www.czasopisma.pan.pl PAN POLSKA AKADEMIA NAUK www.journals.pan.pl

A R C H I V E S O F M E T A L L U R G Y A N D M A T E R I A L S

Volume 60 2015 Issue 2

DOI: 10.1515/amm-2015-0099

G.-S. MOON*, T.-J. CHUNG*, S.-H. YANG**, G.-S. HONG**, K.-S. OH*,♯

JOINING OF GREEN BODY AND DENSE SUBSTRATE FOR INDIUM TIN OXIDE UNDER UNIAXIAL PRESSURE IN AN OPEN CONDITION

ŁĄCZENIE ZIELONEJ MASY I GĘSTEGO PODŁOŻA Z TLENKU CYNY INDU W WARUNKACH JEDNOOSIOWEGO ŚCISKANIA W STANIE OTWARTYM

The green body and dense substrate of indium tin oxide was joined by uniaxially pressing at 0.3 MPa at 1300°C to test the restoring of the eroded part of transparent conducting oxide target. The green body was sintered to 98% of theoretical density under the suppression of shrinkage along the boundary below 5%. The boundary between two parts was free of pore but could be recognized from the difference in grain sizes. The joined part had the virtually same density with the substrate, but the grain size was less than one fifth compared with that of substrate.

Keywords: Transparent Conducting Oxide, Indium Tin Oxide, Green body, Joining

1. Introduction

Transparent conducting oxide (TCO) film, which is generally prepared by sputtering process, is essential in various electronic devices such as touch panel or displays. During the sputtering, accelerated ions collide onto target and the peeled off species deposit on the substrate. Therefore, TCO target plays role of material source in the preparation of TCO film [1]. In practice, In_2O_3-SnO_2(ITO) is most widely used TCO material due to its excellent electrical conductivity and optical transparency. In case of ITO, the recycling process of indium is an important issue [2] due to the unstable supply [3].

General route of recycling is the chemical separation of indium after dissolution [4-6]. However, the chemical recycling requires numerous steps and increases the cost of recovered indium. The process and time can be greatly cut down if eroded part in the target can be restored without chemical recycling. In practice, the erosion of target is intense near the magnet [7]. Due to the uneven erosion, the planar target should be replaced long before complete consumption. The restoring of eroded part in the target can thus be a valuable approach to save resources.

The restored part evidently requires a comparable performance with that of the original part. It is desired that the restored part is indistinguishable from the original target in the aspect of density, grain size, and conductivity and so on. However, as the bulk ceramic is prepared via consolidation of powder compact, the shrinkage is inevitable. As long as the green body shrinks along the boundary, the green part is unable to maintain the join with the substrate [8]. Therefore the shrinkage along the boundary (horizontal shrinkage) needs to be suppressed, while vertical shrinkage needs to be maximized until the full density is attained.

Approaches to join the green tape with bulk substrate are available [9-10], but attempt to join the bulk green body and dense substrate is rare [11]. In this work, joining of green body and used target was attempted for ITO by hot pressing in an open condition, while seeking the dense state suitable for sputtering.

2. Experimental

2.1. Preparation of ITO Green body

The ITO powder used in the work was supplied by Heesung metal. The powder contained 90 wt% of indium and spray dried to have the average granule size of 40 μm. The mean primary particle size was 0.2 μm. The ITO powder was uniaxially pressed at 0.5 MPa for 1 min using the mold with a diameter of 1 cm. The green body was subsequently cold isostatically pressed at 100 MPa for 3 min.

2.2. Hot press in open conditions

The ITO green body was uniaxially pressed between upper and lower rams. The green body could expand or shrink horizontally depending on the experimental conditions such as magnitude of pressure or sintering temperature. The green body was sintered at 1300, 1325 or 1350°C for 2 h. During the sintering, the pressure was kept at 0, 0.098, 0.294

* SCHOOL OF MATERIALS SCIENCE AND ENGINEERING, ANDONG NATIONAL UNIVERSITY, ANDONG, REPUBLIC OF KOREA
** HEESUNG METAL LTD., INCHEON, REPUBLIC OF KOREA
♯ Corresponding author: ksoh@anu.ac.kr

or 0.490 MPa. The specimen was in an 'open' condition, which meant that ITO green body was not constrained by the side wall of mold. After the sintering under pressure, both the horizontal and vertical shrinkages were measured using vernier caliper. The density of the specimen was measured by Archimedes immersion technique. For a specimen exhibiting appropriate shrinkage, the ITO green body was placed on the ITO substrate as shown in Fig. 1. The substrate was actually a piece of ITO target and had the almost full density (7.0 g/ml).

