Effect of Alloying Element of S, Se or Te on Oxidation Resistance of Cu at 573-873 K

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Abstract: The influence of alloying element S, Se or Te on the oxidation resistance of pure Cu was studied by oxidizing in 0.1 MPa pure oxygen atmosphere at 573-873 K in comparison with a 6N Cu (99.9999 wt.%). The addition of S, Se or Te is found to improve the oxidation resistance of Cu remarkably. This improvement is contributed from the accumulation of alloying element at the Cu_2O/Cu interface and segregation of alloying elements at grain boundaries in Cu_2O.

Keywords: Pure Cu, oxidation resistance, oxygen family element.

1. INTRODUCTION

Cu is usually employed in cooling devices, including water-cooled Cu fingers, panels and tapholes, because of its high strength and high thermal conductivity at elevated temperatures [1]. The development of electronics industry has led to the Cu/low-*k* dielectric materials, which have been rapidly replacing conventional Al-based interconnects due to its excellent electric conductivity (1.67 $\mu\Omega$cm) for bulk and superior electro-stress-migration resistance. These applications require Cu components with unique high reliability conductivity coupled with thermal stability. Cu has been also extensively studied as a typical metal to understand the oxidation resistance (OR) mechanism of metals at high temperature. Hence, knowledge on and understanding of the high temperature oxidation of Cu alloys is important in experimentally and theoretically as referred above [2, 3].

Recent papers [4-10] revealed that the oxidation activation energies of Cu were very different as reviewed in Table **1**. As can be seen that the value of oxidation activation energy at 623-823 K for OFHC Cu [7] is 84 kJ/mol, which is higher than that of 52 kJ/mol for a 2N Cu [9] and 40 kJ/mol for a floating zone refined Cu [9-10] a 6N Cu [10]. Thus, it has to consider the effect of the impurity on the OR of Cu. Especially, Zhu *et al.* [6] found that the OR of Cu with small amounts of impurity is better than that of the high-purity Cu owing to the possible impurity layer formed at the Cu/Cu_2O interface.

It is well-known that trace amounts of S, Se or Te are the main non-metallic impurity in pure Cu. Their incorporation into pure Cu is possibly caused by two ways [9]: one is that the impurity elements are released and dissolved in Cu when melting because of the product of about 80% pure Cu

coming from the Cu_2S ore; the other is that Cu reacts with S (Se or Te) or S (Se or Te)-containing materials in surroundings. As known, the effect of the metallic alloying elements, such as Al, Mg, Fe and Ni, on the high temperature OR of Cu has been studied extensively. Among them, the alloying element Al has been found to improve the OR of pure Cu [11-13]. However, few attempts have been made to study the effect of the oxygen family elements as S, Se or Te. To further enlarge the application of Cu, it is therefore, necessary to study how the oxygen family elements will affect the oxidation behaviors of Cu at 573 - 873 K because of high temperature of encapsulation in microelectronics.

Table 1. Values of Oxidation Activation Energy for Pure Cu at 573-873 K. Noting that the Results of the Present Work were Given for Comparison

Type of Cu	Temperature (K)/ Atmosphere (10^5MPa)	Oxidation Activation Energy (kJ/mol)	Reference
5N	723-1023 / O_2 or air	84	Park and Netasen [4]
OFHC	573-773 / air	39	Tylecote [5, 6]
OFHC	573-823 / O_2	84	Valensi [7]
FZR	623-823 / O_2	40	Zhu [8-10]
6N	623-873/ O_2	40	
2N	623-773 / O_2	52	
6N	623-873 /Ar + 1% O_2	57.8	
6N	573-873 / O_2	48.8	Present work
Cu-S	573-873 / O_2	77.5	
Cu-Se	573-873 / O_2	105.4	
Cu-Te	573-873 / O_2	87.5	

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In literatures, Medved [14] found that Se diffuses towards the surface of Cu - 1.65 wt % Se alloys oxidized at

