Single Crystals and Oxidation of $\text{Cu}_x\text{Mo}_6\text{S}_8$

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Single Crystals of $\text{Cu}_x\text{Mo}_6\text{S}_8$ ($1.4 \leq x \leq 1.7$) are grown by the Bridgman method. SIMS, RBS, and X-ray analyses reveal that the oxidation on the $\{100\}_R$ cleaved surfaces in air at ~ 473 K (200°C) forms two layers, copper oxides ($\sim 0.1 \mu\text{m}$ deep) and "dilute zone" (a few μm deep) in order from the surface. Total variation of copper component in the bulk of $\text{Cu}_{-1.5}\text{Mo}_6\text{S}_8$ crystals is 0.002/h in oxidation at 463 K (190°C).

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I. Introduction

Crystal structure and physical properties, especially superconductivity, of numerous Chevrel-phase compounds have been examined and discussed⁽¹⁾⁽²⁾, but their chemical properties have not been almost paid attention.

Copper Chevrel compounds $\text{Cu}_x\text{Mo}_6\text{S}_8$ is of the first kind: Cu concentration x may vary continuously between the two limits ($1 \leq x \leq 4$)⁽¹⁾. These Cu ions can enter the chalcogen "channels" which are running in the direction of the rhombohedral axes⁽²⁾.

Recently we have observed by DTA and TG analyses, and X-ray diffractometry that $\text{Cu}_{-2}\text{Mo}_6\text{S}_8$ powders change into $\text{Cu}_{-1}\text{Mo}_6\text{S}_8$ by oxidation in atmosphere at high temperatures up to 573 K (300°C)⁽³⁾. It is interesting to investigate whether such a structural change is peculiar to powder samples or not.

The present paper reports on the preparation of $\text{Cu}_x\text{Mo}_6\text{S}_8$ ($1.4 \leq x \leq 1.7$) single crystals, the existence of copper oxides very near the crystal surface, and the reduction profiles of Cu ions near the surface and in the bulk, after heat treatment in air at 463–473 K (190 – 200°C).

II. Experimental

Single crystals of $\text{Cu}_x\text{Mo}_6\text{S}_8$ were grown by Bridgman technique using a high-temperature

and high-pressure furnace (DP-100MP, Kokusai Electric Co.) in the same manner as reported in the previous work⁽⁴⁾. First, the powder reagents of Cu (99.99%, 300 mesh, Mitsuwa Chemical Co.), Mo (99.9%, sintered up to 200 mesh in a vacuum, High Purity Chemetals Co.), and S (99.999%, 200 mesh, Mitsuwa Chemical Co.) were mixed to be $x=1.8$ with a mixer (Model S-1, Tsutsui Rigaku Kikai Co.) for 1 h, isostatically pressed, sealed in a Mo container ($20^{d\phi} \times 80^h$), and then heated up to 1773 K (1500°C) for 12 h. Next, it was put into a high quality Al_2O_3 crucible (SSA-S, $16^{d\phi} \times 80^h$), heated up to 2123 K (1850°C) at the center of the crucible under He gas pressures of 2.94–3.43 MPa (30 – 35 kg/cm^2), and then lowered at the rate of 2 mm/h.

A boule with large grains was obtained (see Fig. 1). The X-ray powder analysis for the grains revealed that the concentration of Cu is ~ 1.4 near the top, ~ 1.7 near the bottom, and ~ 1.5 for the most part of the remains⁽⁵⁾. The dimensions of the $\{100\}_R$ cleaved surfaces were more than $5 \times 5 \text{ mm}^2$, where the suffix R means rhombohedral. The surfaces were polished very carefully by alumina abrasive (5 to $0.05 \mu\text{m}$, Buehler Ltd.) until they showed no scratch under a metallurgical microscope (SZH-151, Olympus Optical Co.), because the crystal is brittle and the cleavage is strong.

Three samples were oxidized for 1, 10 and 20 h, respectively, at 463–473 K, using an electric furnace with an air flow of $\sim 20 \text{ l/h}$.

Distribution of oxygen and the other

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Fig. 1 Broken-out section of the Cu-Chevreol boule grown by the Bridgman method. Five large $\{100\}_R$ cleaved surfaces are shown by Roman numerals.

elements, particularly copper, near the surfaces was investigated by SIMS (Secondary Ion Mass Spectroscopy), RBS (Rutherford Backscattering Spectrometry), and X-ray diffractometry.

