Original article

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Effect of small amounts of chalcogen alloying elements on the oxidation resistance of copper

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Abstract: The effect of small amounts of chalcogen alloying elements (S, Se and Te) on the oxidation resistance (OR) of Cu has been investigated at 300–800 °C in 0.1 MPa oxygen atmospheres. Compared to pure copper, the addition of S, Se and Te could effectively improve the OR below 600 °C mainly owing to the chalcogen-element inclusions which hinder the diffusion of Cu. However, it becomes weak above 800 °C. In contrast, the failure at 800 °C is associated with the absence of those inclusions. The results are discussed in detail by the thermodynamic methods.

Keywords: chalcogen; copper; oxidation resistance; thermodynamic.

1 Introduction

As an oldest metal, copper possesses a very wide range of properties that makes it invaluable in the socio-economic development. Up to now, Cu and its alloys are still important in serving lives of people in many applications, such as micro-electric, cooling devices and the effective antimicrobial materials due to their excellent properties as high electrical and heat conductivity and good machinability (Shinato et al. 2020; Tan and Roy 2007). Upon these applications, however, Cu easily suffers from serious oxidation. Hence, ways should be found to address this issue.

In previous publications (Birks et al. 2006; Hauffe 1956; Sarrazin et al. 2000; Tylecote 1950; Zhou 2009; Zhu et al. 2006, 2014), much attention has been made to investigate the oxidation resistance (OR) of Cu and its alloys. It was reported that the OR of Cu can be influenced by the presence of impurities. By oxidizing 99.9999 wt% Cu (6N Cu), oxygen-free Cu (99.99 wt%, 4N), and electrolytic touch-pitch Cu (TPC, 2N Cu) (Valensi 1948; Zhu 2003; Zhu et al. 2003, 2004a, 2005, 2002), it was found that, compared to 6N Cu, the OR of 4N Cu is enhanced slightly below 800 °C (Zhu et al. 2004b). This enhancement is contributed from the relative fast grain boundary diffusion of Cu and O, since the trace impurities result in slow lateral growth of Cu₂O grains. In contrast, the oxidation rate of 2N Cu was enhanced at 800 °C but impeded at 400 °C, owing to the main impurities such as Ni (1090), Sb (960), As (890), Pb (600), Se (420), Bi (375), Te (240), Sn (140) and Au (120 ppm) (Zhu et al., 2003, 2005). The accumulation of impurities at the Cu₂O/Cu interface can effectively slow down the oxidation rate of Cu. In particular, the non-metallic impurities of chalcogen elements Se and Te are believed responsible for the different ORs by impeding the diffusion of both Cu and O regarding the temperature. The exciting result suggests that the chalcogen elements (S, Se and Te) should play an essential role in protecting Cu from oxidation. Moreover, since Se is an environment-friendly element and beneficial to the human health. Thus, it is necessary to study how small amounts of S, Se and Te affect the oxidation behaviour of pure Cu.

In fact, the chalcogen alloying elements (S, Se and Te) are the main non-metallic impurities in Cu introduced primarily by smelting because of the product of about 80% pure Cu coming from the Cu₂S ore. It is thus of much interest to investigate how S, Se and Te would influence the OR of Cu (Medved et al. 2004; Zhu et al. 2005). Medved studied the OR of Cu-1.65 wt% Se alloys at 800 °C, where the internal oxidation of Cu₂Se took place, increasing the oxidation rate when compared to pure Cu (Faes et al. 2019; Medved et al. 2004). However, the effect of Cu₂Te and Cu₂S on Cu oxidation process was not discussed in the paper. According to the phase diagrams (Chakrabarti and Laughlin 1983; Okamoto 2017; Pashinkin and Fedorov

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2003), the dissolution of Se and S in Cu is 9 and 4.5 ppm at 400 °C, while they are 150 and 80 ppm at 800 °C, respectively. Moreover, the dissolution of Te in Cu is 3 ppm at 600 °C and 75 ppm at 800 °C. In light of this, when 0.1 wt % chalcogen alloying element is added in pure Cu, Cu-M (M: S, Se and Te) compounds or inclusions will form. This means that Cu₂M inclusions should be present in specimens on the basis of phase diagrams. However, how the Cu₂M alloys (M: S, Se and Te) influence the oxidation behaviour of the Cu alloys is still not clear.

