxidation was omitted. However, metal rolled from blooms prepared by both the above procedures, yielded a high percentage of brittle sheets. Micro-sections indicated oxygen between 0·05 and 0·07%. Brittle sheets retained brittleness after annealing.

Laboratory estimation of hydrogen revealed the presence of 0·2 to 0·22 cc of hydrogen in 100 gm of as-cast samples and 0·26 cc in the brittle sheet. These values are quite low and cannot cause brittleness.

Spectroscopic analysis of sheets showed Bi, Te and As all below 0·01% and Sb below 0·005%. Chemical analysis for Bi alone indicated the presence of 0·005–0·007% bismuth.

Metallographic examination of the as-cast samples showed presence of Cu-Cu_2O eutectic in grain boundaries in normal quantities. The size, shape and distribution of oxide in sheet samples were normal.

That the inclusions are mainly Cu_2O particles was confirmed under polarised illumination when these particles appeared ruby red. Cu_2S, which would appear black under these conditions, was not found in any significant quantity.

THE metal copper is traditionally considered quite ductile, malleable and amenable to hot and cold working. India has meagre deposits of its ores and it is very essential that these resources are used judiciously and to the fullest extent possible.

In this context the subject of brittleness in copper is quite timely so that our melts do not reach the scrap yard in the production stage but do go out in the market as good quality products.

Impurities in copper

While melting copper hydrogen pick-up should be avoided. A slag cover will effect this. The main undesirables in copper are sulphur, silicon and the oxides of all metals present. Silicon and sulphur present in the form of silica and sulphides give rise to hot-shortness, hot-tearing, leakers, drossy and dirty fractures and the oxides also tend to impair the fluidity of the metal. The removal of these impurities can be achieved by fluxing. Sodium-calcium carbonates combine with silica and copper oxide to form sodium and calcium silicates and give off carbon dioxide. The former pass into slag and the latter acts as an inert mechanical degassing agent. Borax will combine with almost all metallic sulphides to form complex sodium and sulphur salts, which are either taken into the slag or in the gaseous form.[1]

Calcium introduced in the form of calcium copper will successfully deoxidise commercial copper, while for high conductivity copper it is generally accepted that either lithium or calcium boride is more efficient as a degassing and deoxidising agent.

The blister copper, which is sent to the refinery[2] may contain varying amounts of S, Fe, As, Al, Se, Te, Bi, Ni, Co, Au, Ag.

Bismuth can be reduced to 0·001% in the converter by prolonging the blowing at the slagging stage, and a concentrate, with a precentage higher than normal, is produced to enable this to be done. Bi, if allowed to remain in the blister copper cannot be removed by fire-refining.

In fire-refining sulphur is eliminated almost at once. Iron is readily removed in the slag, so also is aluminium. As and Sb if present are removed by using soda-ash and lime, the lime being added to reduce the wear and tear on the furnace lining.

Se and Te cannot be removed by fire-refining, although there are possibilities of some success using soda-ash under reducing conditions. However, these elements are normally removed by electrolysis together with the precious metals.

Dissolved copper oxide is reduced by 'poling'.

Electrolytic methods of refining remove the difficult elements, such as Ni, Co, Se, Te together with Au, Ag.

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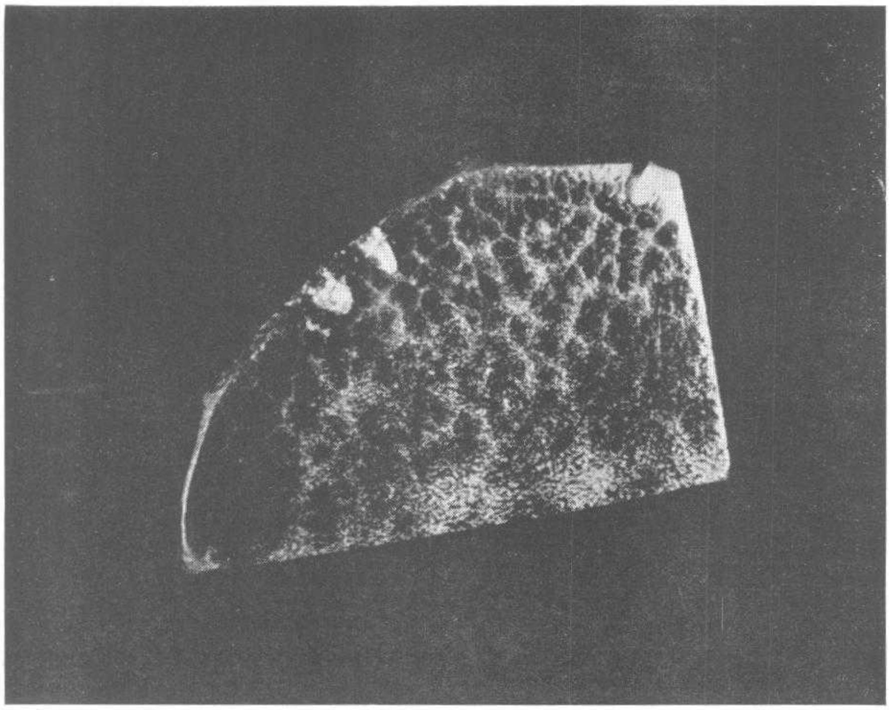