The hot pressed specimens were then vertically bisected with a diamond saw for the microstructural analysis. The exposed surface was sequentially polished with SiC abrasive paper and diamond pastes (6, 3, and 1 μm). The polished specimens were thermally etched at 1200~1250°C for 1 h to develop the microstructures. Scanning electron microscopy (JSM-6300, JEOL, JAPAN) was used at 20 kV for the observation. The density and porosity of the bulk specimen were also estimated using the image analyzer from the microstructure.

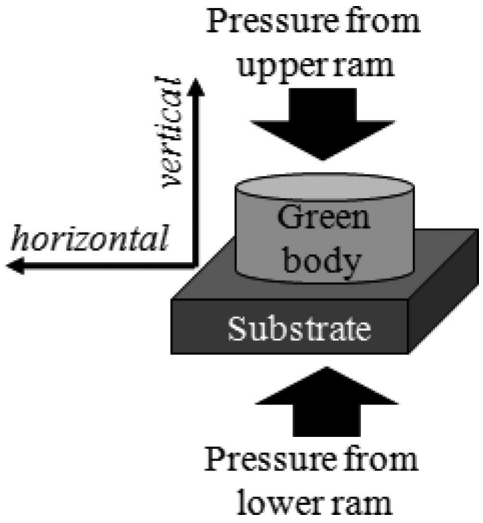


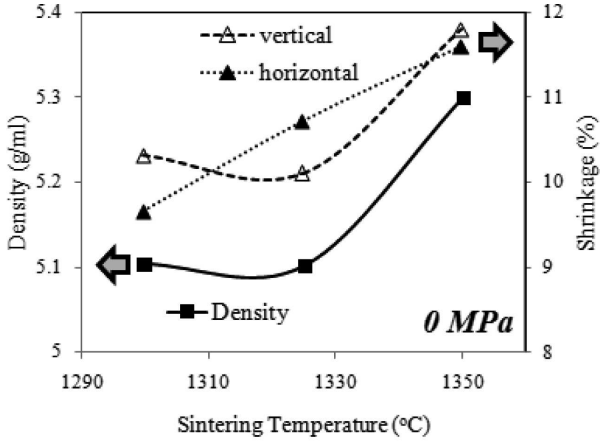
Fig. 1. Schematic illustration of the ITO green body setup for sintering under uniaxial pressure in an open condition

3. Results and discussion

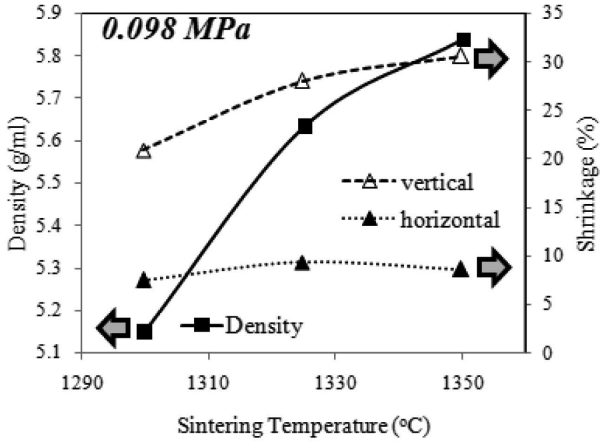
3.1. Shrinkage with respect to pressure and temperature

Fig. 2 shows the change of density and shrinkages with the increase in temperature for various pressures (0, 0.098, 0.294, 0.490 MPa). Without applied pressure (Fig. 2a), the density generally increased with temperature. At 1350°C, the best density (5.3 g/ml) was obtained but it is far less than the theoretical density (7.1 g/ml). The shrinkages were ranged between 9 and 12%, regardless of the direction.