In the field of materials science, traditional thermodynamics is a powerful tool to predict stable phase structure and surface properties of macroscopic materials under a certain ambient condition (Jiang et al. 2002; Su et al. 2011; Zhu et al. 2009). Since the actual content of the elements in Cu are very low, the concentration of Cu₂M should be very less. It is very difficult to observe directly the reactions between Cu₂M and O₂/CuO as well as the products of CuO or Cu₂O. However, thermodynamics affords a possible method for explanation on these reactions and the products. Considered that the oxidation of metals is essentially a thermodynamic process, the corresponding thermodynamic data can therefore be used to analyse the possible reactions and the products during oxidation process (Zhu et al. 2005). Thus, the thermodynamic method is beneficial to understand how the chalcogen alloying elements affect the oxidation behaviour of Cu by investigating the role of the Cu-M compounds. Moreover, there is a very low solubility of the chalcogen elements in Cu (Chakrabarti and Laughlin 1983; Okamoto 2017; Pashinkin and Fedorov 2003) according to the Cu-M binary phase diagrams. Therefore, the alloying elements, including S, Se and Te, are usually present as Cu₂M compounds in Cu as aforesaid. If Cu₂M react with O₂ and/or CuO to form Cu₂O without any other new solid inclusion formed, a thin CuO film and a thick Cu₂O layer will normally form near the surface. Consequently, the effect of chalcogen elements on the OR of pure Cu would be weak. However, if the Cu₂M inclusions cannot react with O₂ and CuO, or some new additional solid inclusions formed, such as TeO₂, the outward diffusion of Cu should be deleteriously hindered, lowering the oxidation rate of Cu. Such a prediction can be performed with the thermodynamic method. A previous work (Zhu et al. 2005) predicted the influence of Se and Te on the OR of 2N Cu using the thermodynamic method, and concluded that the different ORs are attributed to Cu₂Se and Cu₂Te inclusions which can react with O and facilitate the oxidation process. It should be pointed out that, however, such a result is somewhat arbitrary, because the investigation on the effect of other impurities was not provided. Furthermore, the influence of the S element or the Cu₂S inclusions on the

oxidation of pure Cu was not provided either. Besides these, the influence from the change in entropy before and after the reaction was not given either in the thermodynamic approach. To better understand the effect of the chalcogen alloying elements on the OR of pure Cu, a systematic investigation is still necessary.

In this paper, the effect of small amounts of chalcogen alloying elements (S, Se and Te) on the OR of Cu has been investigated systematically by experiments and discussed using the thermodynamic method. The surface/cross-sectional morphologies of the specimens oxidized at both 500 and 800 °C in 0.1 MPa O₂ atmospheres have been observed. The Gibbs free energy of Cu-O-S, Cu-O-Se and Cu-O-Te systems for standard state and the change in entropy in the thermodynamic reaction are also discussed. The theoretical prediction has an ability to provide an in-depth comprehension.

2 Materials and methods

2.1 Experimental characterization

The experimental Cu-0.1 wt% M (M: S, Se and Te) alloys were fabricated by pure Cu (99.9999 wt%, 6N) with Se (99.9 wt%), S (99.9 wt%) or Te (99.9 wt%) as alloying elements using a hydrogen plasma arc melting technique (Liu et al. 2008). Herein, the alloys are marked as CuS, CuSe and CuTe, respectively. The actual concentrations of the added elements were 0.038 wt% for S, 0.089 wt% for Se and 0.084 wt % for Te. The specimens were prepared by cutting the ingots, cold-rolling into 0.5 mm sheets and punching into a diameter of 5 mm discs. Before punching, the sheets were grounded by 2000-grit SiC then mechanically polished with 0.5 µm diamond sprays. Also, the specimens were completely cleaned in acetone and ethanol solution by an ultrasonic bath after every treatment process.