1 *As-cast grain structure revealed by macro-etching*

Copper is extremely malleable at temperatures between 600 and 920°C.

Lead is the most harmful of the common impurities[3] in its effects on hot-rolling copper and its alloys, owing to the fact that it precipitates at the grain boundaries during solidification after casting and at the normal rolling temperature of 700 to 870°C it is present in the molten state, thus markedly lowering the cohesion of the grains. Lead should, therefore, preferably be restricted in copper and its alloys to not over 0·03%.

The physical structure of the cast slabs is also important in hot rolling. A long, columnar, grain structure produced by high temperature pouring and slow cooling is undesirable, as cohesion of this structure is less than in the more equiaxed type produced by lower pouring temperature and more rapid cooling. A columnar structure tends to produce intercrystalline fissures, which develop into surface cracks as the structure is changed from a vertical to a horizontal position during the rolling operation. The harmful effects of columnar structure are most pronounced during the first three or four passes ; once recrystallisation takes place, the slabs become more homogeneous and malleable.

Hot rolling is also limited to large sheet bars as large masses retain heat over a period long enough to permit reduction to the required gage. Smaller sections can be rolled in high speed tandem mills.

Brittleness in copper sheet

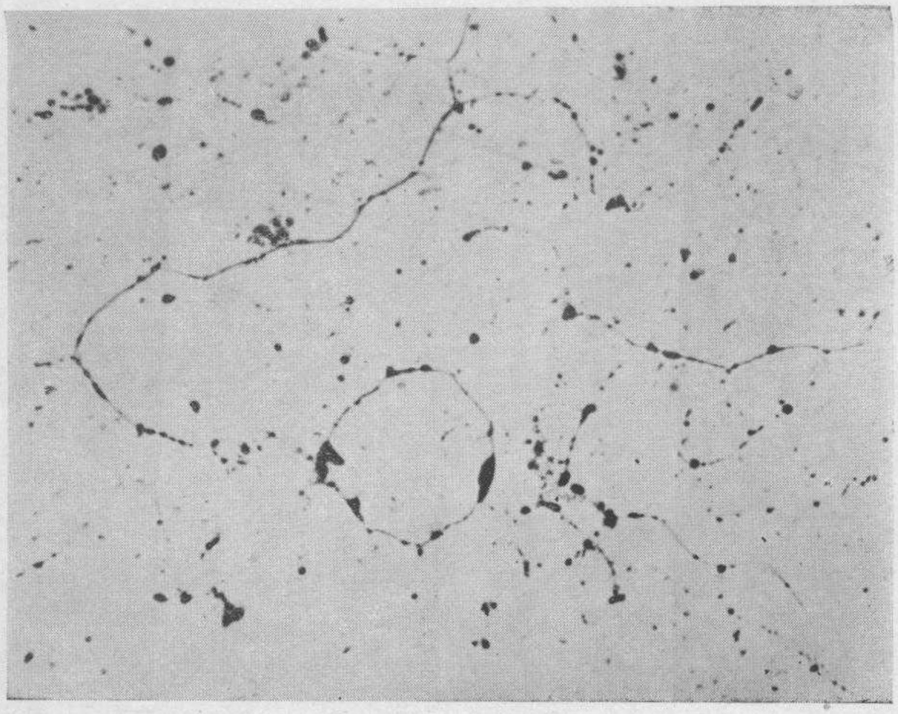
This paper outlines investigations carried out at the National Metallurgical Laboratory to find out possible causes of brittleness in copper sheet made by the Indian Copper Corporation Ltd., at their Ghatsila Works.

