Methods of hydrogen charging and effect of hydrogen charging on physical properties of copper

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ABSTRACT

Hydrogen charging of copper can be possible by three different methods, first is cathodic charging, second gaseous or high temperature charging and third electroless copper plating. The effect of hydrogen on copper is that it changes physical and mechanical properties. Above three methods concluded that hydrogen effect shows two different courses first, the development of high pressure molecular hydrogen in voids and second formation of defect, such as dislocation due to precipitation of absorbed atomic hydrogen in the form of hydrogen molecules and due to this region physical and mechanical property of copper changing with hydrogen charging.

KEY WORDS: Hydrogen charging, hydrogen contents, high temperature, strain rate, mechanical properties, physical properties.

1. INTRODUCTION

Hydrogen in Copper: Hydrogen enters in copper in the atomic form and not as molecular hydrogen. Rogers (1968), has shown in general any process producing atomic hydrogen at metal surface can easily absorbed by the metal. As described already cathodic charging, gaseous charging and electro less copper plating causes hydrogen absorption into copper. Here detail of these processes describe and attempt to explain results in terms of molecular hydrogen effects.

Hydrogen has been found in the three different form (a) Molecular H_2 method of detection calorimetry and hydrogen gas analysis (Graebner and Okinaka, 1986), (b) Atomic H method of detection Resistivity (Wampler, 1976), permeation (DeWulf and Bard, 1969; Ishikawa and McLellan, 1985) and (c) Protonated H^+ method of detection positron annihilation (Graebner and Okinaka, 1986).

Cathodic hydrogen charging: Cathodic charging can be done at ambient temperature. In general (DeWulf and Bard, 1969; Okinaka, 1986) shown that hydrogen recombination inhibitor such as As_2O_3 is needed to inject hydrogen into copper. During cathodic charging charge hydrogen is detectable at room temperature (DeWulf and Bard, 1969; Ishikawa and McLellan, 1985). To understand the hydrogen effect author (DeWulf and Bard, 1969; Ishikawa and McLellan, 1985), conducted a cathodic charging experiment on copper foil catholically charged at 10mA cm^{-2} for 24h in 0.1N H_2SO_4 containing 0.001M As_2O_3. After charging in scanning electron microscopy (SEM) image found that copper foil contain a number of large voids inside the grains as well as at the grain boundaries shown in Figure.1.

Further examination of sample by TEM shows that voids are hydrogen gas bubbles, which are precipitation of atomic hydrogen.

Gaseous hydrogen charging: Gaseous hydrogen charging in an attractive approach for controlling the microstructure, mechanical and physical properties of copper. In this study copper was hydrogenated with hydrogen level of 8 ppm to 20 ppm. The microstructures, fractograph, and chemical composition analysis were investigated by optical microscope (OM), scanning electron microscopy and inductively coupled plasma-atomic emission spectrometer (ICP-AES). Hydrogenation of copper was carried out vacuum annealing furnace (Sievert's apparatus) Figure.2. Material used for this study was copper sheet tensile test sample. The chemical compositions in weight percent were 95.48% Cu, 3.501% Zn, 0.677% P, 0.136% Fe, 0.0854% S, 0.577% Sn, 0.026% Pb and 0.0204% Ni. The hydrogenation treatment of the specimens was carried out in Sievert's apparatus, which is known as gaseous hydrogen charging system.

This procedure is as follows, sample was weighed and inserted in to the sample holder made quartz which was further kept inside the reaction chamber. A high vacuum of the order of 10^{-6} torr was created inside the system using rotary diffusion pump. The sample was heated at 1073 K temperature and pressure varies from 650 to 850torr under dynamic vacuum conditions for some hours to activate the sample surface. Hydrogen was flushed out through the system at temperature 1073 K and then system was evacuated again. After that hydrogen gas was introduced inside the system from the hydrogen generator at a constant temperature and at a particular pressure level. The sample started absorption of hydrogen at a fixed temperature and drop in the system was absorbed. This shows that charging of sample is taking place. After charging furnace was switch off and removed it away from the reaction chamber and the valve connecting the sample holder to the remaining system was disconnected. The reaction chamber was rapidly cooled by quenching so that hydrogen absorption during cooling is minimized. Sample was taken out from the tube. Sample with different hydrogen contents (8ppm to 20ppm) were obtain by controlling pressure. The amount of hydrogen contents of sample was determined by pressure drop method as well as inert gas fusion technique. The microstructures and fractograph were investigated by optical microscope (OM) and scanning electron microscopy.

The samples were polished by using emery papers of different grades starting from 600# to 4000#. Emery paper polishing was followed by disc polishing. Diamond pest and Carochin is used during cloth polishing. Echent used for copper samples were ferric chloride ($FeCl_3$) 3gm, hydrochloric acid 10ml and ethanol 96 ml. Flow and fracture behaviour studied at constant strain rate 10^{-3} S^{-1} at the room temperature, were carried out on a floor model screw driven Universal Testing Machine.

