

Manufacturing High Conductivity Copper : Part– II



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“Lithium is most effective in removing the oxygen combined with Copper, leading to considerable enhancement in conductivity”

In the last article, it was discussed that under most industrial conditions, the charge is always melted under oxidising conditions. Due to the complimentary nature of the solubility of hydrogen and oxygen, oxygen is always present in the melt as Cu_2O in relatively large quantities that later on becomes detrimental to the electrical conductivity, and hence requires treatment for elimination from the melt.

Effect of Impurity Elements in High conductivity Copper

Fig. – 3 shows the effect of dissolved elements in copper on electrical conductivity. It may be noted that all of the elements dissolved in copper decrease the conductivity, some of which by a great extent. Phosphorous, though used for de-oxidation treatment can be detrimental if it is dissolved to the tune of 0.02 percent.

In general, it is best to avoid these impurities from entering copper melt through meticulous analysis of the charge, especially if it mainly comprises of scrap. Because once these enter the melt, it is very difficult to eliminate them through treatment. Oxidation treatment (called “Fire Refining”) is recommended in such cases, when these metallic impurities are oxidised in preference to copper, but it invariably leads to high amount of dissolved oxygen in melt, and the subsequent de-oxidation treatment becomes extremely critical to the operation.

Cadmium, silver and lithium are the only elements that do not have any remarkable effect on conductivity in small quantities.

Lithium, amongst these, offers the most interesting possibility due to its extremely high affinity for oxygen. Not only can it combine with the

dissolved oxygen, but also reacts with the Cu_2O formed in the melt, and takes away the oxygen from the Cu_2O molecule, thereby de-oxidising the melt in a true sense. Since the reaction is carried out in the molten stage, unlike the gas/metal degassing reaction, the dwell time of the lithium added to the melt is sufficiently large. While most of the lithium oxide formed during the de-oxidation reaction floats on the surface and is removed as slag, the minor amount of residual lithium, according to the Fig. – 3, are inconsequential. De-Oxidisation of copper melt with lithium is therefore, becoming an accepted practice in most of the bulk high conductivity manufacturing processes of continuous / semi-continuous billet casting, or vertical / upward rod casting plants.

Treatment for Removal of Oxygen from Copper Melt

There are several methods being practised in the industry for treatment of melt of high conductivity copper.

Graphite flakes and powders are added on top of the melt. This helps in breaking the constant contact with oxygen in air, and further ingress of oxygen is curtailed. However, the graphite powder floating on the surface is in no way capable of removing the oxygen already

dissolved in the melt, nor can it take care of the Cu_2O formed in the process.

The use of “Green poles” was an ancient process, which produces smoke, and is hardly used in the present.

Addition of phosphorous is the most widely used method as it reduced Cu_2O to copper and the oxygen is removed as P_2O_5 , which is a poisonous and obnoxious gas. This is a clear-cut health hazard that certainly does not meet any of the pollution control norms (though it is practised very much with hardly any measures to protect the work force) and the residual phosphorous can be detrimental even in minute quantities.

Other degassing compounds (Calcium Carbide, Carbonates, etc.) have only a degassing effect: These remove only the dissolved gasses, and not the oxygen that is chemically bonded to copper as oxide.

The exact mechanism and effectiveness of calcium boride is not known, though it is reported to have some effect on the conductivity. However, the amount of calcium boride prescribed to be added is of the order of 600 grams per metric ton (MT) of melt, which turns out to be expensive. In many plants, only few tens of grams of calcium boride are added, which cannot be effective at all in such small quantities.

Lithium, on the other hand does not pose any of these problems, and in fact, is most effective in removing the oxygen combined with copper as oxide, which is the main reason for drastic reduction in conductivity.

When encapsulated in copper tube, it can be easily added to the copper melt using a simple plunger, and the quantities to be added are also very small – about three or five tubes of 4 gram potency are sufficient to eliminate oxygen from one MT of copper.

As stated earlier, lithium has such high

affinity to oxygen that it can even remove the oxygen that is combined with copper. This drastically reduces the amount of copper oxide in the melt, and the conductivity is improved considerably.