The specimens were annealed in the high purity hydrogen atmosphere at 600 °C for 1440 min. The oxidation tests were conducted between 300 and 800 °C in 0.1 MPa O₂ atmospheres at the flow rate of 200 ml/min from 8 to 80 h. Mass gained of the specimens was recorded before and after oxidation using an HXD-1000 electro-balance with the precision of 0.1 µg. The ratio of Cu-M alloys to pure Cu was calculated according to the mass gained. The surface and cross-sectional morphologies of samples were carefully observed using scanning electronic microscope (SEM, JSM-5600). Before observation, the cross-section of the specimens was etched by a 0.05 M HCl and 0.1 M FeCl₃ solution, where the solvent consists of 67 vol% water and 33 vol% ethanol. As a comparison, the samples of pure Cu were examined at the same experimental conditions.

2.2 Thermodynamic prediction

The Gibbs free energy ΔG of all the possible reactions between Cu-M compounds and O₂/CuO was calculated to judge if the Cu₂S, Cu₂Se and Cu₂Te inclusions can react with O₂ or CuO converting to CuO or Cu₂O or if there are any additional solid inclusions newly formed. All the

data required for calculation of ΔG were obtained in reference (Barin et al. 1977).

3 Results and discussion

3.1 Experimental results

To express the OR of specimens, Figure 1 shows the ratios of the mass gain of Cu-M alloys to that of pure Cu oxidized at 300–800 °C. Obviously, the ratio values of Cu-M alloys are lower than one between 300 and 600 °C, demonstrating that ORs of Cu-M alloys can be improved below 600 °C. Note that, the improvement of CuS is less obvious than those of CuTe and CuSe while CuSe exhibits the best OR. When the oxidation temperature increased above 700 °C, the ratio values become larger than one indicating the ORs turn weak at these tested temperatures. At 700 °C, the addition of S renders Cu to have the fastest oxidation rate in contrast with that of CuSe exhibiting the maximum mass gain at 800 °C. In one word, the addition of chalcogen alloying elements improves the OR of pure Cu below 600 °C, but impairs it above 700 °C.

Figure 2 displays the typical surface and cross-sectional morphologies of pure Cu oxidized at 500 °C (Figure 2A, B) and 800 °C (Figure 2C, D) respectively. At 500 °C, high-density-long whiskers are observed on the surface of pure Cu (Figure 2A). The corresponding cross-sectional morphology shows that the oxide layer consists

of the double-layer structure including an outer thin CuO layer and an inner-columnar-thick Cu₂O layer (Figure 2B) (Su et al. 2011). By careful measurement, the thickness of the Cu₂O layer is ~190 μm. When the temperature increased to 800 °C, the surface morphology changes from the whiskers (Figure 2A) to the irregular shape with ridges along the grain boundaries (Figure 2C), comprising CuO grains (Zhu et al. 2005). The corresponding cross-section of alloys oxidized at 800 °C for 4 h (Figure 2D) shows similar oxide layer appeared at 500 °C (Figure 2B). But the thickness of the oxide layer seems thicker compared to that of 500 °C, obviously, a thick columnar and continuous Cu₂O layer formed beneath an outer thin CuO layer in Figure 2D.

To compare the OR, Figure 3 shows the typical surface and cross-sectional morphologies of CuS oxidized at 500 (Figure 3A, B) and 800 °C for 4 h (Figure 3C, D), respectively. It can be seen that the relative long whiskers appear on the surface of CuS alloy (Figure 3A) compared to pure Cu (Figure 2A). Some cavities also can be found on the surface as pointed by arrows. The microstructure of the cross-section is similar to that of pure Cu containing an external thin CuO layer and an interior thick Cu₂O layer. However, the oxide layer is ~133 μm (Figure 3B), which is thinner than that of pure Cu (Figure 2B). This indicates that the addition of S could improve effectively the OR of pure Cu at 500 °C, accordance with results in Figure 1. When the temperature increased to 800 °C, the surface is rougher (Figure 3C) than the case of pure Cu (Figure 2C). By contrast, the oxide layer on CuS alloys is denser than pure Cu, implying that the oxidation rate of CuS is relatively higher than pure Cu. Moreover, the oxide scale of CuS is thicker than that of Cu, which manifests that the addition of S accelerates the oxidation at high temperature.

