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Effect of sintering atmospheres on the densification behavior of CuO ceramics

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Abstract

In this study, the effect of oxygen partial pressure on the densification and the resultant microstructure change of CuO were examined. When CuO green bodies were heated up to 1100 °C for sintering in air, denser CuO samples were obtained than the samples sintered in oxygen. When the samples were kept at 1100 °C for a prolonged period of time, however, the densification of the sample in oxygen was accelerated whereas that of the sample in air was hindered. This is attributed to the phase transformation from CuO to Cu_2O which accompanies oxygen release during sintering in air. On the basis of the results, dense CuO samples could be obtained by switching the sintering atmosphere from air to oxygen at the suitable stage so that oxygen release by reduction could be suppressed.

Keywords: A. Sintering; B. Microstructure-final; C. Diffusion; Phase transformation

1. Introduction

In recent years, CuO thin films have attracted much attention due to their p-type conductive characteristics as well as their potential applications for solar cells and sensors [1–3]. However, there were no systematic or fundamental reports on the target manufacturing which is important for high quality film growing. Gehman [4] emphasized the importance of the target properties which directly affect film properties, processing efficiency and consistent film quality. In thin film deposition by sputtering methods, density of oxide targets is one of the most important factors to be considered since the density is proportional to deposition velocity and life cycle of the target. For the preparation of highly dense oxide sintered body, fine powders having high driving force of sintering could be considered. However, in the case of CuO, the fundamental variables of phase equilibrium such as temperature and oxygen partial pressure are of importance since CuO is unstable at high temperature and low oxygen partial pressure. According to the CuO phase diagram [5], CuO transforms to Cu_2O at 1050 °C and 1100 °C in air and oxygen, respectively. Therefore, the optimum sintering condition could be suggested as 1100 °C in oxygen which is the highest temperature without phase transformation. If CuO is sintered at 1100 °C in air, low oxygen partial pressure will trigger the formation of Cu_2O and single phase CuO is no longer affordable. In this study, the effect of sintering atmosphere on phase transformation and microstructural development processes was examined. Particularly, the reversible phase transformation between CuO and Cu_2O by reducing and oxidizing was correlated with the densification behaviors. On the basis of the experimental results, a sintering process for the preparation of dense CuO sintered body is deduced.

2. Experimental procedure

CuO (99.9%, Kojundo Chemicals, Japan) was used as the raw material. The powder compacts were formed into cylindrical pellets in a steel die 10 mm in diameter by cold isostatic pressing (CIP) at a pressure of 100 MPa for 5 min. Sintering of the compacts was conducted at 1050 °C and 1100 °C for 0–4 h with a heating rate of 5 °C/min. After sintering, the samples were furnace cooled. In order to analyze the effects of sintering atmosphere (oxygen and air) on densification behavior of the compacts, the sintering

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atmosphere was changed when the temperature reached the target sintering temperature. When the whole sintering process (heating and holding) was conducted in O_2 or air, it is denoted as $S_{O_2-O_2}$ and $S_{air-air}$, respectively whereas, when the compacts were kept in air during heating up and kept in O_2 during holding at the sintering temperature, it is denoted as S_{air-O_2}.

The densification behavior of the compacts was monitored using a thermo mechanical analyzer (TMA, TD5000SA, BRUKER, Germany) at the same sintering conditions, i.e., heating rate and gas atmosphere. Powder XRD patterns were analyzed for phase identification (Mac Science, MO3XHF, Japan). The microstructure of the fractured section of the samples was observed by using a field emission scanning electron microscopy (FE-SEM, JEOL, JSM-6701 F, Japan).

3. Results and discussion

Fig. 1(a) shows the shrinkage curves of the CuO samples during sintering depending upon the sintering atmosphere of the $S_{O_2-O_2}$, $S_{air-air}$ and S_{air-O_2}. Fig. 1(b) represents the shrinkage rate, i.e. the linear shrinkage differentiated by time. The shrinkage of the samples was also monitored during the 4 h of holding process at 1100 °C. Comparing the degree of shrinkage for $S_{O_2-O_2}$ and $S_{air-air}$ samples at low temperatures, the shrinkage of the $S_{O_2-O_2}$ sample was faster than that of the $S_{air-air}$ sample. But the high density of $S_{O_2-O_2}$ at low temperature reversed at 1100 °C that $S_{air-air}$ sample revealed higher density than $S_{O_2-O_2}$. When considering the effect of the holding time at sintering temperature in different atmospheres, oxygen contributed to a gradual densification of the sample, while air resulted in the expansion of the sample. Among the samples, S_{air-O_2} showed the highest densification. From the shrinkage rate in Fig. 1(b), it can be determined that densification of every sample started at around 850 °C. In the case of $S_{O_2-O_2}$, a maximum shrinkage rate was reached at around 1050 °C, and the degree of shrinkage decreased as the temperature increased. The shrinkage of both $S_{air-air}$ and S_{air-O_2} samples was much more prominent showing deeper curves than $S_{O_2-O_2}$, and those revealed their maximum shrinkage rate at around 1100 °C. However, in the case of $S_{air-air}$, positive shrinkage rates were observed during the 4 h of holding period at 1100 °C in air, which signifies that the samples were expanding. In the case of S_{air-O_2}, small negative shrinkage rates maintained throughout the holding period suggesting that a slow densification proceeds.

