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Estimation/Assessment of Oxygen content in copper by Metallographic method

Devdutt Singh[1], Vivek Mittal [2], Subodh Rana[3]

[1,2] Material Research Laboratory, BHEL Haridwar, Uttrakhand, India
[3]Metallurgy Engineering department, BHEL Haridwar, Uttrakhand, India

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Abstract - *This methodology is related to the development of a method for estimating oxygen content qualitatively and quantitative approximation (to know the content of oxygen present in copper). This may be used to differentiate ETP (electrolytic tough pitch) & OFC (oxygen free Copper) copper. This method can also be used for determining the presence of Cuprous Oxide (Cu2O) (hydrogen embrittlement susceptibility) in products made from deoxidized and oxygen – free copper. In other ways, the extent of oxygen is determined by heating the test specimens in a hydrogen-rich atmosphere and rapidly cooling the specimens without undue exposure to air followed a microscopic examination and/or a bend test.*

***Key Words*: Hydrogen Embrittlement, ASTM B577, DLP Copper, Oxygen Free Copper, ETP Copper**

1. INTRODUCTION

In power generation industry, oxygen free copper, electrolytic tough pitch and deoxidized copper are used for manufacturing generator components. Copper alloys which contain higher amount of oxygen can get embrittled during brazing due to reaction of hydrogen with the oxygen. Hydrogen diffuses through the copper and reacts with inclusions of Cu_2O, forming H_2O (water), which then forms pressurized bubbles at the grain boundaries. This causes the grains to literally be forced away from each other i.e. developing cracks, and this phenomenon is known as hydrogen embrittlement. Thus hydrogen embrittlement test is required to assess the presence of oxygen or cuprous oxide in copper products made from oxygen free and deoxidized copper. The copper products, which need to be welded/brazed/hot formed, should be free from oxygen which is not practically possible but should contain less amount of oxygen or cuprous oxide.

Standard test method for determination of oxygen in copper and copper alloys is specified in ASTM 2575 (withdrawn in Jan 2017) and standard test methods for detection of cuprous oxide (Cu_2O) which is also known for causing hydrogen embrittlement susceptibility in copper are in ASTM B577. Test method A of ASTM B577 stipulates the microscopic examination without thermal treatment. In this method when specimen of copper is seen using polarized microscopy at minimum 75X magnification then cuprous oxide will appear as ruby-red particles and cuprous oxide will appear as blue particles under white light (Refer Fig.1).

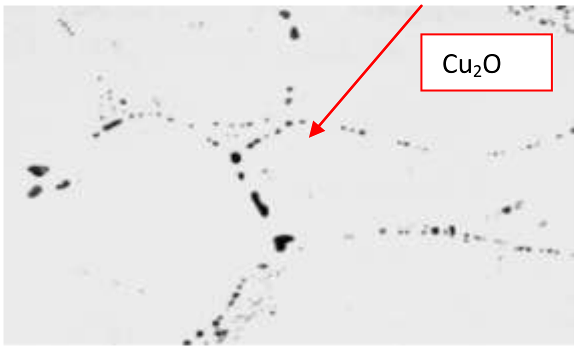

Fig .1 Oxygen in copper present at the grain boundaries in the form of copper oxides

Test method B of ASTM B577 specifies microstructural examination after thermal treatment (Refer Fig.2). In this the specimen is heated for 850oC for 20 to 40 min in a furnace with at least 10% hydrogen inside that. After heating the specimen is cooled very fast to room temperature and for this water quenching is generally done. As the reaction between hydrogen and cuprous oxide leads to formation of pressurized water vapor, the grains look separated as can be seen in figure below.

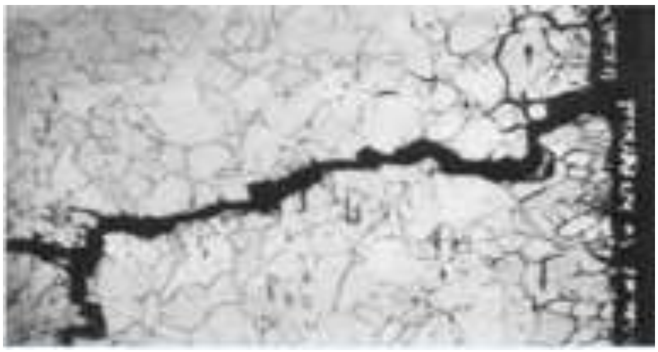

Fig .2 Long chain of Voids along the grain boundaries due to hydrogen embrittlement.

Test method C ASTM B577 preaches closed bend test after thermal treatment. (Refer Fig.3). Heat treatment is same as specified in the test method B. After heat treatment cooling is done very fast without much contact with air. Then, U shaped bend test with two legs completely touching each other is done being kept the surface of interest outside during bend. If cracks start to appear on the outside surface then it tells about presence of Cu_2O.

