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Effect of O_2 on copper-water vapor interaction near critical point

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A significant weight loss of copper plate was observed after copper-water vapor interaction near critical point. This leads to the acceleration of the ceramic layer formation on SUS surface during granite-water vapor interaction in the presence of copper. In this paper, we have determined the chemical state of copper at which the mass transfer takes place through reaction with H_2 and O_2+N_2 gas mixture at the different O_2 amount. Obtained results indicate that the weight loss of copper plate occurs at Cu_2O (+1) state due to a complex processes. The morphology of copper species on the surface of mesh and granite suggests that the Cu_2O was dissolved in water vapor and recrystallized on the surface of mesh and granite. Copper species were characterized by X-ray diffraction(XRD), scanning electron microscopy (SEM) equipped with an energy dispersive X-ray (EDX).

1. Introduction

Water vapor near critical point which has no coexisting equilibrium liquid water, is a high-enthalpy, low-density reaction field [1] and its properties are controlled by temperature and pressure in water vapor generator, such as an autoclave. A number of studies [1–4] have been made in this region to understand the reaction of water vapor with materials, such as SiO_2, granite. Our research team has studied the formation of ceramic layer on metal surface using mass transfer at conditions above, and reported that a highly protective amorphous aluminum silicate layer formed on SUS surface after granite-water vapor interaction in the presence of copper [5–7]. In this process, we found a phenomenon that the mass transfer of aluminum and silicon species from the granite surface to the SUS surface was accelerated by the presence of copper species on the granite surface which were transferred from copper plate surface. However, a mechanism, providing the acceleration of mass transfer by copper, still remains unknown. Moreover, it is important, firstly, to understand the mechanism of weight loss of copper plate occurring during copper-water vapor interaction near critical point.

The mechanism of high temperature oxidation of copper has been thoroughly investigated due to its ideal model system. Previous works [8] on high temperature oxidation of Cu in dry and wet air (H_2O partial pressure in the range $\sim 1 \times 10^{-5}$ to 0.023 atm) indicated that the weight gain of Cu plate occurs due to the formation of oxides scale of Cu_2O and CuO even at the 0.0001 atm of O_2 partial pressure. The measured gravimetric parabolic rate constants are higher in wet air than in dry air at temperature below 700°C. The author interpreted these results on the basis of that the majority defects in the Cu oxides governing the parabolic oxidation are Cu vacancies, which at higher water vapor pressure are seemingly become partly compensated by protons from water vapor in the temperature range of 400~700°C.

Bharadwaj *et al.* [9] investigated the role of moisture in the reactions of Cu oxidation at 350°C by UHV transmission electron microscopy (TEM), and reported that Cu_2O spots, formed on Cu surface after exposure to O_2, were reduced by subsequent H_2O supply under similar temperature and pressure conditions. They also observed that wet O_2 significantly slower oxidized the Cu than dry O_2 at research conditions. These results are different from another investigation [8] that have shown that presence of water vapor often enhances the rate of oxidation versus dry oxygen. The author [9] also explained the discrepancy

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between bulk thermochemical data and the phenomenon of Cu_2O reduction observed with the interfacial and surface energies.

Pocock *et al.* [10] studied the solubility of Cu and its oxides Cu_2O and CuO in pure supercritical steam, and obtained data indicate that cupric oxide has the most solubility from three tested materials. The solubility of copper in supercritical steam is a function of pressure primarily, and temperature effect appeared to be negligible in the tested range. Sue *et al.* [11] measured the solubility of CuO in subcritical and supercritical water in a flow apparatus, and reported that the solubility of CuO comes to maximum at 350°C and constant pressure of 28Mpa.