The Indian Copper Corporation had from time to time been getting a high percentage of brittle sheets in certain heats. As-cast samples from one such heat cast in the beginning, middle and end of casting, brittle sheets and ductile sheets were received at the National Metallurgical Laboratory for examination. It was also communicated that normally copper is cast in vertical water cooled moulds with a 'flaming' dressing and phospho-copper is used as a deoxidiser prior to casting. Reported brittleness was initially thought to occur when casting conditions were modified wherein mould dressing changed to bone-ash and phospho-copper deoxidation was omitted. However, metal rolled from blooms prepared by both the above procedures yielded a high percentage of brittle sheets. Micro-sections indicated oxygen content between 0·05 and 0·07%.

Samples studied

As-cast

No. 1.	Beginning of casting period.	from a 10-ton heat cast under modified conditions described in preceding para and resulting in brittle sheets.
No. 2.	Middle of casting period (5)	
No. 3.	End of casting period (12)	



2 *As-cast microstructure* ×150

Sheet samples

No. 1. 1/8″ good sheet (annealed)
No. 2. 1/4″ good sheet (annealed)
No. 3. 1/8″ brittle sheet (annealed). Brittle after annealing.

Brittle sheets retain brittleness on re-annealing.

Experimental

Qualitative spectroscopic analysis of the as-cast samples indicated :

Major constitutent	...	Cu
Appreciable	...	Ni 0·1 – 1·0%
Traces	...	Fe, Si, Pb, Ag, Te, Bi All 0·01%
Minutes Traces	...	Sn, Sb, As

Results of chemical analyses are given in Table I.

The above table indicates presence of 0·06 to 0·007% Bi whereas the maximum permissible amount as per B. S. 1172-1952 is 0·003%. Bismuth is known to cause brittleness as this metal, insoluble in solid copper beyond 0·002%, forms films around grains.

Spectroscopic analysis of sheet No. 1 and 3 indicated Bi, Te and As all below 0·01% and Sb below 0·005%. Chemical analysis for Bi alone showed presence of 0·005% in sheet No. 1 and 0·007% in sheet No. 3.

TABLE I Chemical analysis

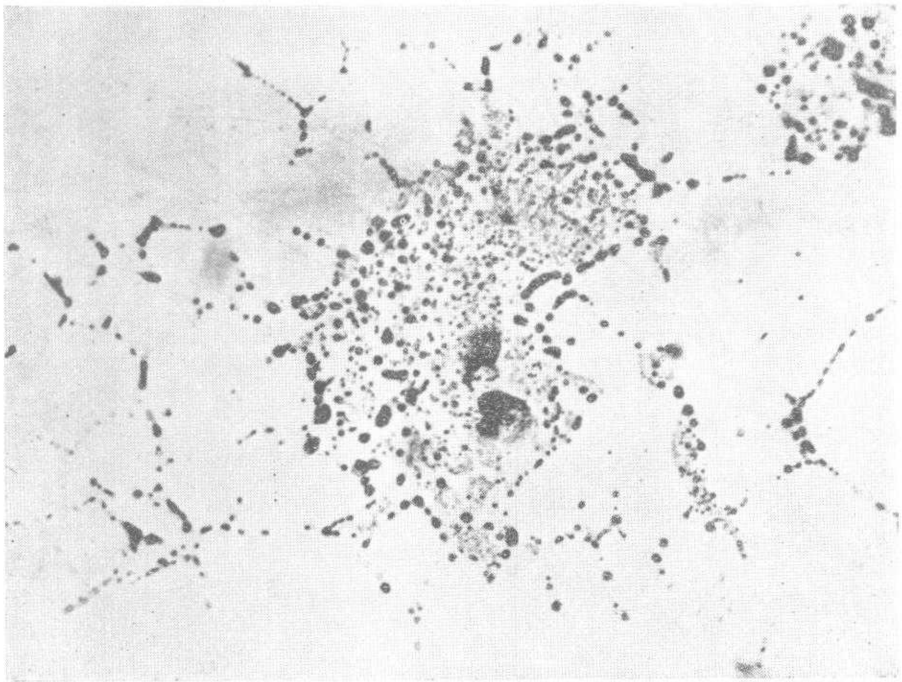
% Element	As-cast 1.	5.	12	Brittle sheet (unnumbered)
Ni	0·613	0·586	0·573	0·555
Fe	0·0036	0·0026	0·0036	0·0030
Bi	0·007	0·0056	0·006	0·0061
As	0·001	0·001	0·001	0·0012
Ag	Trace	Trace	Trace	Trace
Pb	,,	,,	,,	,,
P	Not found	Not found	Not found	Not found
Sb	,,	,,	,,	,,

Metallographic examination of as-cast samples

Macro-etching of an as-cast sample in 75% nitric acid and 25% acetic acid revealed gas porosity in centre and equiaxed chilled grain in the periphery. No columnar grains were present (Fig. 1).