3.2 Theoretical prediction

According to previous papers (Wagner 1940; Zhu et al. 2004a), a thin and uniform CuO film might be formed on the surface of Cu by the reaction $\text{Cu} + 1/2\text{O}_2 = \text{CuO}$ usually for the oxidation of pure Cu. With gradual growth of CuO layer, the oxygen potential will descend at the CuO/Cu interface. Once it reaches the potential where Cu₂O can exist stably (McKewan and Fassell 1953), Cu₂O will nucleate and grow in terms of the formula, $\text{Cu} + \text{CuO} = \text{Cu}_2\text{O}$. Then, Cu₂O grow in volume and coalesce to form the Cu₂O islands. Subsequently, continued oxidation will result in a successive Cu₂O layer under CuO. Refer to the oxidation mechanism of pure Cu (Zhu et al. 2005), the role of the Cu₂S inclusions in the development of the thin

Figure 1: Ratio of the mass gain of CuS, CuTe and CuSe alloys to that of pure Cu oxidation at 300–800 °C from 4 to 48 h.

Figure 2: Surface and cross-sectional morphologies of pure Cu at 500 and 800 °C: (A) surface, 500 °C – 8 h; (B) cross-section, 500 °C – 48 h; (C) surface, 800 °C – 4 h; (D) cross-section, 800 °C – 4 h.

Figure 3: Surface and cross-sectional morphologies of CuS alloy at 500 and 800 °C: (A) surface, 500 °C – 8 h; (B) cross-section, 500 °C – 48 h; (C) surface, 800 °C – 4 h; (D) cross-section, 800 °C – 4 h.

CuO films will be discussed on the basis of the probable reactions as below:

The calculated Gibbs free energies ΔG and entropy change ΔS of Equations (1)–(4) were plotted as a function of

temperature in Figure 4 according to the thermodynamic data obtained from the reference (Barin et al. 1977). Data used in Equations (1)–(4) have been listed in Tables 1 and 2. As for the data are not available in the reference, such as G at 95.15 °C, $G_{95.15} = (G_{126.85} - G_{26.85}) \times 68.3/100 + G_{26.85}$. Therefore, $\Delta G_{(1)} = G_{\text{S(s)}} + 2 \times G_{\text{CuO(s)}} - G_{\text{O}_2(\text{g})} - G_{\text{Cu}_2\text{S(s)}}$, $\Delta G_{(2)} = G_{\text{S(l)}} + 2 \times G_{\text{CuO(s)}} - G_{\text{O}_2(\text{g})} - G_{\text{Cu}_2\text{S(s)}}$, $\Delta G_{(3)} = G_{\text{S(g)}} + 2 \times G_{\text{CuO(s)}} - G_{\text{Cu}_2\text{S(s)}}$, $\Delta G_{(4)} = G_{\text{SO}_2(\text{g})} + 2 \times G_{\text{CuO(s)}} - 2 \times G_{\text{O}_2(\text{g})} - G_{\text{Cu}_2\text{S(s)}}$; similarly, $\Delta S_{(1)} = S_{\text{S(s)}} + 2 \times S_{\text{CuO(s)}} - S_{\text{O}_2(\text{g})} - S_{\text{Cu}_2\text{S(s)}}$, $\Delta S_{(2)} = S_{\text{S(l)}} + 2 \times S_{\text{CuO(s)}} - S_{\text{O}_2(\text{g})} - S_{\text{Cu}_2\text{S(s)}}$, $\Delta S_{(3)} = S_{\text{S(g)}} + 2 \times S_{\text{CuO(s)}} - S_{\text{O}_2(\text{g})} - S_{\text{Cu}_2\text{S(s)}}$, $\Delta S_{(4)} = S_{\text{SO}_2(\text{g})} + 2 \times S_{\text{CuO(s)}} - 2 \times S_{\text{O}_2(\text{g})} - S_{\text{Cu}_2\text{S(s)}}$.