Fig .3 Samples failed in Close bend test after heating in hydrogen atmosphere at a temperature of 850 deg C for 30 minutes (ASTM B 577 Method C). Cracking during bend test shows the presence of hydrogen embrittlement

The above three methods are normally followed but there are some drawbacks which will be discussed one by one. The method is highly subjective as no quantitative criterion is specified in all three cases. It is basically stating about the presence of Cu_2O and not exactly the amount of Cu_2O. If test method C is seen then there may be chances that the specimen would contain some amount of Cu2O and this amount is not sufficient to cause embrittlement i.e. failure during bend test. After analyzing this there is a scope for improvement or addition of a method to tell about the approximate amount of Cu_2O in the sample. The test method B and C are also very time consuming and each involves hazards and risk of injury and since heat treatment is also involved so it becomes bit costly.

To overcome these difficulties, a new testing method has been tried to develop. The testing will be done by means of metallography which primarily involves the collection of known samples with known value of oxygen in PPM and develop metallographic comparator. The microstructures of samples with increasing order of oxygen content will be used as Atlas to compare the microstructure of unknown oxygen content and approximate oxygen content will be assessed. This method will not be able to exactly tell the ppm level but can easily give us a range in which we can predict and get the idea of the oxygen content.

Copper has highest electrical conductivity after silver, it is possible to convert in to any shape. Some alloys of copper (Cu-Zr-Cr) have very high strength comparable to steel. These alloys coupled with high conductivity make them ideal for power plant rotating components. Copper has good corrosion resistance, good machinability, strength, ease of fabrication and non- magnetic. Most commonly used coppers are ETP grade copper (ETP), Oxygen free copper (Cu-OFC), High conductivity phosphorous de-oxidized (Cu-HCP), Silver bearing copper (Cu Ag x) and Silver bearing oxygen free copper (Cu Ag x P).

An advantage of ETP copper is that it does not lose electrical conductivity on cold working. Fully hard copper may have electrical conductivity around 97 %. IACS. Tensile strength up to 350N/mm2 can be obtained in copper by cold working. Hard coppers e.g. copper bars of AC motor, Commutator segments of DC motor. The oxygen content is very important and is carefully controlled during manufacture. As shown in Fig 4 and Fig 5, the presence of impurities in solution reduces conductivity but, if oxygen is also present (Fig 5 & 6), many impurities form oxides which then exist as inclusions within the material. Because the impurities are no longer in solution, the effect on conductivity is reduced. However, the amount of oxygen that can be tolerated is limited for two reasons. Firstly, oxygen itself reduces conductivity by forming particles of copper oxide and, secondly, a high oxygen content gives rise to hydrogen embrittlement if the material is heated in a reducing atmosphere, such as during welding, brazing or hot bending operations. Traditionally, copper castings and refinery shapes for subsequent fabrication contain sufficient oxygen to give a level 'set' to the casting on solidification. This has two main advantages:

- The presence of oxygen ensures that most impurities are present as oxides, reducing their effect on conductivity and ductility.
- The oxygen reacts with hydrogen, which is picked up from the furnace atmosphere, forming steam. The micropores resulting from the steam counteract the shrinkage which would otherwise occur during solidification and this leads to the level set (correct pitch) of the casting. Further hot processing reduces the porosity. With the correct pitch and oxygen content, the properties are good and said to be 'tough', hence the term tough pitch copper for the most widely used high conductivity copper.

More recently improvements in refinery techniques have resulted in a reduction in impurity levels, making the presence of oxygen less necessary. Meanwhile, improvements in casting techniques, such as improved control of the melting atmosphere to reduce hydrogen pickup, has enabled the oxygen content to be reduced from about 0.06% to 0.02% or less. Today, all copper is continuously or semi-continuously cast so there are no longer static refinery shapes. The copper is fed continuously and a rolled product is produced at the end of the process. These improvements have resulted in high conductivity oxygen-free copper becoming commonly available these days. High Purity copper (ETP) copper may contain up to 400 PPM oxygen. Higher oxygen content may cause defects like cracks, laps, seams. ETP copper grades are extensively used in almost applications which require high conductivity.

A normal commercial copper may contain oxygen up to 400 PPM without impairing its electrical properties. However presence of oxygen may cause cracking of copper when it is processed in hydrogen atmosphere during some metal working processes requiring heating like hot bending operation, welding, brazing etc.

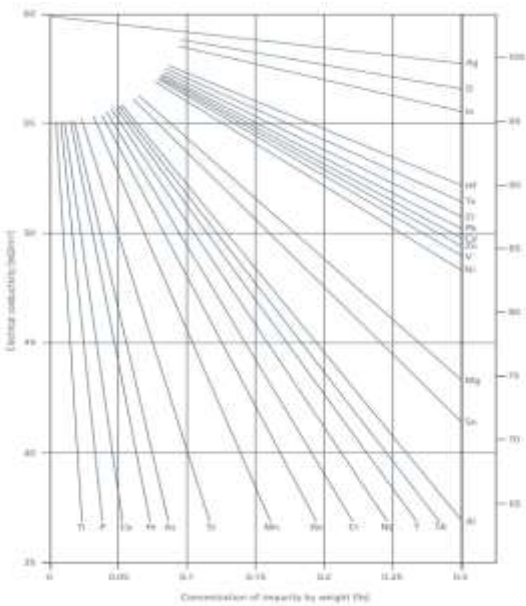

Fig 4: Effect of various elements (impurities or intentional additions) on the conductivity of copper (Source: European Copper alliance docs))