Electro less copper plating: In the electro less copper deposition process, the deposition of 1 mole of copper accompanies the evolution of 1 mole hydrogen.

$$Cu (II) + 2HCHO + 4OH^- \rightarrow Cu + 2HCOO^- + 2H_2O + H_2$$

It is seen that the formation of hydrogen gas is an integral part of the overall deposition reaction. The hydrogen gas is produced from the combination of hydrogen atoms which are formed on the surface of copper as a result of splitting of the C - H bond in the formaldehyde molecules. Some of the hydrogen atoms or molecules can be entrapped and deposited in the interstitial space as gas bubbles.

The effect of on the ductility has been shown in (Okinaka, 1986; Nakahara, 1983). Figure.3, is an SEM image shows surface of electroless copper which was electropolished and enlarges shows hydrogen gas bubbles. This cause low ductility of electroless copper (Graebner and Okinaka, 1986; Okinaka, 1986; Nakahara, 1983).

Graebner and Okinaka (1986) found that the nature of electro less copper using calorimetry and hydrogen gas analysis all hydrogen in electroless copper is present in the molecular form.

Hydrogen charging effect on physical properties of copper: Hydrogen charging affects physical as well as mechanical properties. According to Rudee and Huggins (1964) stacking fault energy changes, Martin (1967); Waterhouse (1969), shows change in specific heat, Okinaka and Nakahara (1976) shows change in ductility, Butt (1983) found change in tensile yield stress and Kim and Byrne (1983) found change in hardness.

After analysis of gaseous hydrogen charged sample it was found that ultimate tensile strength varies from 350 MPa to 365 MPa and ductility from 0.45 to 0.40 for 0 ppm to 20 ppm hydrogen levels. Thus, gaseous hydrogen charging resulted in decrease in strength and ductility at room temperature with an increase in hydrogen contents.

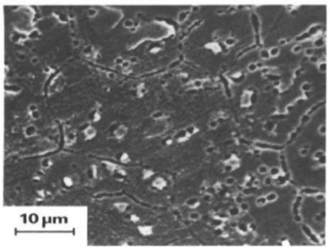

Figure.1. SEM micrograph showing the surface of copper catholically charged with hydrogen

Figure.2. Sievert's apparatus setup for gaseous hydrogen charging

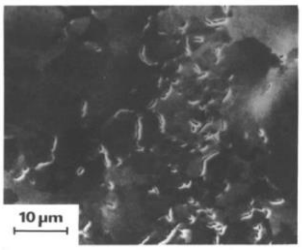

Figure.3. SEM image of the electro polised surface of electro less copper

2. METHODS & MATERIALS

Material used for this study is copper sheet sample which dimensions are 50 mm length, 12 mm width, and 12.5 mm gauge length and 1.60 mm thickness. The chemical compositions in weight percent were 95.48% Cu, 3.501% Zn, 0.677% P, 0.136% Fe, 0.0854% S, 0.577% Sn, 0.026% Pb and 0.0204% Ni. The hydrogenation treatment of the specimens was carried out in sievert's apparatus, which is known as gaseous hydrogen charging system. Its procedure is as follows. Sample was weighed and inserted in to the sample holder made quartz which was further kept inside the reaction chamber. A high vacuum of the order of 10-6 torr was created inside the system using rotary diffusion pump. The sample was heated at 1073 K under dynamic vacuum conditions for some hours to activate the sample surface. Hydrogen was flushed out through the system at temperature 1073 K and then system was evacuated again. After that hydrogen gas was introduced inside the system from the hydrogen generator at a constant temperature and at a particular pressure level. The sample started absorption of hydrogen at a fixed temperature and drop in the system was absorbed. This shows that charging of sample is taking place. After charging furnace was switch off and removed it away from the reaction chamber and the valve connecting the sample holder to the remaining system was disconnected. The reaction chamber was rapidly cooled by quenching so that hydrogen absorption during cooling is minimized. Sample was taken out from the tube. Sample with different hydrogen contents (9ppm to 17ppm) were obtain by controlling pressure. The amount of hydrogen contents of sample was determined by pressure drop method as well as inert gas fusion technique. The microstructures and fractograph were investigated by optical microscope (OM) and scanning electron microscopy. The samples were polished by polished by using emery papers of different grades starting from 600# to 4000#. Emery paper polishing was followed by disc polishing. Diamond pest and Carochin is used during cloth polishing. Etchant used for copper samples were ferric chloride (FeCl3) 3gm, hydrochloric acid 10ml and ethanol 96 ml. Flow and fracture behavior studied at constant strain rate 10-3 S-1 at the room temperature, were carried out on a floor model screw driven Instron Universal Testing Machine.