Figure 4: (A) The Gibbs free energy ΔG of the reaction of Cu-S-O system. Considering the standard state is essential for all the components. (1) $\text{Cu}_2\text{S(s)} + \text{O}_2(\text{g}) = 2\text{CuO(s)} + \text{S(s)}$; (2) $\text{Cu}_2\text{S(s)} + \text{O}_2(\text{g}) = 2\text{CuO(s)} + \text{S(l)}$; (3) $\text{Cu}_2\text{S(s)} + \text{O}_2(\text{g}) = 2\text{CuO(s)} + \text{S(g)}$; (4) $\text{Cu}_2\text{S(s)} + 2\text{O}_2(\text{g}) = 2\text{CuO(s)} + \text{SO}_2(\text{g})$; (5) $2\text{CuO(s)} + \text{Cu}_2\text{S(s)} = 2\text{Cu}_2\text{O(s)} + \text{S(s)}$; (6) $2\text{CuO(s)} + \text{Cu}_2\text{S(s)} = 2\text{Cu}_2\text{O(s)} + \text{S(l)}$; (7) $2\text{CuO(s)} + \text{Cu}_2\text{S(s)} = 2\text{Cu}_2\text{O(s)} + \text{S(g)}$; (8) $6\text{CuO(s)} + \text{Cu}_2\text{S(s)} = 4\text{Cu}_2\text{O(s)} + \text{SO}_2(\text{g})$. (B) The entropy change ΔS of the corresponding reactions in (A).

It can be shown that at both 500 and 800 °C, ΔG of Equation (3) is positive, while these of Equations (1), (2) and (4) are negative. These reactions of Equations (1), (2) and (4) are supposed to occur towards the positive side, and Equation (4) should proceed most easily because of the most negative ΔG . Considering that small amounts of liquid S may volatilize at 800 °C, however, it can hardly affect the formation of the thin CuO film. On the other hand, the influence of Cu_2S inclusions below the CuO layer on the formation of Cu_2O nucleation is discussed according to the probable reactions as below:

The Gibbs free energy values, ΔG , of Equations (5)–(8) were also plotted in Figure 4A. It can be seen that ΔG values of Equations (5)–(7) are positive at both 500 and 800 °C, while that of Equation (8) is negative, showing that Cu_2S can be converted to Cu_2O at both 500 and 800 °C. Furthermore, ΔG of Equation (8) is more negative at 800 °C than that at 500 °C, suggesting its oxidation is more serious at 800 °C.

Figure 4B plots the entropy change of reactions (1)–(8). It can be figured out that the entropy changes ΔS of reactions (1)–(4) are negative while those of reactions (7) and

Table 1: The thermodynamic data used in Equations (1)–(4) (Barin et al. 1977); (G: kJ/mol).

$T(^{\circ}\text{C})$	$G_{\text{Cu}_2\text{S(s)}}$	$G_{\text{O}_2(\text{g})}$	$G_{\text{CuO(s)}}$	$G_{\text{S(s)}}$	$G_{\text{S(l)}}$	$G_{\text{S(g)}}$	$G_{\text{SO}_2(\text{g})}$
25	-115.801	-61.165	-168.762	-9.557	–	226.942	-370.820
26.15	-116.016	-61.544	-168.841	-9.617	–	226.631	-371.279
95.15	-124.617	-75.8727	-172.222	-11.984	–	214.920	-388.671
102.85	-125.587	-77.488	-172.603	-12.322	–	213.600	-390.632
115.21	-127.411	-80.081	-173.215	-12.762	-12.762	211.480	-393.779
126.85	-129.129	-82.523	-173.791	–	-13.277	209.484	-396.743
226.85	-145.325	-104.262	-179.915	–	-18.181	191.759	-423.297
326.15	-163.442	-126.626	-187.029	–	-23.867	173.582	-450.787
426.15	-183.097	-149.528	-194.995	–	-30.124	155.034	-479.099
446.85	-187.188	-154.203	-196.738	–	-31.470	151.371	-484.907
526.85	-204.137	-172.901	-203.709	–	-36.856	136.717	-508.140
608.97	-222.294	-192.442	-211.413	–	-42.710	120.552	-532.528
626.85	-226.247	-196.697	-213.091	–	–	117.032	-537.838
726.85	-249.275	-220.875	-223.077	–	–	97.651	-568.131
826.85	-273.125	-245.402	-233.618	–	–	78.052	-598.970
926.85	-297.720	-270.251	-244.669	–	–	58.256	-630.309

Table 2: The thermodynamic data used in Equations (1)–(4) (Barin et al. 1977); (S: J/mol).