Above mentioned literature indicate that there may be some competitive processes—the formation and growth of copper oxide and the dissolution of such oxide in the water vapor at high temperature and pressure. In previous research, we observed the significant weight loss of copper plate in water vapor near critical point. These results and above-mentioned literature references show that Cu-O_2-H_2O interaction system at high temperature and pressure has a lot of interesting no studied phenomena yet. The goal of this paper is to investigate the effect of O_2 on the mass transfer process of copper species during copper-water vapor interaction near critical point, due to the possible chemical state of Cu species-Cu(0), $Cu_2O(+1)$, and $CuO(+2)$ at high temperature and pressure.

2. Experimental details

Some experiments were conducted in order to reveal a role of granite in the process of weight loss of copper plate in water vapor near critical point, and results showed that granite does not affect on the weight loss of copper.

Copper plate 7 × 7 × 0.3 mm with 99.96% purity was used in our experiments. The size of granite sample is 9.35 × 7 × 6 mm. Their mineral and chemical composition at starting state were presented elsewhere [6]. The polished pipe-shaped specimen of austenitic type-304 stainless steel (SUS-304), with 21.65 mm in outer diameter, 1.5 mm wall thickness and 68.5 mm in height, was used in these experiments. The granite sample and copper plate were placed on the top of steel pipe in the autoclave, divided by a steel mesh (SUS-304). A schematic illustration of the autoclave and location of starting specimens inside the apparatus is shown in Fig. 1. The schematic representation of the hydrothermal equipment is presented elsewhere [12].

In all experiments the autoclave (an effective volume of 39ml after subtracting the volume of starting specimens) was filled in the range of 4–12% with distilled water. For example, it corresponds to 9 MPa pressure at 4% water content and temperature 340°C.

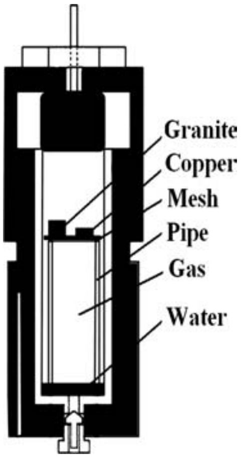

Figure 1 Schematic representation of autoclave and starting sample location inside an autoclave.

The various O_2 ratio of gas mixture in the autoclave at starting stage were achieved with a complex flowmeter controlled gas mixer, where the autoclave with starting materials was placed. At first step, the gas mixer was evacuated, and then filled with pure O_2 and N_2 gases at the prearranged rate of flow controlled by the flowmeter. The evacuation and filling operation was repeated two-times, and then the gas mixer was filled with the gas mixture corresponding to each experiment. Finally, the autoclave was tightly closed, then placed into a oven with fan, and heated to temperature of 330 or 340°C. The exposure time was 170 hours.

H_2 gas was generated in the autoclave using the reaction of Fe powder with water at experiment conditions. The amount of Fe powder and water was calculated for the H_2 generation process. It was enough to reduce the oxides formed on the surface of copper plate with H_2 gas generated at the experiment condition.

The weight of copper plate was measured before and after each experiment. The morphology and component of Cu species on the surface of Cu, mesh, and granite, was examined by scanning electron microscopy (SEM) equipped with an energy dispersive X-ray (EDX, Model S-4700T, Hitachi, Tokyo, Japan). The species formed on Cu surface was also examined by X-ray diffraction (XRD; Model JDX-3530, JEOL, Tokyo, Japan).

3. Results and discussion

3.1. Chemical state of Cu at which the weight loss phenomenon occurs

In order to study the chemical state of Cu at which the observed weight various occurs, we have conducted experiments in H_2, O_2+N_2 gas mixtures with lower O_2 concentration, and the air respectively. The Cu, Cu_2O, and CuO stable phases prevail at the tested reaction atmosphere respectively.