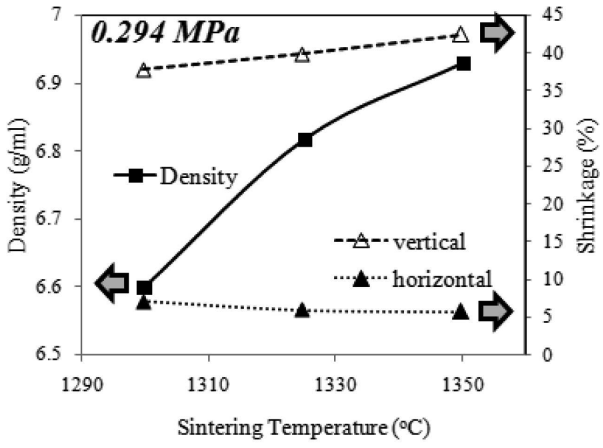
Under 0.098 MPa shown in Fig. 2b, the density considerably increased to 5.9 g/ml as result of sintering at 1350°C. The density increased with the increase in sintering temperature also. The application of pressure increased the vertical shrinkage as 20~35%, but decreased the horizontal shrinkage as 5~10%. The application of greater pressure (0.294 MPa) in Fig. 3c led to the density at 1350°C as 6.9 g/ml. At 0.294 MPa, the vertical shrinkages increased as 35~45%. On the contrary, the horizontal shrinkage was suppressed near 5%. Under 0.490 MPa in Fig. 3d, density of 7.0 g/ml was achieved by the sintering at 1250°C. The density obtained at 1250°C was already close to the theoretical density (7.1 g/ml) and improvement of density was hardly observed with the increase in temperature. The vertical shrinkages were ranged at 40~45% and the horizontal shrinkage was less than 5%. However, the shrinkages could not be measured at 1350°C due to the fracture of specimen.



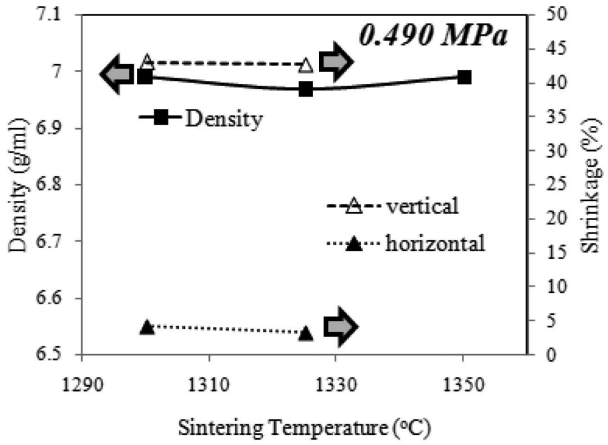
(a)



(b)

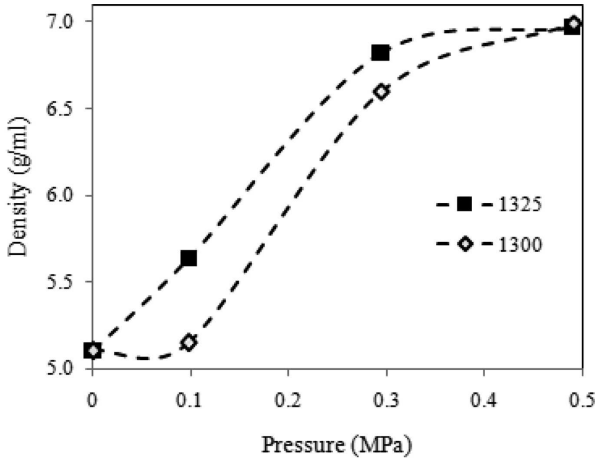


(c)

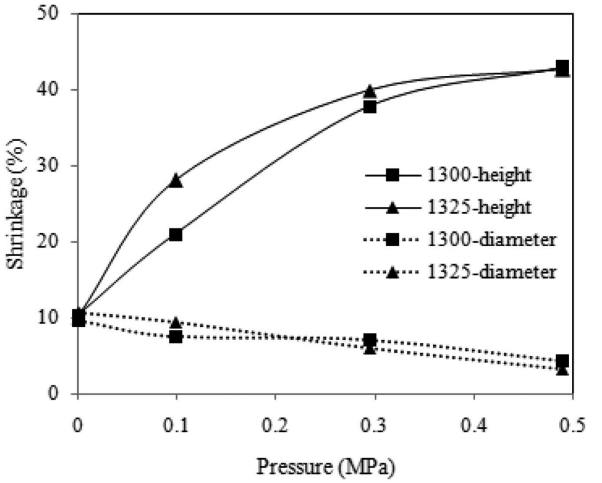


(d)

Fig. 2. Change of the density, vertical and horizontal shrinkages (%) of ITO green body with sintering under pressure at (a) 0, (b) 0.098, (c) 0.294 and (d) 0.490 MPa



(a)



(b)

Fig. 3. Change of (a) density and (b) shrinkages with the increase in applied pressure during sintering of ITO

Change of density and shrinkages is shown in Fig. 3 with the pressure. The abrupt increase in density is observed with increase in pressure from 0.098 to 0.296 MPa. The increase in density is more effective at elevated temperature. The increase in pressure greatly improved the vertical shrinkage and suppressed the horizontal shrinkage.