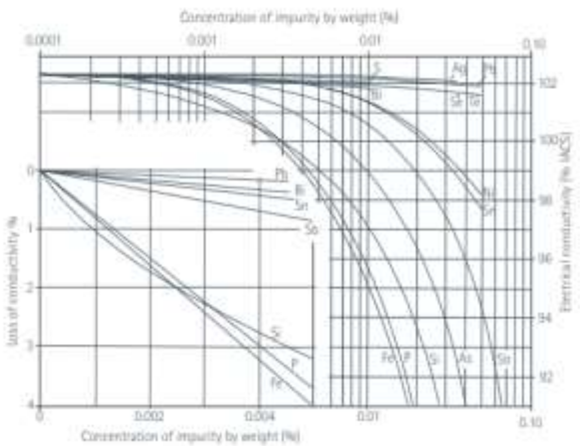

Fig 5: Effect of various elements (impurities or intentional additions) on the conductivity of oxygen-free copper (Cu-OF) (Source: European Copper alliance docs)

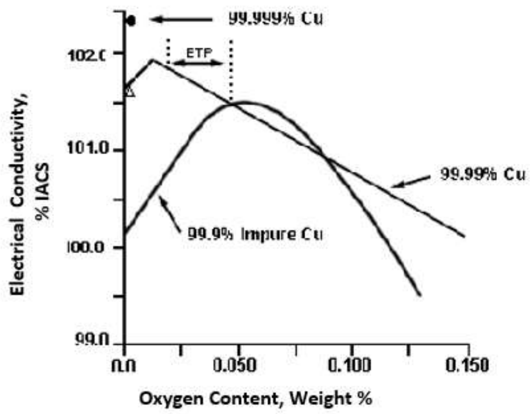

Fig 6. Effect of oxygen content on the electrical conductivity of annealed copper (Source: www.copper.org)

To avoid the phenomenon of Hydrogen embrittlement of copper, the content of oxygen in the copper material is reduced. Such copper materials are called oxygen free copper materials. Such coppers have maximum oxygen content of order of 10 PPM, achieved by double/triple electro refining. The removal of oxygen can also be done by de-oxidation of copper by phosphorous (also called DLP coppers). De-oxidation by phosphorus ensures complete removal of oxygen, But it is also very risky as slight increase in Phosphorus may cause drastic fall in conductivity

Procedure & Evaluation of Oxygen Content

The setup was designed with the following in-house efforts-

2.1 Collection of different samples of copper obtained from different heats.

2.2 Samples should be preferably of same grade and same dimensions.

2.3 Oxygen content testing by spectroscopy

2.4 Collection of samples of oxygen content of from 10 PPM to 1000 PPM.

2.5 Preparation of Metallographic samples for each sample tested for oxygen content using spectroscopy

2.6 Capturing the metallographic images at magnification 100X for each samples.

2.7 Preparation of Metallographic Atlas of copper samples having different level of oxygen content (Refer Images enclosed as Annexure)

2.8 By comparison method, new samples can be qualitatively assessed for oxygen content and also quantitative near approximation of the oxygen content.

It is pertinent to mention here that in quantitative analysis of copper oxides / voids, if seen in metallographic context ,are akin to inclusions in steel, for which standard micro photograph are available in ASTM E45 /IS 4163

ACKNOWLEDGEMENT

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ANNEXURE:

(a) Oxygen Content 27 PPM

(b)Oxygen Content 46 PPM

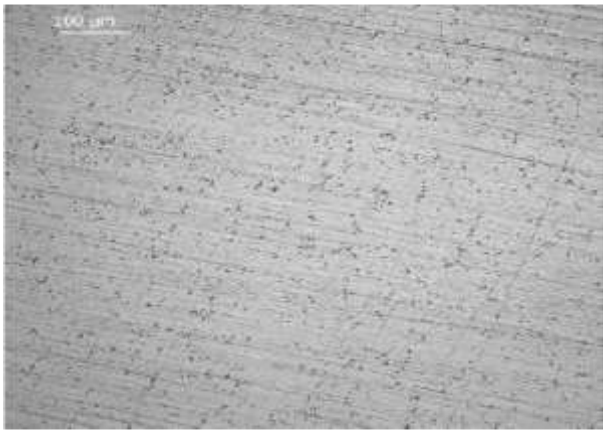
(c) Oxygen Content 81 PPM

(d)Oxygen Content 155 PPM

(e) Oxygen Content 253 PPM

(f) Oxygen Content 500 PPM

(g) Oxygen Content 672 PPM



(h) Oxygen Content 1061 PPM