1073 and 1273 K. Zhu *et al*. [15] have demonstrated that 0.2 - 0.5 wt % Te can improve the OR of commercial Cu at 773 K. As for S, although no paper has been reported to study its effect on the OR of pure Cu until now, its influence on the OR of other metals/alloys was studied [16-20], such as Cr, Fe-20Cr-4Al alloys and Fe-15% Cr (with 160 ppm S) alloy. It was found that S segregated not only to the surface but also to the scale-metal interface and the OR can be improved by hindering the diffusion of reacting species [17]. On the contrary, Smark [19] considered that the alloying element S at the metal/oxide interface may reduce the bonding force between scale and metal, deteriorating the OR. However, few studies have been made to study the influence of S, Se and Te on the OR of Cu systematically.

This work presents an investigation on how S, Se or Te affect the OR of Cu by oxidizing at 573-873 K in 0.1 MPa dry O_2 in comparison with a 6N Cu (99.9999 wt.%). The surface and cross-section morphologies of oxidized samples were examined, and the distribution of the alloying element at the oxide/metal interface was checked. The results were discussed by considering the oxidation activation energy and the diffusion rates of Cu cations, O anions and the oxygen family alloying elements.

2. EXPERIMENTAL

The nominal composition of Cu-0.1 wt.% M (M = S, Se or Te) alloys were obtained by melting Cu (99.9999 wt.%, 6N) with S (99.9 wt.%), Se (99.9 wt.%) or Te (99.9 wt. %) [21], which are hereafter referred to as Cu-S, Cu-Se and Cu-Te, respectively. The actual chemical composition was analyzed by glow-discharge mass spectrometry (GDMS) as shown in Table **2**. The concentration of the added elements was 0.0376 wt.% for S, 0.0898 wt.% for Se and 0.0844 wt.% for Te, respectively. The oxidation tests for 6N Cu were also conducted under the identical conditions as the reference specimen.

The sample ingots were cut and cold-rolled into 0.5 mm sheets, which were degreased and cleaned in acetone and ethanol using an ultrasonic bath. The sheets were ground with 1000-grit SiC and mechanically polished with 0.5 μm diamond spray until a mirror-like surface appeared, and then cleaned in acetone and ethanol in an ultrasonic bath again. The samples for oxidation were prepared by punching into 5 mm diameter discs, during which the sample sheet was covered by high-quality parchment paper to prevent any contamination from the metallic punching tool. The specimens were annealed in high-purity H_2 atmosphere at 873 K for 24 h. Both annealing and oxidation tests were performed in a tube furnace, where the temperature is controlled by a sensitivity of 0.2 K. The samples were oxidized isothermally at 573, 673 or 773 K for 8, 16, 24, 48 or 80 h and 873 K for 4, 8, 12, 24 or 48 h. After oxidation, the specimens were cooled quickly in dry air. The sample mass was recorded before and after oxidation using a HXD-1000 electro-balance with the precision of 0.1 μg. The cross-sections of the samples were encapsulated in epoxy resin for solidification. The surface for observation was polished with 0.5 μm colloidal silica and etched by a 0.05 M HCl solution for 3-30 minutes, where the solvent was composed of 67 vol % water and 33 vol % ethanol.

**Table 2.   Analytical Results of Cu-S, Cu-Se and Cu-Te Alloys by GDMS**

Cu-0.1wt % S		Cu-0.1 wt %Se		Cu-0.1 wt %Te	
Element	ppm	Element	ppm	Element	ppm
C12	4.224	C12	4.835	C 12	181.764
N14	72.617	N 14	99.920	N14	223
O16	0.604	O16	0.489	O 16	7.666
Na23	0.008	Mg24	0.001	Mg24	0.006
Mg24	0.001	Al27	0.324	Al27	0.952
Al27	0.112	Si28	1.539	Si 28	17.959
Si28	0.058	P31	0.008	P31	0.012
P31	0.062	S32	0.130	S32	0.159
S34	376	Ca44	0.005	Ca44	0.007
Ca44	0.017	Cr53	0.042	Cr53	0.003
Ti49	0.002	Mn55	0.002	Mn55	0.009
V51	0.000	Fe56	0.030	Fe56	0.124
Cr53	0.007	Ni58	0.024	Ni 58	0.038
Mn55	0.034	Co 59	0.001	Co59	0.001
Fe56	12.562	Cu63	998967	Cu 63	998816
Ni58	0.457	Zn68	0.011	Zn 68	0.775
Co59	0.017	As75	0.030	As75	0.101
Cu 63	999645	Se82	898	Se77	0.589
Zn 67	0.650	Ag107	0.023	Se82	0.729
As75	0.056	Sb121	0.003	Sb121	0.003
Se82	0.625	Te125	0.008	Te124	844
Ag107	0.088	Pb207	0.118	Pb207	0.032
Sb121	0.052	Bi209	0.000	Bi209	0.001