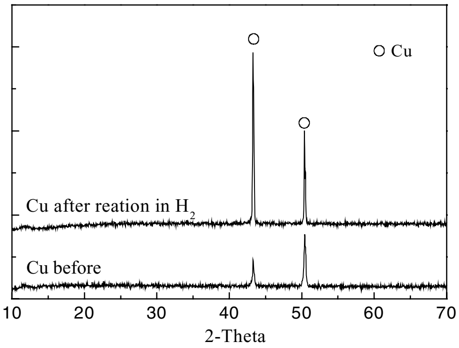

Figure 2 XRD patterns of Cu plate before and after copper-water vapor interactions near critical point in the presence of H_2 gas.

3.1.1. Cu (0)

The weight loss of Cu plate was not observed at the copper-water vapor interaction in the presence of H_2 gas under tested conditions. The XRD examination of Cu plate before and after the reaction, shown in Fig. 2, did not reveal the formation of any oxide scale on Cu surface. There was no a change in the surface color of Cu plate. According to this result we assume that Cu species do not transfer at this chemical state.

3.1.2. CuO (+2)

Like previous investigations of the high temperature oxidation of copper [8, 13], the weight gain of Cu plate also occurred during experiments in the air atmosphere. The color of the copper surface was black. The morphology and XRD pattern of Cu plate (Fig. 3) indicates that CuO whiskers were formed. Moreover, according to XRD data it is possible to suppose that Cu_2O phase was formed under the scale of CuO. These results conform with the Haugsrud's observations [8], where oxide scale was roughly divided into four regions: (1) surface oxide whiskers, (2) an outer fine-grained CuO layer, (3) an underlying columnar region of Cu_2O, and (4) a thin, fine-grained and porous Cu_2O region near the metal. Thus, it was confirmed that the interaction between CuO and water vapor is not a reason of the weight loss of Cu plate, because if the mass transfer resulted from weight loss of Cu plate occurs, this should take place at the interface of water vapor and the outer copper oxide scale.

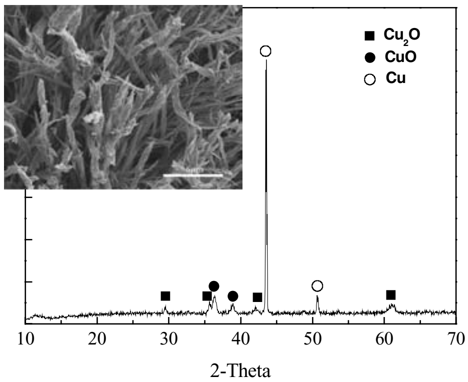

Figure 3 Morphology of Cu plate surface and XRD pattern of Cu plate after copper-water interactions near critical point in higher O_2 ratio (air atmosphere) gas mixture at starting state.

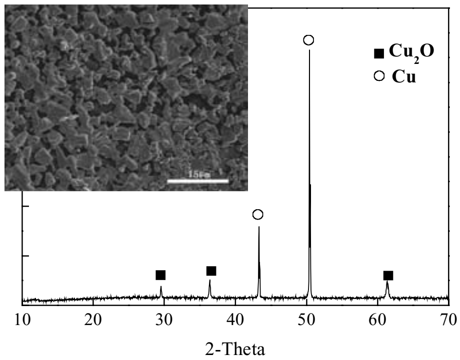

Figure 4 Morphology of Cu plate surface and XRD pattern of Cu plate after copper-water interactions near critical point in 3.75% O_2 ratio gas mixture, 12% water contents at starting state.

3.1.3. Cu_2O (+1)

According to references mentioned above, at the higher oxygen ratio in gas mixture a two-phase scale is formed during copper-water vapor interaction near critical point. An outer layer is CuO, and inner layer is Cu_2O. Some experiments were conducted in order to find out the conditions where the oxygen ratio of gas mixture at starting state supports the formation of Cu_2O stable phase after copper-water vapor interaction. The XRD examination of Cu plate after copper-water vapor interaction, shown in Fig. 4, indicates that only Cu_2O scale was formed on the Cu plate surface in the O_2+N_2 gas mixture with lower O_2 ratio. The color of Cu plate was red that also confirms the formation of Cu_2O at test conditions. The measurement of Cu plate weight before and after experiment reveals that the weight loss of Cu plate occurred at lower O_2 concentration of the gas mixture at starting state condition. The morphology of oxide particles formed on Cu plate surface, shown in Fig. 4, demonstrates that Cu_2O crystal growth takes place in this case. During this interaction the mass transfer from copper surface to water vapor phase provides the weight loss of copper plate. These data indicate that the weight loss of Cu plate occurs at the Cu_2O (+1) chemical state.