As-polished and oxidized samples were analyzed by SIMS (IMA-3, Hitachi Ltd.) with primary ions C_s^+ (5 keV)[†]. After the analysis, the depth of sputtered craters was measured by a depth profilometer to determine the sputtering rate. The composition of the other samples in deeper regions was measured by RBS (Dynamitron, Radiation Dynamics Ltd.) with a He^+ beam of 2.7 MeV.

The relation between the lattice spacing d_{100} and the Cu component x is given by Tovar *et al.*⁽⁵⁾ as shown in Fig. 2. The value of x was determined by comparing the value of d_{100} with the five- and six-fold values of d_{500} and d_{600} , respectively, obtained from the higher index reflections of the X-ray crystal diffraction ($CuK\alpha_1$ and α_2 , 525 W, Geigerflex 2027, Rigaku Corp.) on the $\{100\}_R$ surfaces, because the oxidation of single crystals changed only the Cu component in the bulk in the same manner as that of the powders⁽³⁾ as shown by SIMS and RBS measurements.

III. Results and Discussion

The values of Cu component x determined by the X-ray crystal diffraction are listed in Table 1. The changes of x in the samples C-2 and C-3 suggest that the decrease of Cu concentration in the bulk is proportional to the oxidation time. The total variation of Cu component in the bulk is evaluated to be 0.0018–0.0020/h at 463 K.

The concentration-distribution profiles of four elements in the sample C-1 obtained from SIMS measurement are shown in Fig. 3, where each profile illustrated by a narrow line represents a reference obtained for the as-polished $\{100\}_R$ surface of another crystal ($x=1.46$). Comparing the two profiles for each element, it is found that copper oxides exist in a narrow range of $0.15 \mu m$ at maximum from the surface, because only copper and oxygen show significant deviations from the reference profiles which represent that both copper and oxygen are enriched very near the surface.

The results of RBS measurement for the as-polished C-2 and the oxidized C-3 samples are shown in Fig. 4(a) and (b), respectively. These are analyzed by the relation⁽⁶⁾,

$$N_i = (I_i/S_i)(S_{Mo}/I_{Mo})N_{Mo} \quad (1)$$

[†] 1 eV = 1.6022×10^{-19} J.

Fig. 2 Relation between Cu component x and lattice spacing d_{100} given by Tovar *et al.*⁽⁵⁾.

where N_i , I_i and S_i mean the concentration, backscattering yield, and ion beam cross-section for 2.7 MeV, respectively, of the i -th element. Numerical values normalized by the Mo concentration $N_{\text{Mo}}=6.00$ are listed in Table 2. From the comparison of the values in Table 2 with those in Table 1, the followings are derived:

(i) Cu component x in the as-polished C-2 sample shows no difference between the X-ray and RBS data, $x=1.51$ (1) and 1.52.

(ii) Cu component x of the oxidized C-3 sample shows a clear difference between them, $x=1.460$ (5) and $x=1.20$.

In order to explain these differences, the depth of the regions measured by the X-ray diffrac-

Fig. 3 Concentration-distribution profile of the elements on the $\{100\}_R$ surfaces of Cu-Chevre single crystals by SIMS analysis. Oxidized sample (—), and as-polished sample as a reference (—).

tion with $\text{CuK}\alpha$ and the RBS with He^+ is estimated.

Mass absorption coefficient μ/ρ for the X-rays is given by

$$\mu/\rho = \sum_i (\mu/\rho)_i a_i x_i / \sum_i a_i x_i \quad (2)$$

where $(\mu/\rho)_i$, a_i and x_i mean mass absorption coefficient⁽⁷⁾, atomic weight, and chemical com-

Table 1 Cu component x in copper-Chevre compounds estimated from the x vs d_{100} curve in Fig. 2. Numerical values in the parentheses represent errors.

Samples	As-polished		After heat treatment		Remarks
	d_{100}/nm	x	d_{100}/nm	x	
C-1	—	—	0.6436(2)	1.45 (1)	473 K, 1 h
C-2	0.64476(17)	1.51 (1)	0.64446(16)	1.49 (1)	463 K, 10 h
C-3	0.64456(10)	1.495(5)	0.64375(11)	1.460(5)	463 K, 20 h

Fig. 4 RBS spectra with a He^+ beam of 2.7 MeV for the $\{100\}_R$ surfaces of Cu-Chevrel single crystals. As-polished C-2 sample (a), and C-3 sample oxidized for 20 h at 463 K (b).