Scanning electronic microscope (SEM, JSM-5600) with EDX (Energy Dispersive X-ray Detector) was adopted to observe the morphologies of surface and cross-section, and to detect the distribution of the alloying elements in oxidized samples. Secondary ion mass spectroscopy (SIMS, UHVAC-PHI SIMS6600) was utilized to characterize the distribution of Cu, Se and O at the region near the Cu_2O/Cu interface.

3. RESULTS AND DISCUSSION

3.1. Oxidation kinetics

Fig. (**1**) shows the mass gain as a function of time for 6N Cu, Cu-S, Cu-Se and Cu-Te oxidized at a temperature range from 573 to 873 K. The oxidation rate of 6N Cu was highest, while that of Cu-Se was the lowest. This indicates that the oxygen family element can improve OR of Cu at 573 - 873 K. The OR for all samples was in the order of Cu-Se, Cu-Te, Cu-S and 6N Cu, inferring that Se has a significant effect on improving OR of Cu. In the case at 573 K, Cu-Se exhibits excellent OR and is seven times better than that of 6N Cu. Almost no difference in the mass gain at 673 K was
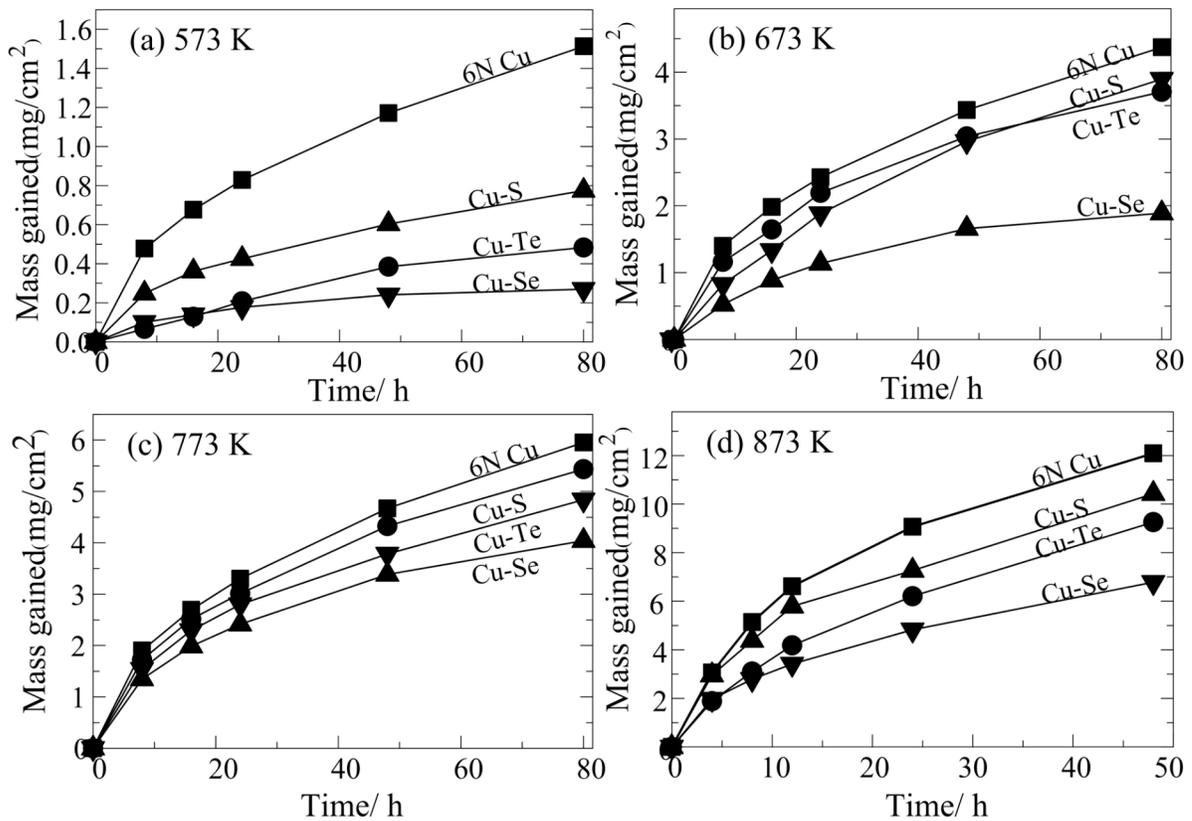
Fig. (1). Mass gain as a function of time for samples oxidized at 573-873 K in 0.1 MPa O_2. (**a**) 573 K, 80 h; (**b**) 673 K, 80 h; (**c**)773 K, 80 h; (**d**) 873 K, 48 h.