Methodology for De-Oxidation and Improved conductivity:

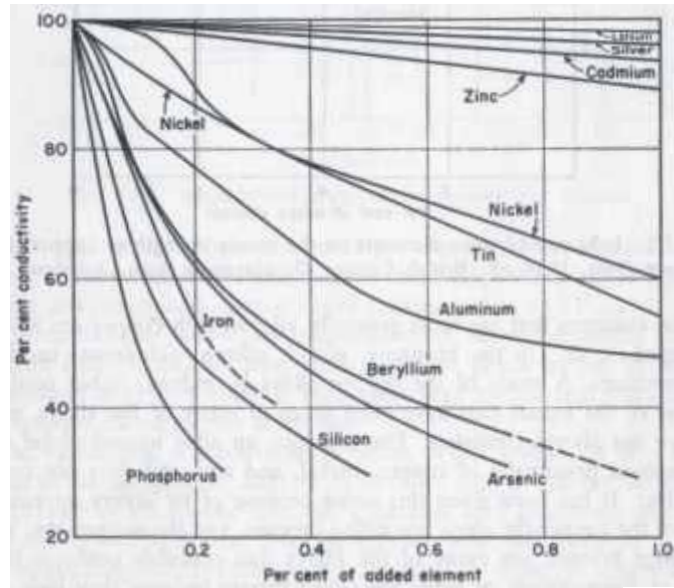
Firstly, samples may be drawn from the scrap as also the cathodes, to ensure that the impurity elements in the charge would not exceed the limits to affect the conductivity. Accordingly, a charge / recipe may be computed and it should be weighed and kept in batches, to be loaded into the furnace.

Once the melting is completed, samples may be drawn to test the impurity elements, and the charge may be balanced by adding cathodes to reduce the impurity levels further.

Samples may be tested for conductivity, and the melt should be treated with Lithium Tube Copper Deoxidiser (LiTube). Depending on the Oxygen content, between three and five LiTubes will have to be added per MT of the melt.

In induction furnaces attached to continuous casting lines, the first melt should be treated with LiTube as per the method described above, and after addition of every 250 kilograms of top-up charge, one piece of LiTube should be added to take care of oxygen that might enter through this new charge.

Care must be taken to ensure that the LiTubes are plunged deep down into the melt, and that these do not merely



“The measuring instruments should not be taken for granted”

“A simpler method is to plunge the LiTube along with heavy cathode plates / scrap such that it sinks to the bottom.”

float on the surface of the melt, trapped in the cover slag / fluxes, in which case the treatment would be ineffective.

The plunger material should be suitably coated with refractory / graphite, or even sleeves may be used to minimise contact of steel with the melt to avoid iron pick up. A simpler method is to plunge the LiTube along with heavy cathode plates / scrap such that it sinks to the bottom.

Laboratory Practice in High conductivity Copper:

There are many areas in the measurement of properties of Copper and their correlations in the laboratory. The general trend is to take the measuring instruments for granted; there are a number of areas of concern.

1. Chemical Analysis:

Optical emission spectrometer is the preferred method for chemical analysis, though there can be quite some confusion in terms of the following:

- ✦ Selection of correct spectral lines: Depending on the matrix elements / alloy, type has to be suitably created and stored in computer. The correct programme should be recalled for analysis of specific alloys, otherwise the readings could differ considerably.
- ✦ Availability of multiple standard samples in the range of interest for Oxygen analysis
- ✦ Data on precision should be generated, without which the analytical results are questionable, particularly in times of failure analysis, or disputes.

2. Measurement of Oxygen:

Presently, no methods of measurement of Oxygen in the melt are available, though an on-line probe should be available very soon, that could aid in decisions for dosing of de-oxidant.

3. Measurement of Electrical

Conductivity :

The analogue / partially digitised eddy current conductivity measurement device is a good device for quick measurement of electrical conductivity on shop floor, even by unskilled operators. However, the value of electrical conductivity measured is only as good as the calibration. There are two problems here: Firstly, it requires a periodic re-calibration in the instrument manufacturers' facility. This necessity becomes evident when the metre shows a different reading on the same sample, when taken at different times. The variation can be as high as five percent on IACS scale.

The other problem is more serious and has not been properly addressed: That there is always a curvature in the signal to conductivity calibration, leading to a positive or negative deviation in the reading. The problem is aggravated by the fact that the instrument is calibrated using two samples that are apart by about 60 percent IACS. Typically, the samples offered are aluminium alloy with conductivity of about 40 percent IACS, and High conductivity Copper of about 99 percent IACS. Instead, if the two samples are in a close range of 92 and 98 percent IACS, it is possible to minimise the deviation from linearity in the calibration, which would not make any measurable difference on the reading.

This issue can be critical especially when the samples are on the borderline of the acceptance levels of customers. Cross-check with classical method (of using a Whetstone bridge on a one metre long sample) is highly recommended under such circumstances.

Another solution is to use the hand-held, modern conductivity meters that are based on microprocessors that are intelligent and circumvent many a problems, while offering many other possibilities of data logging / communication. ■ ■ ■