3.2. Microstructure after joining

Through a proper manipulation of temperature and pressure, almost fully dense specimen could be prepared, while suppressing the horizontal shrinkage below 5%. The joining with dense substrate was attempted for the ITO green body at 1300°C for 2 h under 0.294 MPa. The union of two bodies was successful as shown in Fig. 4. Fig. 5 was taken at the boundary between the two parts from the cross section of the specimen after union. The upper half of Fig. 5 is the sintered ITO green body and the bottom half shows the dense target. The boundary could be recognized from the difference in grain sizes between the two regions. The boundary was free of pores. Table 1 summarizes the grain size after the union. The target part was composed of grains with the average size of 5.0 μm and newly consolidated part was composed of grains less than 1 μm.

Fig. 4. ITO green body joined with used target by sintering at 1300°C for 2 h under 0.296 MPa

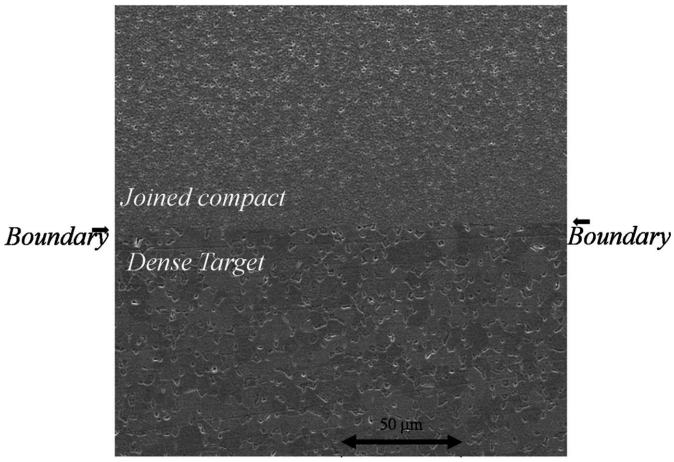


Fig. 5. Boundary between ITO green body and dense target joined by sintering at 1300°C for 2 h under 0.296 MPa

As shown in Table 1, the difference of density between joined part and substrate was very small as 1.6%. However, the grain size was more than 5 times larger at the substrate. The difference in grain size can affect the erosion rate and also the formation of nodule [12].

TABLE 1
Comparison of density and grain size between joined green body and substrate

	Density (g/ml)	Grain Size (μm)
Joined green body	6.93	1.0
Substrate	7.04	6.5

3.3. Qualitative stress analysis during union

Fig. 6 shows schematic analysis on the forces acting on the specimen during joining. Compressive stresses are transmitted from the rams as arrow 1 in Fig. 6. As the specimen shrinks with the increase in temperature, the shrinking force (sintering stress) was expressed as arrow 2. At the boundary between the ram and specimen, frictional forces (arrow 3) exist opposite to the shrinking force. The frictional force is proportional to the magnitude of uniaxial pressure of arrow 1.

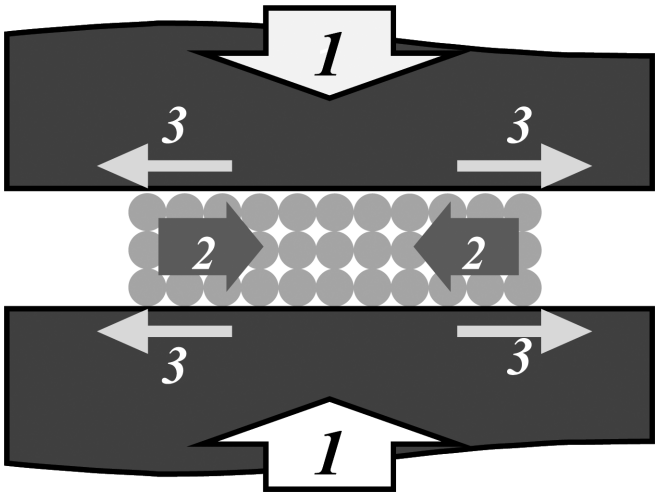


Fig. 6. Schematic illustration of forces acting on the specimen during the joining: Arrow 1 denotes the uniaxial pressure from upper and lower rams, arrow 2 shows the sintering stress of powder compact, and arrow 3 represents the friction force by the rams