observed between Cu-S and Cu-Te, while their ORs were poorer than Cu-Se but better than 6N Cu.

Interestingly, the mass gain of the Cu alloys was lower than that of 6N Cu at all experimental temperatures, indicating that the added elements play a beneficial role on the OR of Cu. To further understand the OR results, the values of oxidation activation energy calculated according to Wagner's theory [5, 6] were also presented in Table **1**. It can be seen that the value of Cu-Te was higher than that of Cu-S but lower than that of Cu-Se, which was even as twice as that of 6N Cu. Generally, when metals oxidize at low temperatures, the outward diffusion of metals is dependent on the grain boundary diffusion. Since a reaction with low activation energy will proceed faster than that with high activation energy due to rapid outward diffusion of Cu through grain boundary, the grain boundary diffusion should be slowed down for Cu alloys because of the segregation of oxygen elements, which will be discussed later.

The surface morphology for all samples initially oxidized at 573 K for 8 and 48 h were observed as shown in Fig. (**2**). After oxidation for 8 h, long whiskers (marked by arrows) appeared on both 6N Cu and Cu-S alloy, while the whisker density was larger for the former. In contrast, only a few short whiskers can be found on the surface of Cu-Se and Cu-Te alloys. This indicates that Se in Fig. (**2c**) and Te in Fig. (**2d**) were more useful to improve the OR of Cu than S in Fig. (**2b**) possibly because of low S concentration. When the oxidation time was extended to 48 h, all whiskers became longer and coarser especially for Cu-S and 6N Cu as marked

by arrows in Fig. (**2e**, **f**). In case of 6N Cu, whiskers are long as 20 μm in Fig. (**2d**), while high density whiskers for Cu-Te were short but rather coarse, suggesting the growth of the CuO oxide scale for all samples after long time oxidation.

By considering the results of both oxidation kinetics and oxidation activation energy together with the surface morphologies for all samples, it can be deduced that the improvement of OR should be related to impediment role of the oxygen family elements on the grain boundary diffusion rate of Cu cations. Park and Natesan [4] suggested that the decreased oxidation activation energy for pure Cu oxidized at 773-973 K is attributed to the increasing grain boundary diffusion. However, Zhu *et al.* [10] have studied the oxidation behaviors of 4N (99.99 wt.%) Cu at 623-773 K and considered that the higher oxidation activation energy value is due to the impurity segregation or agglomeration at the grain boundary hindering the grain boundary diffusion. In light of the latter case, our results can be understood. Note that since no intermetallic compound between Cu and S (Se, Te) formed during annealing or oxidation process because of the low content of S (Se, Te) according to binary alloy phase diagrams [22], thus there is no occurrence of oxidation of intermetallic compound during oxidation.

