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BRITTLENESS IN COPPER (*)

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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 go out in the market as good quality products.

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 released in the gaseous form.

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 may contain varying amounts of S, Fe, As, Al, Se, Te, Bi, Ni, Co, Au, Ag. Bi can be reduced to 0.001 in the converter by prolonging the blowing at the slagging stage, and a concentrate, with a

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percentage 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 limes, the lime being added to reduce the wear and tear on the furnace lining. Se & 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. Copper is extremely malleable at temperatures between 600 to 920°C.

Lead is the most harmful of the common impurities in its effect on hot-rolling these 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 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 horizonal position during the rolling operation. The harmful effects of structure are most pronounced during the first three or four passess 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.

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

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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 phospho-copper is used as a deoxidiser prior to casting. Reported brittleness was initially though to occur when casting conditions were modified wherein mould dressing was 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 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 gms 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 boundries in normal quantities. The size, shape and distribution of oxide in sheet samples was normal. That the inclusions are mainly Cu_2O particles was confirmed under polarised illumination when these particles appear ruby red. Cu_2S which would appear black under these conditions was not found in any significant quantity.

Bend test as per B.S. 899:1952 through 180° over 1/2 t indicated that brittle sheets could hardly be bent through 90° whereas the specification lays down bending upon itself. Zone of fracture on microscopic examination revealed inter-crystalline failure. Autographic stress/strain curves plotted were found typical of ductile and brittle failure in the tensile test over samples.

It was concluded that presence of Bi 0.005 - 0.007% which is much above the permissible limit of 0.003% laid in B.S. 1172 - 1952 specification, is responsible for the brittleness in the present investigation. Although the material could be hot-rolled it fell much short of bend test requirements wherein the mode of failure was intergranular thus indicating presence of weakening films of bismuth in the grain boundaries.

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