3.2. The effect of O_2 on copper-water vapor interactions

As above mentioned, the properties of water vapor near critical point were controlled by temperature and pressure inside autoclave, and the pressure in the autoclave varied with the change of water content in the volume of the autoclave at starting state. Therefore, the effect of O_2 concentration on copper-water interaction near critical point was determined at the constant content of water. For example, the water content in the range 4–12% and the 330∼340°C temperature interval were selected.

3.2.1. Weight loss of copper plate

The weight loss data of Cu plate under different conditions were placed in Table I. According to several testing measurements of weight change of copper plate before and after drying, we can conclude that new phases of Cu species was not formed during drying process. The curve in Fig. 5 shows the experimental weight loss and calculating weight loss of copper plate with respect to the amounts of O_2 presenting in the autoclave at the temperature 340°C, and 8% water contents. The calculating weight loss of copper plate implicates that if oxygen presenting in the autoclave was all used to form cuprous oxide and the whole cuprous oxide formed were removed from copper plate to water vapor phase, the weight loss of copper plate will abbey the calculating weight loss curve. At high temperature and pressure, the possible consumption of O_2 presenting in the autoclave at starting state of reactions is to form oxides on the polished SUS pipe surface and copper surface. At the constant temperature and water concentration, which ensure that the effect of H_2O on Cu-O_2 interaction at tested conditions is equivalent. There is a maximum weight loss of copper plate at 3.75% O_2. This indicates that there is a competitive process that nucleation and growth of copper oxides on Cu surface take place while the copper oxides formed on Cu surface are transferred to water vapor phase due to the Cu-water vapor interactions near critical point. Obviously, this process provided the maximum weight loss of copper plate at 3.75% O_2 ratio and tested conditions, and could be used for the interpretation of the difference in weight loss between experimental and calculating results.

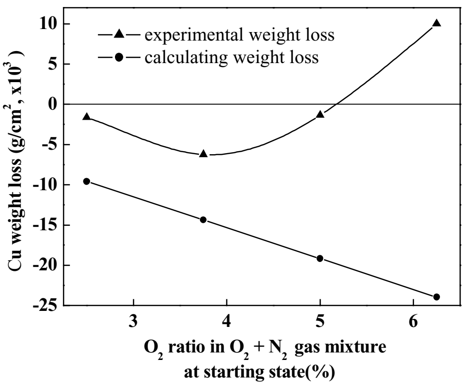

Figure 5 Practical and calculating weight loss of Cu plate after copper-water vapor interactions in various O_2 ratio gas mixture at 8% water contents, 340°C.

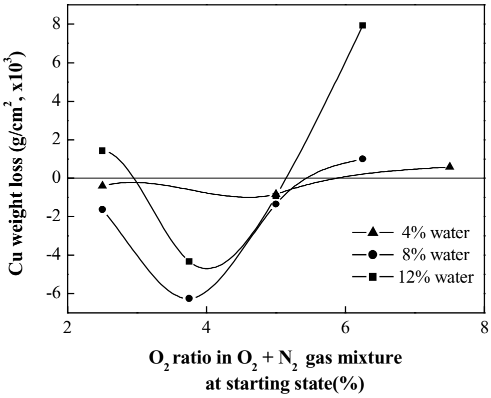

Figure 6 Weight loss of Cu plate in various O_2 ratio gas mixture at various water contents of 4%, 8%, and 12%, 340°C.