To further reveal the reason for the low diffusion of Cu, the distribution of Se and Cu over the cross-section was investigated by SIMS for Cu-Se alloys after annealing and oxidation at 773 K as shown in Fig. (**3**). It can be found that the weak Se signal appeared near the surface (Fig. **3a**) indicating that outward segregation of Se to the surface took
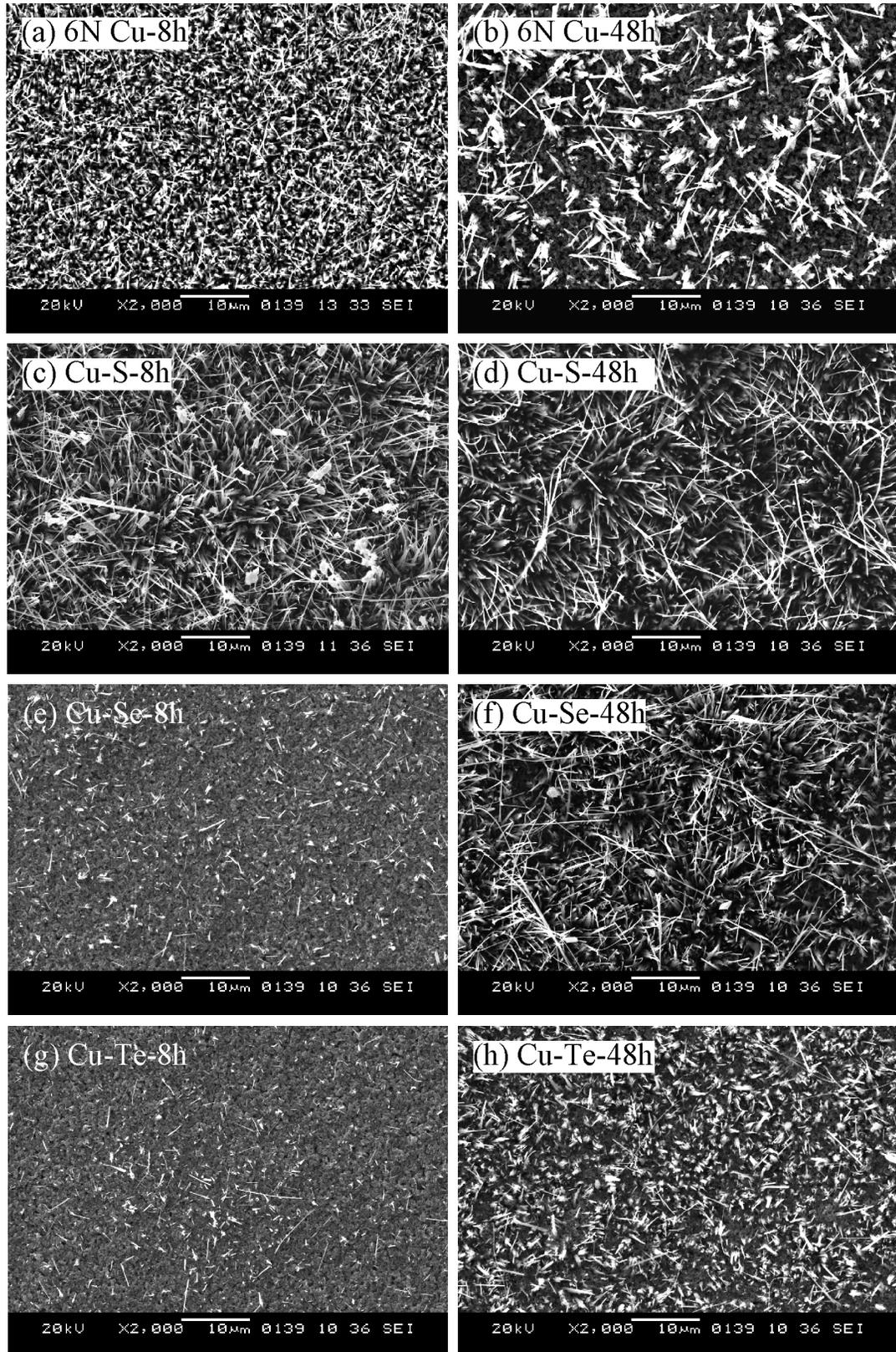
Fig. (2). Surface morphology of Cu-S, Cu-Se, Cu-Te alloys and 6N Cu oxidized at 773 K for 8 and 48 h. (**a**) 6N Cu, 8 h; (**b**) Cu-S alloy, 8 h; (**c**) Cu-Se alloy, 8 h; (**d**) Cu-Te alloy, 8 h; (**e**) 6N Cu, 48 h; (**f**) Cu-S alloys, 48 h; (**g**) Cu-Se alloy, 48 h; (**h**) Cu-Te alloy, 48 h.