Table 2 Composition near the surface of copper-Chevrel crystals C-2 and C-3 shown in Table 1. Concentration of the i -th element N_i is obtained by applying of eq. (1) to RBS spectra shown in Fig. 4, and by normalizing with $N_{\text{Mo}}=6.00$.

Element i	S_i [10^{-28} m^2]	As-polished C-2		Oxidized C-3	
		I_i [counts]	N_i	I_i [counts]	N_i
Mo	1.2989	3330	6.00	8400	6.00
Cu	0.6166	400	1.52	800	1.20
S	0.1835	630	8.04	1600	8.09

position of the i -th element, respectively. The coefficient μ/ρ of $\text{Cu}_{1.5}\text{Mo}_6\text{S}_8$ for the X-ray of $\text{CuK}\alpha$ is evaluated to be $130.6 \times 10^{-4} \text{ m}^2/\text{g}$ by eq. (2). The density is also given to be 5.80 Mg/m^3 from the lattice parameters reported previously⁽⁵⁾. Thus, the total linear absorption coefficient μ is determined to be $758 \times 10^2 \text{ m}^{-1}$. Since the X-ray emergent intensity is given by $I=I_0 \exp(-\mu t)$, the effective range t is estimated by $\mu t=1$, i.e. $t=13.2 \mu\text{m}$. On the other hand, the depth scale in RBS spectra with a He^+ incident beam of 2.7 MeV, Δx is given by the relation⁽⁶⁾,

$$\Delta x = \Delta E / \left[\frac{dE}{dx} \right] \quad (3)$$

where ΔE is the energy interval per one channel, and dE/dx is the stopping cross-section. Replacing $\Delta E=3.6 \times 10^3 \text{ eV}$ and $dE/dx=6.97 \times 10^{10} \text{ eV m}^{-1}$ for Cu in $\text{Cu}_{1.5}\text{Mo}_6\text{S}_8$ into

eq. (3), the depth scale Δx is evaluated to be $\sim 5.2 \text{ nm/channel}$. The depth for Cu spectra is estimated to be $\sim 0.6 \mu\text{m}$ corresponding to 120 channels in Fig. 4. Consequently, the difference of the Cu component obtained by X-ray diffractometry and RBS is due to the difference of the depth measured by them. A tentative Cu-concentration profile for Cu-Chevrel crystals oxidized at 463 K is illustrated in Fig. 5. This schematic shows that the oxidized crystal consists of three regions, copper-oxide layer in $\sim 0.1 \mu\text{m}$ thickness, "dilute zone" in a few μm thickness, and the bulk in order from the surface, which were detected by SIMS, RBS, and X-ray measurements, respectively. The dilute zone is named by reason of

Fig. 5 Schematic profile of Cu content for Cu-Chevrel single crystals oxidized at 463 K.

the fact that the Cu component in the zone is lower than that in the bulk. It seems that this zone appears on account of the faster oxidation reaction than the Cu diffusion from the bulk, although the diffusion is thought to be most rapid for the $\{100\}_R$ cleaved surfaces, which are normal to the chalcogen channels. The fact that copper oxides are not detected in the crystals by the X-ray diffraction as well as in the powders⁽³⁾ suggests strongly that the oxides are amorphous.

IV. Conclusion

The oxidation on the cleaved surface in copper-Chevrel crystals was very similar to that in the powders and offered further information:

(i) Only copper diffuses towards the surface and forms amorphous copper oxides on the surface. The copper-oxide layer is $\sim 0.1 \mu\text{m}$ thick.

(ii) There exists a "dilute zone" between the oxide layer and the bulk. The zone is a few μm thick.

(iii) The reduction of copper component from the bulk is $0.002/\text{h}$ in oxidizing at 463 K .

It is attractive to know the accurate dimension of the dilute zone and its temperature-dependence. Although it is difficult to directly determine them because of the lack of an adequate detector for a region of a few μm in

depth, it may be solved by measuring the oxidation reaction and diffusion constants.

It is also interesting to examine whether an "enriched zone" is formed between the diminishing oxide layer and the bulk by annealing in a hydrogen-gas flow, since the reduction reaction might occur in copper-Chevrel single crystals as well as in the powders⁽³⁾.

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