Fig. 6 shows the effect of O_2 on copper-water vapor interactions near critical point at various water contents. These results also explain the competitive process on copper surface. As shown in Fig. 6, there is a critical point of O_2 ratio in gas mixture at starting state, where the competitive process is in balance or the weight gain of copper begins to take place. Obviously, the critical point of O_2 in gas mixture decreases with increasing water content. This tendency may be explained by the increasing partial pressure of O_2 at higher water contents or by the effect of H_2O molecular on the defect properties of copper oxide at high temperature. Fig. 7 shows the effect of O_2 on the weight loss of copper plate at the temperature 330°C. There is no difference in the tendency of the critical point of O_2 ratio at both temperatures, whereas at the temperature 340°C, the weight loss of copper plate is approximately one order of magnitude higher than for 330°C.

3.2.2. Morphologies of copper oxides

The effect of O_2 on the change of Cu_2O morphology on copper surface is shown in Fig. 8. At the Cu_2O stable region, the roughness of copper surface is increased with

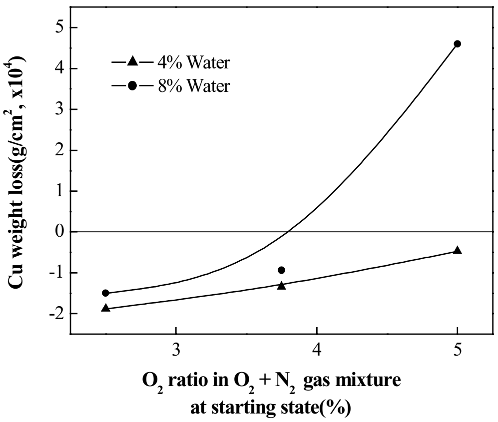

Figure 7 Effect of O_2 on weight loss of Cu plate at 330°C.

TABLE I The weight loss data of Cu plate, (g/cm^2, × 10^3)

		O_2(%)				
	Water(%)	2.5	3.75	5	6.25	7.5
340°C	4	−0.403		−0.836	1	0.583
	8	−1.64	−0.625	−1.35	7.93	
	12	1.42	−4.33	−0.93		
	Calculated at 8%	−9.589	−14.38	−19.18	−23.97	
330°C	4	−0.188	−0.134	−0.047		
	8	−0.15	−0.094	0.46		