Fig. 2 shows the X-ray diffraction patterns of the samples which were sintered at 1050 °C and 1100 °C for 0 h in different atmospheres. In the $S_{O_2-O_2}$ sample, only the diffraction pattern of CuO regardless of the sintering temperature appeared. In the case of $S_{air-air}$ sample, the single phase of CuO was maintained until 1050 °C. However, as soon as the sintering temperature increased to 1100 °C, the diffraction patterns of the Cu_2O began to appear at around $2\theta = 36.4°$ and 42.3°.

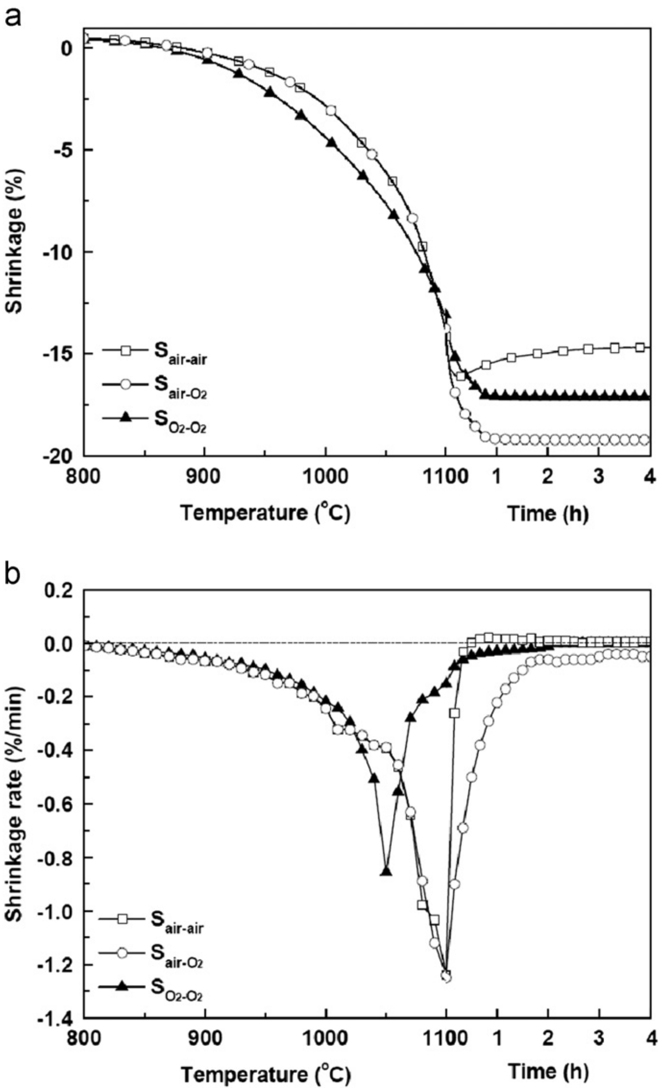

Fig. 1. (a) Shrinkage and (b) shrinkage rate behaviors of CuO compacts heated up to 1100 °C in $S_{air-air}$, S_{air-O_2} and $S_{O_2-O_2}$.

Fig. 3 shows the microstructures of the fractured surface of the samples, which were sintered at 1050 °C and 1100 °C for 0 h in air and oxygen atmospheres. In the case of sintering at 1050 °C, where sintering atmosphere was concerned, oxygen atmosphere was more effective in the densification of the sample than air. However, when the samples were sintered at 1100 °C, air atmosphere led to a higher density and larger grain growth than oxygen atmosphere. Generally, CuO is known to have cation vacancy in the structure which can be expressed with a formula of $Cu_{1-x}O$ in the structure, and the p-type electrical characteristics originated from the Cu vacancies [6,7]. Therefore, the number of Cu vacancies will increase as the oxygen partial pressure increases during sintering.