3. RESULTS

Behavior of true stress - strain curve: True stress-strain curves of specimens with different hydrogen contents are presented in Figure.4. It can be seen that hydrogen content has different effects on room temperature tensile properties. Tensile properties, such as ultimate tensile strength, yield strength, percent elongation and ductility reduces with increasing hydrogen content and variation with different pressure level.

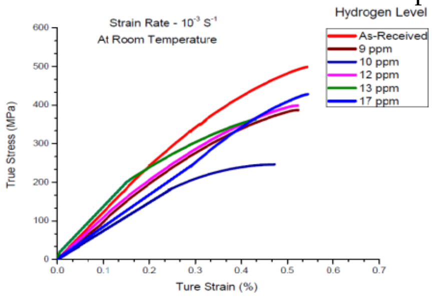

Figure.4. True stress – strain curve

Behavior of Plastic True stress-strain curve at different hydrogen level: Figures 5, 6, 7, 8, 9 and 10 represents plastic true stress-strain curve for unhydrogenated and hydrogenated samples. If we compare all the curves than we can conclude that region from yield strength to ultimate tensile strength for unhydrogenated was higher than hydrogenated samples. Region for this is reduction in ductile property of copper after hydrogen charging because increase in hydrogen contents material is becoming brittle.

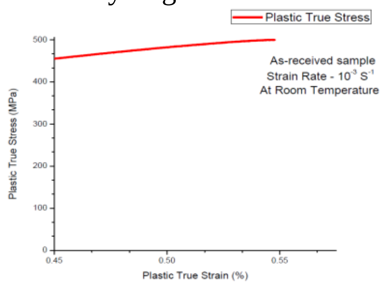

Figure.5. Plastic true stress-strain curve for as - received sample

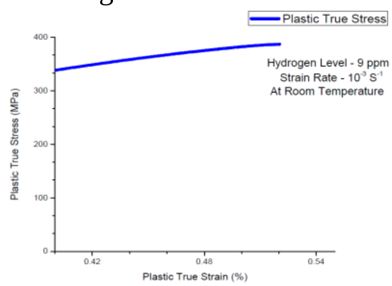

Figure.6. Plastic true stress-strain curve at 9 ppm

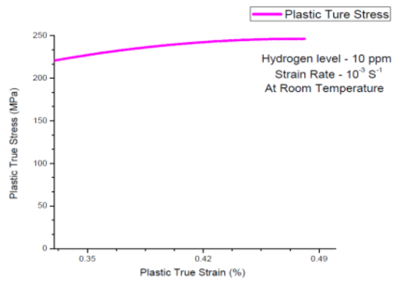

Figure.7. Plastic true stress-strain curve at 10 ppm

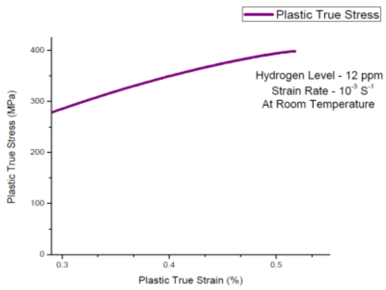

Figure.8. Plastic true stress-strain curve at 12 ppm

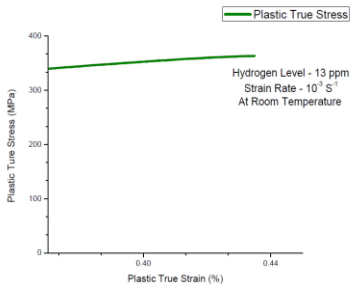

Figure.9. Plastic true stress-strain curve at 13 ppm

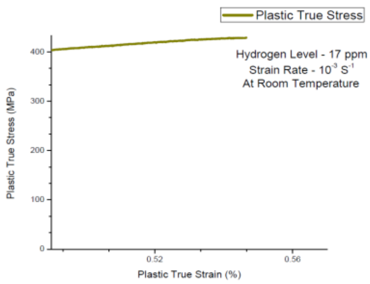

Figure.10. Plastic true stress-strain curve at 17 ppm

DISCUSSION

- Physical and mechanical properties of copper such as stacking fault energy, specific heat, ductility, tensile yield stress, ultimate tensile strength and hardness changes due to hydrogen charging.
- Hydrogen causes the development of molecular hydrogen in the voids and formation of defect such as dislocation due to precipitation of atomic hydrogen in the form of hydrogen molecules.

- With increase in hydrogen contents, the ductile behaviour of copper was found to decrease.
- Ultimate tensile strength, yield strength and percent elongation value were found to decrease with an increase in hydrogen contents in copper.

4. CONCLUSIONS

In this work ductile behavior of metal is reducing and material was becoming brittle with increase in hydrogen content at room temperature and at constant strain rate 10^{-3} S^{-1}.

Hydrogen charging also affects the mechanical and physical properties of copper sample, and region for that is development of high pressure molecular hydrogen in voids.

Tensile test properties like ultimate tensile strength, yield strength, percent elongation and ductility of copper were also decreases with increase in hydrogen contents.

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