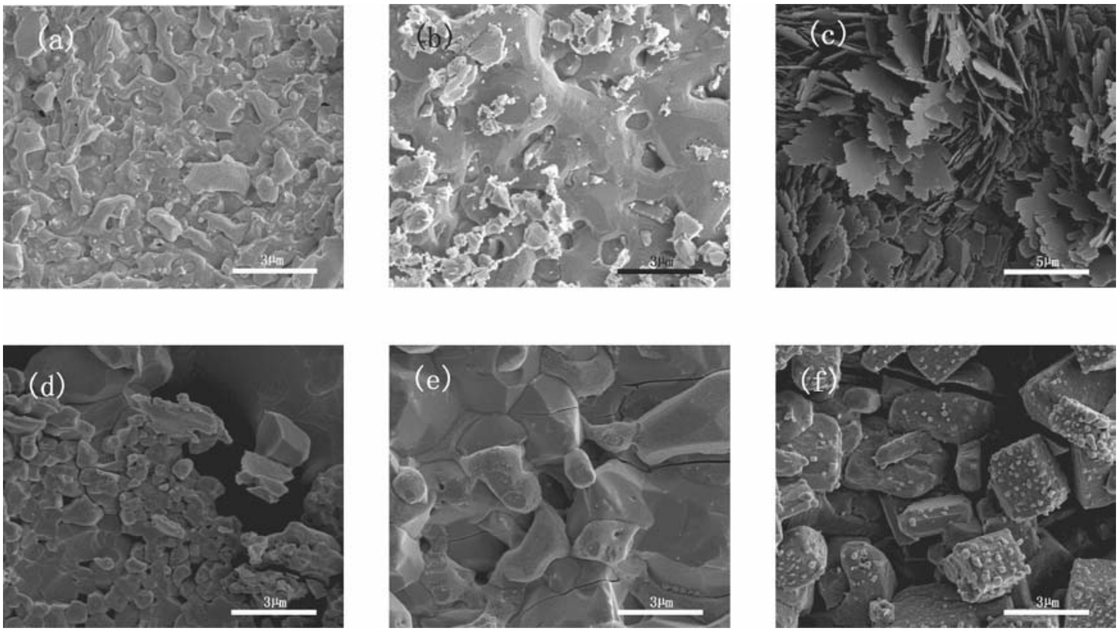

Figure 8 Effect of O_2 on morphology change at 4% water contents, (a) 2.5% (b) 5% (c) 7.5% of O_2 ratio, and at 8% water contents, (d) 2.5% (e) 3.75% (f) 5% of O_2 ratio.

increasing O_2 ratio and water content in the autoclave. It may be due to the boundary growth of Cu_2O in water vapor near critical point. At higher O_2 ratio, the Cu_2O layer formed on the copper surface firstly, and then change into CuO phase. Thus inner Cu_2O layer was protected by outer CuO layer, which made the weight gain occurs.

Fig. 9 shows the morphology of copper species on the surface of mesh and granite after copper-water interaction. The difference in the morphology of copper species suggest that the weight loss of copper plate is not a result of the fracture and spalling of Cu_2O scale formed on the copper surface. EDX point analysis

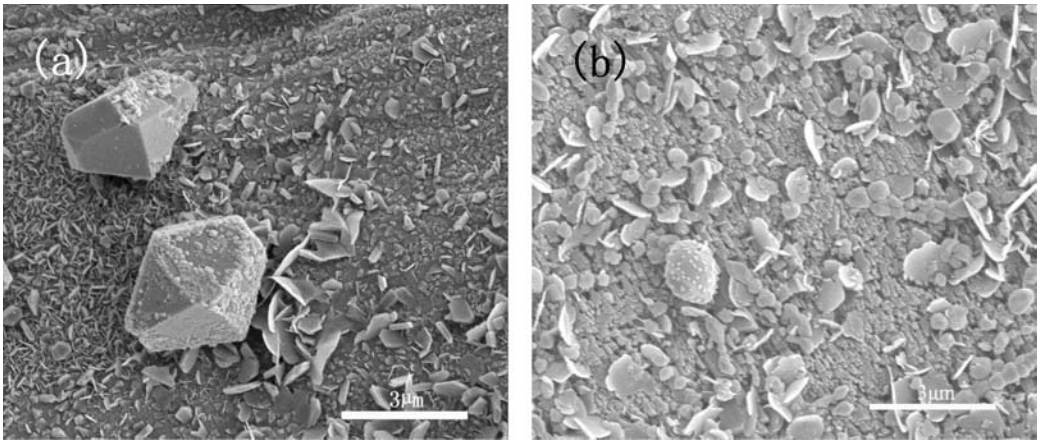

Figure 9 Difference in morphology of copper species on the mesh surface (a) and granite surface (b).