place. Fig. (**3b**) is the SIMS depth profile for the determination of Cu and Se in scales near the surface for Cu-

Se alloy oxidized at 773 K for 8 h, whereas the Se signal was very weak further demonstrating that no intermetallic

compound is formed. Similar SIMS result in scales at/near the Cu_2O/Cu interface for Cu-Se alloy after 48 h of oxidation at 773 K was given as shown in Fig. (**3c**), in which the Se signal is relatively strong, indicating the stable impurity layer (Se) formed during oxidation [10]. Thus, it can be concluded that the improvement of OR was also attributed to the impurity layer formed at the Cu_2O/Cu interface.
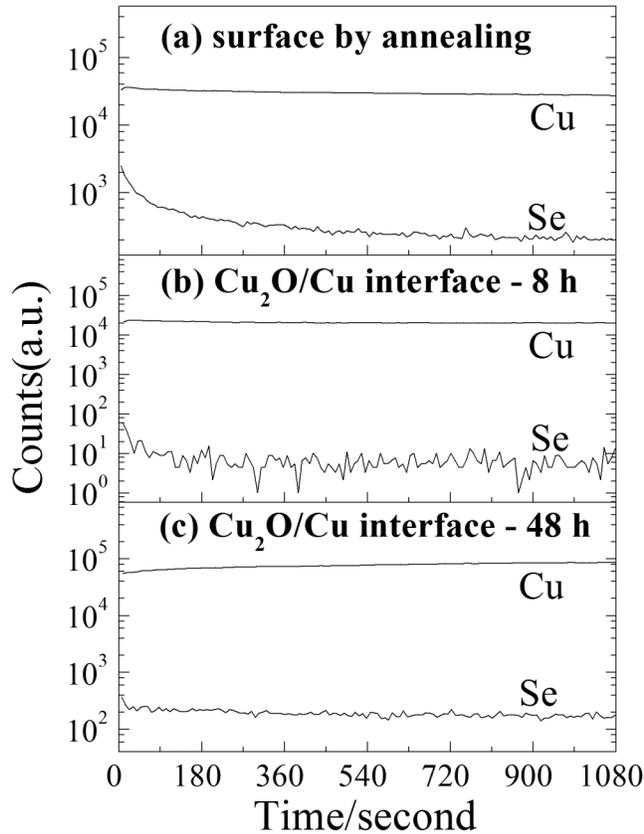

Fig. (3). SIMS depth profiles of Cu and Se for Cu-Se alloys sputtered from (**a**) surface after annealing; (**b**) Cu_2O/Cu interface oxidized at 773 K for 8 h; (**c**) Cu_2O/Cu interface oxidized at 773 K for 48 h.