$T (^{\circ}\text{C})$	$S_{\text{Cu}_2\text{S}(\text{s})}$	$S_{\text{O}_2(\text{g})}$	$S_{\text{CuO}(\text{s})}$	$S_{\text{S}(\text{s})}$	$S_{\text{S}(\text{l})}$	$S_{\text{S}(\text{g})}$	$S_{\text{SO}_2(\text{g})}$
25	116.152(α)	205.147	42.593	32.056	–	167.828	248.221
26.85	118.628	205.329	42.855	32.197	–	167.974	248.468
95.15	133.196	211.163	51.647	37.006	–	172.520	256.614
102.85	134.838	211.821	52.638	38.404	–	173.032	257.533
102.85	144.463(β)	–	–	–	–	–	–
115.21	147.641	212.877	54.229	39.414	43.846	173.854	259.007
126.85	150.634	213.871	55.727	–	44.752	174.629	260.395
226.85	172.331	220.693	66.457	–	53.413	179.668	270.441
326.15	189.378	226.451	75.595	–	59.947	183.731	279.179
426.15	203.292	231.466	83.548	–	65.05	187.137	286.901
446.85	205.786	232.357	84.958	–	65.947	187.724	288.282
446.85	207.414(γ)	–	–	–	–	–	–
526.85	216.142	235.921	90.598	–	69.534	190.07	293.807
608.97	224.128	239.214	95.8059	–	73.01	192.185	298.931
626.85	225.867	239.931	96.939	–	–	192.645	300.047
726.85	234.532	243.578	102.713	–	–	194.939	305.734
826.85	242.342	246.922	108.021	–	–	197.008	310.956
926.85	249.447	250.01	112.941	–	–	198.891	315.781

(8) are positive. This indicates the slope in Gibbs free energy of reactions (1)–(4) is positive but negative for reactions (7) and (8). ΔS of reactions (5) and (6) are almost 0, resulting in the basically constant of Gibbs free energy. Also, from Figure 4B, we can find out that the absolute values of reactions (4) and (8) are relatively large than others, leading to a quick change in the Gibbs free energy as temperature rises.

Similar to Cu_2S , the inclusions of Cu_2Se and Cu_2Te also play a vital role in impeding the oxidation of Cu at low temperature (Zhu et al. 2005). At temperature below 700 °C, Cu_2Se will react with O and convert to CuO on account of the negative ΔG of several possible reactions, such as $\text{Cu}_2\text{Se}(\text{s}) + \text{O}_2(\text{g}) = 2\text{CuO}(\text{s}) + \text{Se}(\text{s})$, $\text{Cu}_2\text{Se}(\text{s}) + 3/2\text{O}_2(\text{g}) = 2\text{CuO}(\text{s}) + \text{SeO}(\text{g})$, and $\text{Cu}_2\text{Se}(\text{s}) + 2\text{O}_2(\text{g}) = 2\text{CuO}(\text{s}) + \text{SeO}_2(\text{g})$. However, further reactions that convert CuO to Cu_2O , involving $2\text{CuO}(\text{s}) + \text{Cu}_2\text{Se}(\text{s}) = 2\text{Cu}_2\text{O}(\text{s}) + \text{Se}(\text{s})$, $4\text{CuO}(\text{s}) + \text{Cu}_2\text{Se}(\text{s}) = 3\text{Cu}_2\text{O}(\text{s}) + \text{SeO}(\text{g})$ and $6\text{CuO}(\text{s}) + \text{Cu}_2\text{Se}(\text{s}) = 4\text{Cu}_2\text{O}(\text{s}) + \text{SeO}_2(\text{g})$, cannot occur by virtue of their positive ΔG values. These results suggest that the addition of Se can hinder the oxidation process at low temperature. Nevertheless, at elevated temperature above 700 °C, the first three reactions proceed towards right side due to the negative ΔG , which converts Cu to CuO. Besides these, the reaction $6\text{CuO}(\text{s}) + \text{Cu}_2\text{Se}(\text{s}) = 4\text{Cu}_2\text{O}(\text{s}) + \text{SeO}_2(\text{g})$ also renders CuO transform to Cu_2O with the negative ΔG at elevated temperature. Therefore, the improvement in OR is weakened at high temperature. As for Cu_2Te in CuTe alloy, in brief, the solid TeO_2 inclusions newly formed at 500 °C will hinder the diffusion for Cu and O, impeding the Cu_2O

nucleation and its growth. Conversely, such an obstruction effect will decrease at 800 °C since TeO_2 from solid becomes to liquid.