Microscopic examination of as-cast samples showed presence of Cu-Cu_2O eutectic in grain boundaries in normal quantities. The size, shape and distribution of oxide in sheet samples were normal.

Fig. 2 shows the as-cast structure of copper ingot.



3 *A populated group of oxide inclusions* ×150

An unusually populated group of oxide inclusions in the as-cast condition is shown in Fig. 3.

That the oxides are mainly Cu_2O particles was confirmed under polarised illumination when these particles appeared ruby red. Cu_2S which would appear black under these conditions was not found in any significant quantity.

Hydrogen estimation of copper

For a copper melted and heated in oxidising atmosphere to 1250°C and poled to 0·015% oxygen, the hydrogen content should not be more than 5×10^{-5}%.

Laboratory estimation of hydrogen revealed the presence of 0·20 to 0·22 cc of hydrogen in 100 gm of as-cast samples of copper which is about $0{\cdot}17 \times 10^{-5}$%. Brittle sheet sample contained 0·26 cc of hydrogen. These values are quite low and cannot cause brittleness.

Laboratory rolling of supplied copper ingots

Maximum sized billets were machined from ingots and hot-rolled to 1/4″ plate. Soaking temperature of billets for rolling was 800°C. The hot rolled plates were descaled mechanically and pickled. These were then cold-rolled to 0·1″ thick sheets.

No difficulty was encountered in either hot or cold working indicating freedom from hot-shortness and cold-shortness.

Metallographic examination of laboratory rolled and supplied sheet

Structure of sheets rolled in the laboratory from ingots supplied by I.C.C. is quite normal. The oxide content and distribution compares with good sheets supplied by the party.

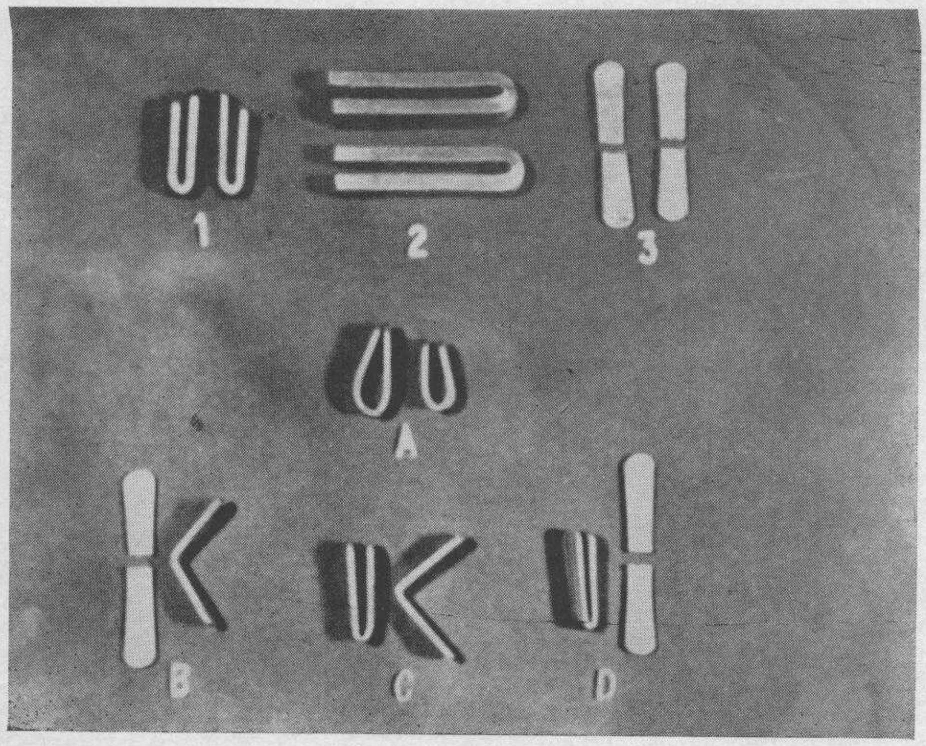
The sheet brittle after annealing supplied by the party shows intercrystalline cracks in the fractured edge. Intercrystalline fracture as a rule indicates either failure above equicohesive temperature or brittleness due to impurities which tend to form films around grain boundaries. These films can cause both hot-shortness and general brittleness persisting at room temperature.