3.2. Cross-Section Morphology

In order to further check the reason for the variance of OR, the corresponding SEM morphologies of cross-section for the Cu-M alloys oxidized at 773 K for 8 and 48 h were shown in Fig. (**4**). After 8 h of oxidation (Fig. **4a-d**), the oxide layer is too thin to distinguish Cu_2O from CuO. In comparison with it, the oxide layers after 48 h oxidation (Fig. **4e-h**) is composed of an outer thin CuO layer and a columnar thick inner Cu_2O layer. For all specimens, the oxide layer of 6N Cu is the thickest corresponding to the mass gain curves in Fig. (**1**). By careful measurement, the thickness of the Cu_2O layer of 6N Cu oxidized for 48 h is 120-148 μm, nine times that of 8 h. The oxide scale tends to exfoliate from the Cu-S alloys in Fig. (**4c**), which may be due to the poor adherence of the Cu_2O scale to the Cu-S alloy substrate. This indicates that S weakens the adherence between the substrate and the oxide layer, similar to the influence of S on the oxidation of Fe-Cr alloys [18-19].
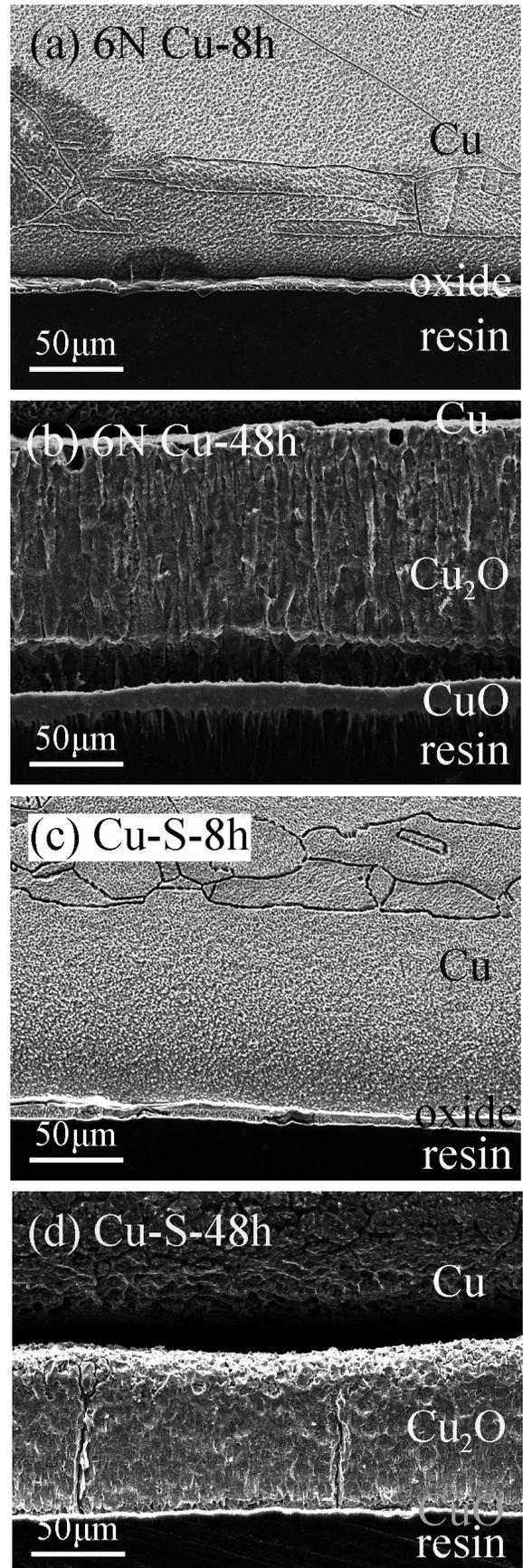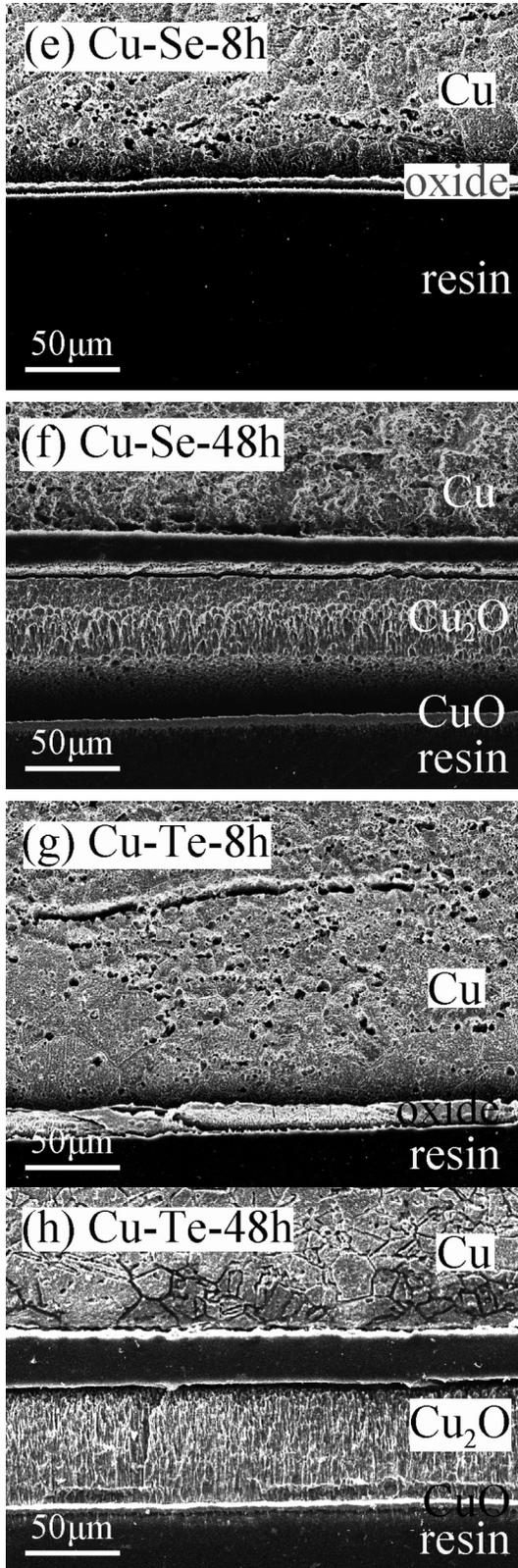
Fig. (4). SEM observation of cross-section of all samples oxidized at 773 K for 8 h and 48 h. (**a**) 6N Cu, 8 h; (**b**) Cu-S alloy, 8 h; (**c**) Cu-Se alloy, 8 h; (**d**) Cu-Te alloy, 8 h; (**e**) 6N Cu, 48 h; (**f**) Cu-S alloys, 48 h; (**g**) Cu-Se alloy, 48 h; (**h**) Cu-Te alloy, 48 h.