The higher densification of the sample sintered at 1050 °C in oxygen (Fig. 3 (b)) is thought to be attributed to the increased number of cation vacancies which accelerated the densification of CuO. [8] On the other hand, concerning the case of sintering in air at 1100 °C (Fig. 3(c)), Cu_2O was formed as observed in

X-ray diffraction in Fig. 2. According to Zhu, the diffusivity of Cu and O ions in Cu_2O is faster than that in CuO. [9–13] Therefore the formation of the Cu_2O in the sample seemed to contribute to the enhanced densification and grain growth.

Fig. 4 shows the X-ray diffraction patterns of the samples which were sintered at 1100 °C for 2–4 h indifferent atmospheres. When the CuO sample was sintered in air ($S_{air–air}$) for 2 h, small peaks from the Cu_2O appeared. A prolonged sintering of 4 h resulted in the development of the large amount of Cu_2O, and a small amount of CuO remained as a minor phase. In the case of S_{air-O_2}, the minor phase of Cu_2O in the sample sintered at 1100 °C for 0 h in air (Fig. 2) disappeared when the sample was kept in oxygen for 2 h. The disappearance of the Cu_2O is believed to be caused by the oxidation of Cu_2O to CuO.

Fig. 5 shows the microstructures of the samples sintered at 1100 °C for 2–4 h in different atmospheres. (a) and (b) correspond to the sample of $S_{air–air}$ sintered for 2 and 4 h, respectively. (c) and (d) correspond to the sample of S_{air-O_2} sintered for 2 and 4 h, respectively. (e) and (f) are the case of $S_{O_2-O_2}$ sample sintered for 2 and 4 h, respectively. In the case of (a) and (b) many large huge pores exist in the sample.

In this case, the pore generation is related to the phase transformation from CuO to Cu_2O which can be expressed as

$$2CuO(s) \rightarrow Cu_2O(s) + 1/2O_2\ (g) \quad (1)$$

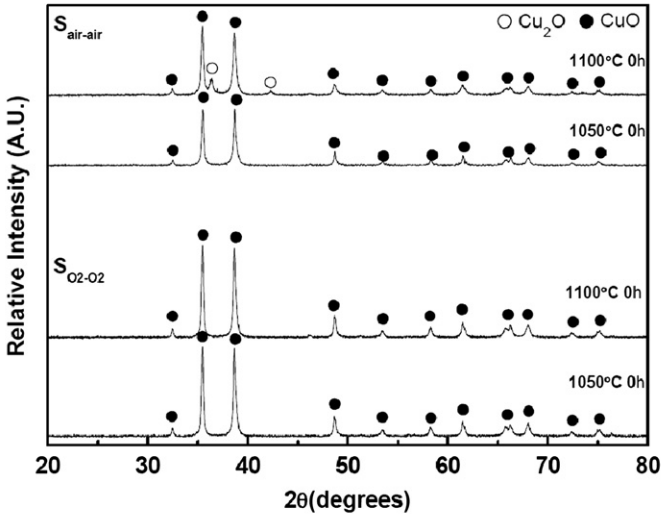

Fig. 2. X-ray diffraction patterns of CuO specimens sintered at 1050 °C and 1100 °C for 0 h in air and O_2 atmospheres.

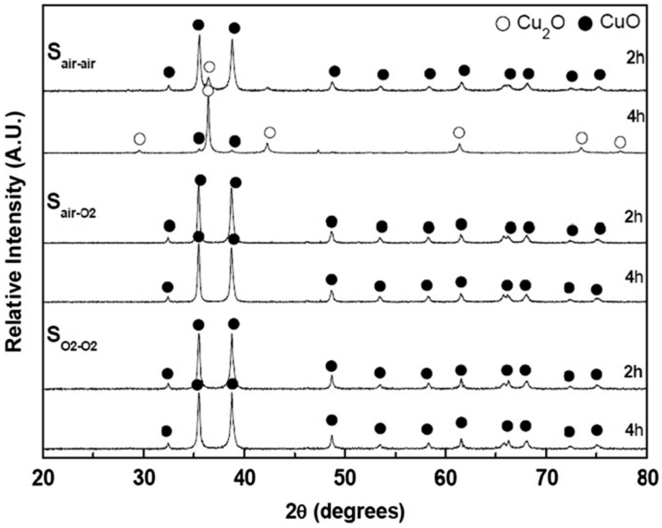

Fig. 4. X-ray diffraction patterns of CuO specimens sintered at 1100 °C for 2 h and 4 h in air–air, air–O_2 and O_2–O_2 atmospheres.