Based on the above calculation and discussion, the Cu_2M inclusions play a different role in the Cu oxidation dependent on the oxidation temperature. Compared to S, small amounts of addition of Se and Te can effectively improve the OR of pure Cu at 500 °C. The reason is that the Cu_2Se and TeO_2 inclusions formed could hamper the formation of the thin CuO layer and/or the nucleation of Cu_2O islands. However, when the temperature is rising to 800 °C, the OR of Cu alloys is weaker than that of pure Cu. This can be explained that Cu_2M will be converted to CuO and Cu_2O during oxidation without producing any additional solid inclusions, accelerating the oxidation. Note that the value of ratio somewhat decrease between 700 and 800 °C, meaning the mass gained decreases during oxidation process. As mentioned, the Equations (4) and (8) will take place preferentially for CuS alloy. Thus, the SO_2 gas will release leading to a little reduction of mass gained and further obtain the relative little value of ratio at 800 °C. This explanation is also effective for CuSe alloy.

3.3 Influence of chalcogen-related inclusions on OR of Cu–M alloys

In view of the experimental results, the OR of Cu–M alloys with small amounts of the chalcogen elements can be enhanced at 500 °C but weakened at 800 °C, especially for

CuSe and CuTe alloys. This is validated by the thermodynamic prediction. Compared to Cu-S alloy, the obviously improved OR for the CuSe and CuTe alloys at 500 °C should be ascribed to the presence of the Cu₂Se and TeO₂ inclusions, respectively. On the other hand, the failure in the OR at 800 °C for all the Cu-M alloys should be related to the absence of those inclusions, which are conducive to the diffusion of Cu atoms. This result suggests that the thermodynamic method is effective for characterizing the effect of chalcogen alloying elements on the OR of the pure Cu.

The oxidation of these Cu alloys is dominated by the grain boundary diffusion at low temperature below 600 °C, while by the lattice diffusion at high temperature above 700 °C (Zhu et al. 2006). This is induced by the fact that the columnar oxide grains are long but thin at low temperature, while they become coarse at high temperature. On the other hand, the impurities in Cu will be segregated to grain boundaries during solidification process for stabilizing the grain boundaries and releasing the local stress there (Hu et al. 2017; Yamakov et al. 2003). Owing to these, the improvement in the OR of CuSe and CuTe alloys at low temperature should be induced by the reason that the grain boundary diffusion is impeded by the segregation of the M-related inclusions near the grain boundaries (Zhu et al. 2003). The accumulation of the M-related inclusions at the Cu₂O/Cu interface should also have contribution to the improvement in the OR (Medved et al. 2004).

Note that, although the thermodynamic prediction shows that S has a less influence on the OR of pure Cu, the actual OR of CuS alloy measured in Figure 1 is still somewhat improved at low *T* below 700 °C compared to pure Cu. This improvement might be relevant to the segregation of S-related inclusions at grain boundaries, hindering the diffusion of Cu and O.

Owing to the above discussion, the chalcogen elements should play an essential role in protecting Cu from oxidation at the temperature below 600 °C. Especially, as an environment friendly and human healthy element, one may expect that Se is preferential for taking such a role.

4 Conclusions

The effect of the chalcogen alloying elements on the oxidation resistance (OR) of pure Cu was examined at 300–800 °C in 0.1 MPa O₂ atmospheres. The chalcogen elements can improve the OR of pure Cu at 500 °C especially for the CuSe and CuTe alloys, but this role is much weakened at 800 °C. According to the thermodynamic prediction, the improved OR at 500 °C is attributed to the Cu₂Se and TeO₂ inclusions presented at the grain boundaries of the alloys hindering the

atomic diffusion. As for the failure at high temperature, it is originated from the reactions of Cu-M (M: S, Se and Te) alloys with O₂ and then with CuO without inclusions newly formed, accelerating the oxidation. The experimental observation agrees well with the prediction results for the oxidation of Cu-M alloys. In addition, the improved OR of Cu-M alloys at low temperature might also be related to the impeded grain boundary diffusion due to the segregation of the M-related inclusions to grain boundaries. As an environment friendly and human healthy element, one may expect that Se is preferential for taking a role in the Cu anti-oxidation.

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