Effect of composition on hot-working

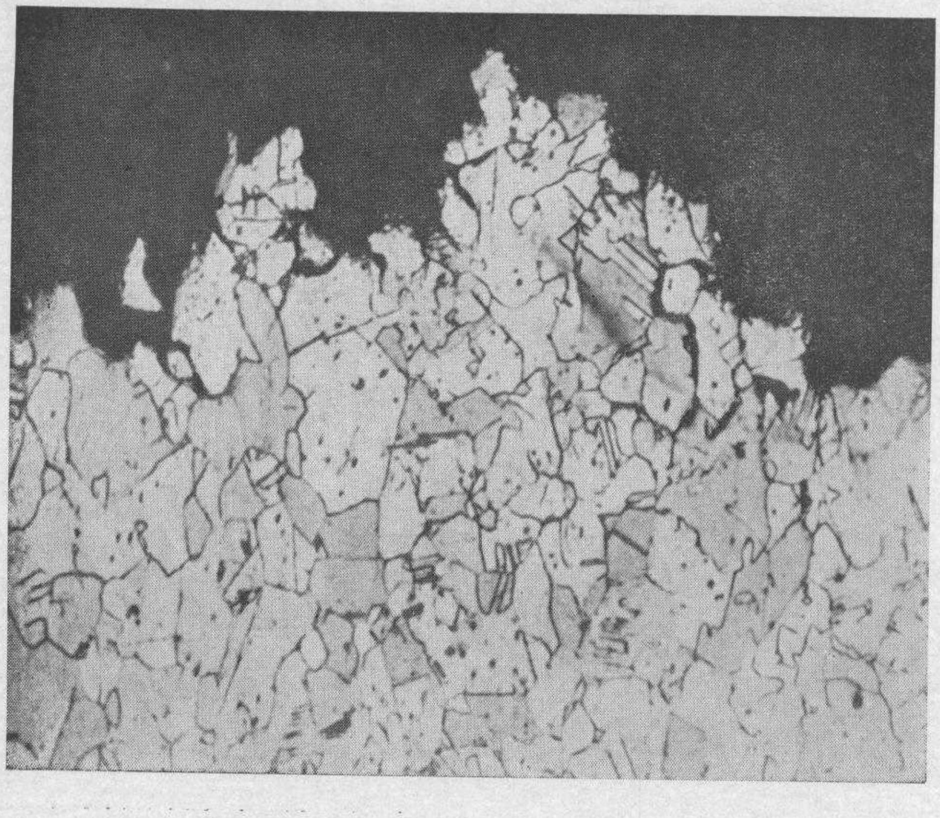
It is known that hot-working of copper is adversely affected by the presence of small quantities of lead and bismuth and it is desirable to maintain other impurities at as low a level as is commercially practical. Within a range of 0·015-0·05%, oxygen has by itself no deleterious effect on hot-rolling.[3] However, its presence changes the chemical form and solubility of other elements that may be present and in so doing affects the hot-working characteristics.

Bend test behaviour

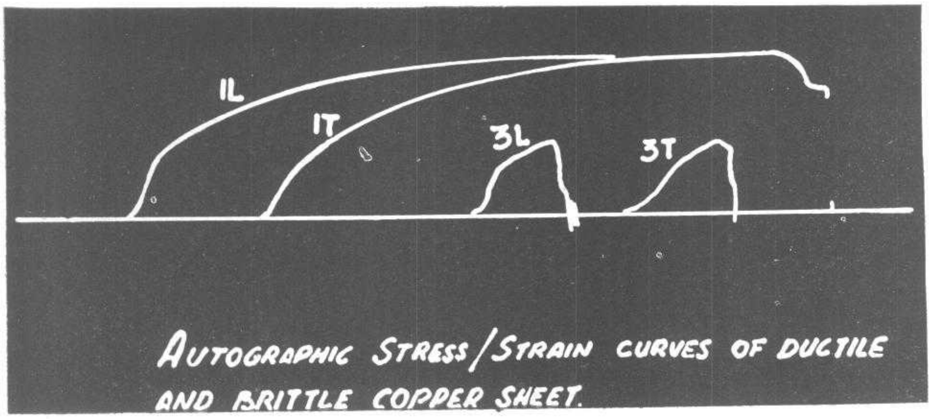
Bend test as per B.S. 899 : 1952 (British Standard 899 : 1952 'Rolled copper sheet and strip for general purposes') through 180° over ½ t (bending upon itself) on ductile 1/8″ and 1/4″ thick sheet samples (Nos. 1 and 2) along as well as across the direction of rolling was satisfactory (Figs. 4 and 5).