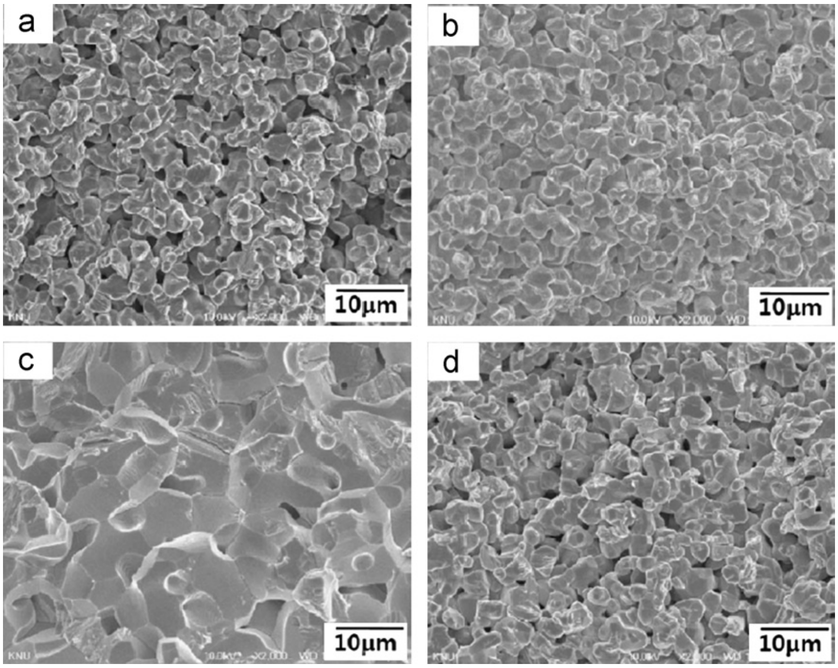

Fig. 3. FE-SEM images of CuO specimens sintered at (a) 1050 °C in air, (b) 1050 °C in O_2, (c) 1100 °C in air and (d) 1100 °C in O_2 for 0 h.