The metal oxidation process may be dependent on the transport or the diffusion process of ions. In the case of Cu oxidation at high temperature, a predominant migration of Cu ions and electrons *via* vacancies and holes, respectively, is expected as a result of the formation of Cu vacancies when a chemical potential gradient of Cu or O exists in Cu_2O according to the lattice defect model of Cu_2O [23]. During metal oxidation process, the transport ways mainly depend on both the grain boundary diffusion at relatively low temperatures and the lattice diffusion at high temperatures through vacancy and interstitial. Therefore, when Cu oxidized at 573 - 873 K, the diffusion rate of Cu cations and O anions mainly depends on the grain boundary diffusion, which was supported by the fine column grains observed in the Cu_2O layer formed on the samples oxidized for 48 h in Fig. (**4**). However, since the addition of S, Se, or Te was segregated to the grain boundary, the diffusion rates of Cu and O were lowered. Moreover, in light of SIMS results in Fig. (**3**), the impurity layer played a more important role in decreasing the diffusion rates for all elements. Thus, both the impurity layer and the impurities at the grain boundary lower the diffusion rates of Cu cations and O anions in Cu alloys resulting in the high OR in comparison with pure Cu. Thus, the new application for Cu by addition of S (Se, Te) that can be employed in cooling devices and microelectric regions was developed. This result will also help us reduce the production cost in Cu-S (Se, Te) alloys compared to that for high purity Cu.

CONCLUSIONS

The effects of small amounts of S, Se and Te on oxidation resistance of pure Cu were examined. The oxidation tests were performed at 573-873 K in 0.1 MPa O_2 atmospheres. The oxygen family elements (S, Se and Te) can improve the OR of pure Cu at 573-873 K. The improved OR was related to both the impurity layer at the Cu_2O/Cu interface and the alloying elements at grain boundaries, which lower the diffusion rates of Cu cations and O anions in Cu alloys.

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