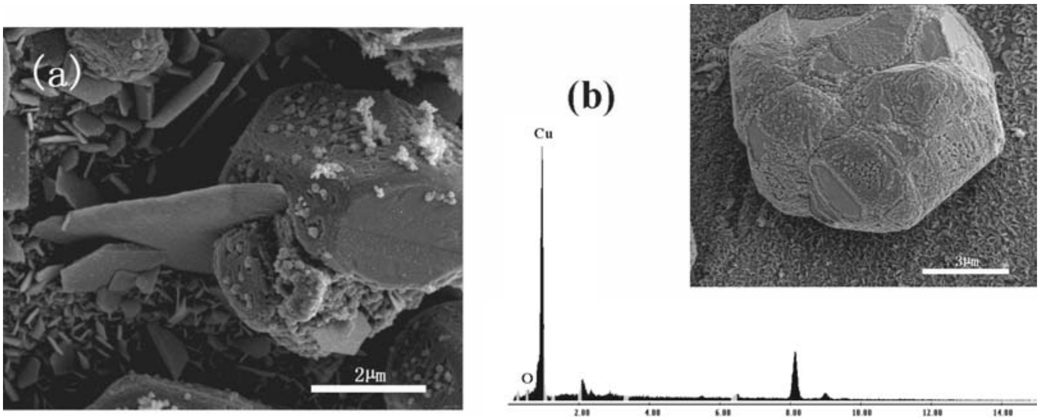

Figure 10 Morphology of copper oxide species on the mesh surface, (a) two combined particles with difference composition, (b) particle on which spot materials exist and its EDX area analysis pattern.

of copper species composition demonstrates that the copper species on the mesh surface consist of 99.51% copper and 0.49% oxygen, while that on the granite surface consist of 98.46% copper and 1.54% oxygen. Compare to Cu_2O composition (88.9% copper and 11.1% oxygen), it is perhaps due to the decomposition of cuprous oxide or a deviation of stoichiometry of Cu_2O [14].

Fig. 10a and b demonstrate the morphology ofcuprous oxide on the mesh surface. From this, one could speculate the process of mass transfer of copper species from copper plate to another place via water vapor phase. EDX area analysis of materials on the mesh surface (Fig. 10 a) indicate that the single sheet like crystal consists of Fe, Ni, Si, and O elements, and the sphere like particle is the copper oxide. This indicates that two particles were combined during crystal growth process. The result of EDX area analysis and morphology of spot materials on the surface of sphere particle (Fig.10 b) suggest the recrytalliztion of copper species from water vapor phase, and this also suggests that the combination of sheet and sphere like species is achieved by crystal growth.

3.3. Images of mass transfer

Previous works have mentioned that the effect of H_2O molecular on Cu–O interaction at high temperature is to accelerate the oxidation rate of copper, or to surprisingly make Cu_2O islands formed on the copper surface reduced immediately. These explain that H_2O molecular significantly influence the physicochemical properties of Cu_2O and accelerate the velocity of formation or decomposition of cuprous oxide at high temperature oxidation process. In this case, one could expect more interesting phenomena in Cu_2O-water vapor interaction near critical point which has no coexisting equilibrium water, and its process is more complex. It is apparent from the weight loss data obtained that copper was firstly oxidized by O_2 to form Cu_2O below the critical point of O_2 ratio at stating state, which [15] is known to be a metal-deficient, p-type semiconductor with cation vacancies and electro holes as the primary defects, and then Cu_2O at the nucleation stage will be dissolved in water vapor after Cu_2O-water vapor complex interactions, and finally the dissolved species of copper are recrystallised on the surface of mesh or granite. This process can be used to interpret why the weight loss of copper is great higher than the reported data with respect to the solubility of cu or its oxides [10], and the competitive process present will make it more complex.

4. Conclusion

It is obvious that the weight loss of copper plate in water vapor is due to the presence of O_2. There is a critical point of O_2 ratio of gas mixture at stating state, and the weight loss of copper will occur due to the formation of Cu_2O below this critical point of O_2 ratio, whereas, if CuO is formed above the critical point, the weight gain of copper plate will occur.

The mass transfer via water vapor phase is carried out at Cu_2O stable state, and Cu_2O will dissolve to water vapor phase during Cu_2O-water vapor interactions at Cu_2O nucleation stage, which makes the weight loss of copper great higher than the reported data with respect to the solubility of Cu or its oxides. The morphology of copper species on the surface of mesh and granite illuminates indirectly that the mass transfer is achieved by dissolution and recrystallization.

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