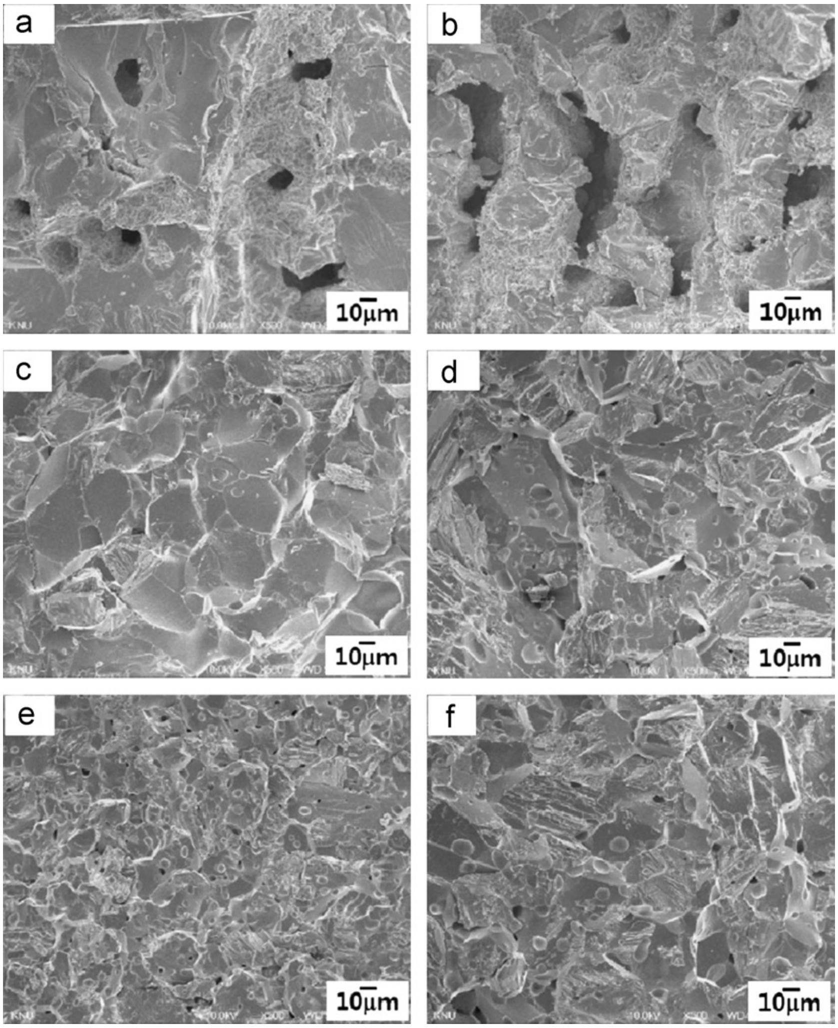

Fig. 5. FE-SEM images of CuO specimens sintered at 1100 °C for 2 h–4 h; (a) $S_{air-air}$, 2 h, (b) $S_{air-air}$, 4 h, (c) S_{air-O_2}, 2 h, (d) S_{air-O_2}, 4 h, (e) $S_{O_2-O_2}$, 2 h and (f) $S_{O_2-O_2}$, 4 h.

As presented above, CuO decomposes (by reduction) into Cu_2O and oxygen ions at 1100 °C in air or in the atmosphere with low oxygen partial pressure. The oxygen development in the relatively dense sample during sintering in air severely deteriorates densification and leaves behind large pores which cannot be removed by normal sintering process. In the case of $S_{O_2-O_2}$ sample, in which phase transformation was not experienced during the whole sintering process, however, a fairly good densification was obtained.

4. Conclusion

When CuO was sintered in air, a maximum shrinkage rate was reached at around 1100 °C, whereas a prolonged sintering at 1100 °C in air resulted in sample expansion due to the phase transformation from CuO to Cu_2O. Switching the sintering atmosphere can effectively enhance the densification of CuO i.e., heating up to 1100 °C in air where maximum density but minimum phase transformation obtained, then holding the sample in oxygen for a continuous densification by suppressing CuO reduction.

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References

[1] A. Chen, H. Long, X. Li, G. Yang, P. Lu, Controlled growth and characteristics of single-phase Cu_2O and CuO films by pulsed laser deposition, Vacuum 83 (2009) 927–930.

[2] T. Itoh, K. Maki, Growth process of CuO(111) and Cu_2O(001) thin films on MgO(001) substrate under metal-mode condition by reactive de-magnetron sputtering, Vacuum 81 (2007) 1068–1076.

[3] G. Yang, A. Chen, M. Fu, H. Long, Excimer laser deposited CuO and Cu_2O films with third-order optical nonlinearities by femtosecond z-scan measurement, Applied Physics A104 (2011) 171–175.

[4] B.L. Gehman, S. Jonsson, T. Rudoph, M. Scherer, M. Weigert, R. Werner, Influence of manufacturing process of indium tin oxide

sputtering targets on sputtering behavior, Thin Solid Films 220 (1992) 333–336.

[5] M. O'Keefee, W.J. Moore, Thermodynamics of the formation and migration of defects in cuprous oxide, The Journal of Chemical Physics 36 (1962) 3009–3013.

[6] Y. Jeong, G. Choi, Nonstoichiometry and electrical conduction of CuO, The Journal of Physics and Chemistry of Solids 57 (1996) 81–84.

[7] T. Serin, A. Yildiz, S. Horzum, N. Serin, Extraction of important electrical parameters of CuO, Physica B-Condensed Matter 406 (2011) 575–578.

[8] N. Kikuchi, K. Tonooka, Electrical and structural properties of Ni-doped Cu_2O films prepared by pulsed laser deposition, Thin Solid Films 486 (2005) 33–37.

[9] D.P. Trauernicht, J.P. Wolfe, Drift and diffusion of paraexcitons in Cu_2O: deformation-potential scattering in the low-temperature regime, Physical Review B 33 (1986) 8506–8521.

[10] Y. Zhu, K. Mimura, M. Isshiki, Influence of oxide grain morphology on formation of the CuO scale during oxidation of copper at 600–1000 °C, Corrosion Science 47 (2005) 537–544.

[11] W.J. Moore, B. Selikson, The diffusion of copper in cuprous oxide, The Journal of Chemical Physics 19 (1951) 1539–1543.

[12] J. Li, J.W. Mayer, Oxidation and reduction of copper oxide thin films, Materials Chemistry and Physics 32 (1992) 1–24.

[13] G.C. Wood, F.H. Stott, The influence of an intermediate annealing treatment on the oxidation of copper and nickel, Oxidation of Metals 14 (1980) 187–205.