The force 2 and 3 induces tensile stress on the specimen. If the tensile stress is greater than strength of the specimen, the fracture should take place. Even if the specimen does not fracture, the force should deform the specimen to relieve the stress. Fig. 7 shows the specimen sintered at 1300°C under 0.296 MPa. It is found that the side wall of the specimen has negative curvature. It suggests that the shrinkages at top and bottom of specimen were restricted due to the friction with rams unlike the middle of specimen. The negative curvature proves the significance of frictional force on the sintering behavior of specimen as expressed in Fig. 6. According to the model in Fig. 6, the sintering at 1350°C induces greater sintering stress and consequently the stronger tensile stress than at 1300°C in Fig. 7. The specimen sintered at 1350°C under 0.490 MPa was actually fractured and it can be the result of the greater tensile stress expressed in Fig. 6.

As shown by Fig. 4 and 5, the joining of ITO green body with dense target was successful via proper selection of temperature and pressure. The joined part had the sufficient density comparable with the substrate. The joining technique in this work can be applied to the restoring of eroded target and save the cost of indium recycling.

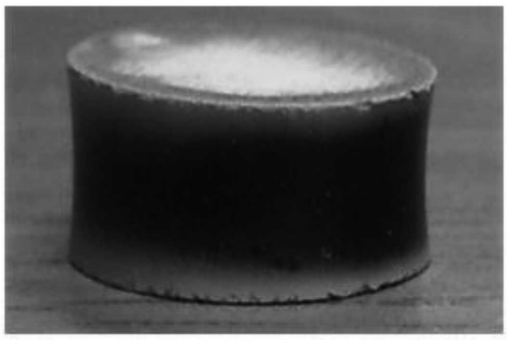


Fig. 7. ITO green body sintered at 1300°C for 2 h under the 0.296 MPa

4. Conclusions

The joining of dense ITO substrate with the same composition of powder compact was successfully carried out in the open hot press condition. By the application of 0.296 MPa at 1300°C, the density of the powder compact could be increased to 98% of theoretical density, while the horizontal shrinkage could be suppressed below 5%. The densification behavior during hot press enabled the union of green body with dense substrate. The boundary was free of pores and could be recognized from the difference in grain sizes between two parts. The density difference between the two parts was less than 1.6%, but the grain size was more than 5 times smaller at the joined part. The successful joining suggests the potential of restoring approach on the eroded sputtering target.

Acknowledgements

This work was supported by a Grant (code #: 20115020100080) in aid for 'Energy and Resource Recycling' under the 'Korea Institute of Energy Technology Evaluation and Planning R&D Programs' of the Korea Ministry of Trade, Industry and Energy.

REFERENCES

[1] D.W. Kim, Y.H. Kim, J.H. Kim, D.G. Kim, J.H. Lee, K.B. Choi, H.T. Son, J. Kor. Powd. Met. Inst. **19**, 264 (2012).
[2] J.G. Kim, J. Kor. Powd. Met. Inst. **19**, 72 (2012).
[3] T. Kato, S. Igarashi, Y. Ishiwatari, M. Furukawa, H. Yamaguchi, Hydrometallurgy **137**, 148 (2013).
[4] Y. He, E. Ma, Z. Xu, J. Hazard. Mater. **263[2]**, 610 (2013).
[5] G. Dodbiba, H. Nagai, L.P. Wang, K. Okaya, T. Fujita, Waste Manage. **32**, 1937 (2012).
[6] J. Yang, T. Retegan, C. Ekberg, Hydrometallurgy **137**, 68 (2013).
[7] T. Fukami, F. Shintani, M. Naoe, Thin Solid Films **151**, 373 (1987).
[8] R.K. Bordia, A. Jagota, J. Am. Ceram. Soc. **76**, 2475 (1993).
[9] A. Roosen, J. Eur. Ceram. Soc. **21**, 1993 (2001).
[10] J. Gurauskis, A.J. Sánchez-Herencia, C. Baudín, J. Eur. Ceram. Soc. **25**, 3403 (2005).
[11] J.H. Han, Ceram. Int. **39**, 239 (2013).
[12] B.L. Gehman, S. Jonsson, T. Rudolph, M. Scherer, M. Weigert, R. Werner, Thin Solid Films **220**, 336 (1992).

Received: 20 November 2014.