4 *Bend test specimens*



5 *Zone of fracture in bend test showing intercrystalline failure in brittle sheets of copper*



6 *Autographic stress/strain curves of ductile and brittle samples during tensile test*

Tensile test behaviour

Tensile test on ductile brittle and laboratory-rolled sheet was carried out and the results are given in Table II.

TABLE II Tensile test

Tensile Test Sample No.	Max. stress T. S. I.	British Standard Flat Test Piece 'A' (G. L. 2″) Elongation %	Remarks
Lab. rolled sheet from ingot 5.	24·60		Broke outside G. L.
Annealed sheet from ingot 5.	15·48	42·18%	Bi 0·0056%
Ductile Sheet (No. 1)			Bi 0·050%
Along direction of rolling	15·59	46·37	Broke off middle half
Across direction of rolling	14·88	45·31	,,
Brittle sheet (No. 3)			Bi 0007%
Along direction of of rolling	7·83		Broke outside G. L.
Across direction of rolling	7·44	3·9	

Autograpic stress/strain curves are typical of ductile and brittle failure in the tensile test (Fig. 6).

Discussion

It is known that hot-working of copper is adversely affected by the presence of small quantities of lead and bismuth and it is desirable to maintain other impurities at as low a level as is commercially practical. Within a range of 0·015%, oxygen has by itself no deleterious effect on hot rolling.[4] However, its presence changes the chemical form and solubility of other elements that may be present and in so doing affects the hot-working characteristics.

Embrittling effects of As, Sb, Pb and Bi are influenced by the oxygen content, the maximum amount permissible being increased by the presence of oxygen. These elements, as well as iron, nickel, sulphur, selenium and tellurium present in fire-refined copper containing a much greater amount of one or more of these elements, affect hot-working.

Although cuprous oxide increases the percentage of most impurities permissible for good hot-working, it is impractical to go beyond the maximum amount (0·05% oxygen) present in commercial copper because it lowers the ductility of the finished products.

Table I indicates presence of 0·006 to 0·007% Bi whereas the maximum permissible amount as per B. S. 1172–1952 is 0·003%. Bismuth is known to cause brittleness as this metal, insoluble in solid copper beyond 0·002%, forms films around grains.

In the opinion of authors brittleness as observed in the bend test behaviour of copper sheet samples under investigation is due to presence of bismuth in the grain boundaries. Separation of this impurity in the grain boundaries in the as-cast structure causes hot-shortness.

In the presence of oxygen bismuth forms oxides below 700°C ; the reaction is reversible at higher temperatures. Consequently, as the temperature decreases during hot-working the separation of injurious metallic impurity is avoided by the reaction forming a much less harmful oxide. Though pitch coppers can be rolled with far greater amounts of bismuth than can be tolerated in the oxygen-free condition, it is doubtful whether as a general rule, the above limits should be more than in practice.[5]

Bismuth impairs the cold-working properties, and in fact, by proper manipulation of heat treatment, it is quite possible to hot-work a copper containing bismuth and produce a very brittle product that would be useless for cold working, bending and deep drawing.

Bismuth can be reduced to 0·001 in the converter by prolonging the blowing at the slagging stage, and a concentrate with a percentage higher than normal is produced to enable this to be done. Bismuth, if allowed to remain in the blister copper, cannot be removed by fire-refining.[2]

A copper containing bismuth can be rolled if additions of phosphorus cadmium and tin are made.[6,7,8]

Conclusions

The copper under investigation contains 0·005–0·007% bismuth and although it can be hot-rolled, the sheet produced is brittle if bismuth exceeds 0·005%. This brittleness is exhibited in bend test and the mode of failure is intergranular ; thus indicating presence of weakening films of bismuth in the grain boundaries.

Acknowledgement

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