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DIRECT ENERGY DEPOSITION OF Mo POWDER PREPARED BY ELECTRODE INDUCTION MELTING GAS ATOMIZATION

Molybdenum (Mo) is used to form a barrier layer for metal wiring in displays or semiconductor devices. Recently, researches have been continuously attempted to fabricate Mo sputtering targets through additive manufacturing. In this study, spherical Mo powders with an average particle size of about 37 um were manufactured by electrode induction melting gas atomization. Subsequently, Mo layer with a thickness of 0.25 mm was formed by direct energy deposition in which the scan speed was set as a variable. According to the change of the scan speed, pores or cracks were found in the Mo deposition layer. Mo layer deposited with scan speed of 600 mm/min has the hardness value of 324 Hv with a porosity of approximately 2%. We demonstrated that Mo layers with higher relative density and hardness can be formed with less effort through direct energy deposition compared to the conventional powder metallurgy.

Keywords: Molybdenum powder, Electrode induction melting gas atomization, Direct energy deposition, Porosity, Hardness

1. Introduction

As the image resolution and size of liquid crystal displays continue to increase, copper (Cu), which has excellent electrical conductivity, is mainly used for wiring connected to thin-film transistors [1-3]. However, since Cu is easy to peel off due to poor adhesion to the glass substrate [4,5], a novel wiring structures consisting of a metallic layer and a barrier layer to improve the adhesion between the glass substrate and the wiring rather than single Cu wiring is applied. Molybdenum (Mo) or Mo alloys are representative materials that can be applied as barrier layers for novel wiring structures [6].

Mo is a typical refractory metal with a melting point of 2,623°C and a density of 10.28 g/cm^3. It is also chemically stable and has excellent thermal and electrical properties [7,8]. Therefore, Mo is deposited by physical vapor deposition (PVD) such as sputtering on the glass substrate to form barrier layers for metal wiring of displays or semiconductor devices [9]. It is also applied in copper indium gallium selenide (CIGS) solar cells as back contacts [10-12]. For this application, Mo sputtering targets with the desired density, purity, etc. are required. Until recently, Mo targets were mostly manufactured through conventional powder metallurgy (PM) and forming processes due to their high melting points. An et al. reported that the Mo sputtering targets fabricated using powder metallurgy. Single hydrogen sintering (SHS) and vacuum pre-sintering followed by hydrogen sintering (VPHS) were compared and analyzed. The impurity contents of VPHS was lower than SHS. As a result, VPHS can utilize for fabricating Mo sputtering targets [13].

However, conventional PM is difficult to control the purity due to the occurrence of impurities during the fabrication process, and Mo has low machinability due to its crystal structure of body-centered cubic (BCC), which makes it difficult to deform. It also has limitations in expanding the size of sputtering targets. Recently, additive manufacturing (AM) has been studied with great effort to overcome these difficulties in manufacturing Mo sputtering targets into desired purity, microstructure and size. However, the extraordinarily high melting point of Mo makes it serious challenges to manufacture spherical powders that are necessary for the AM and apply it to form a uniform and dense deposition layer. Therefore, powder-based direct energy deposition (DED) has been in the spotlight recently. Powder-based DED is additive manufacturing that involves a coaxial feed of particulate materials to high-energy laser beams to form a sin-

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tered layer on a substrate. In particular, it is similar to the laser cladding in terms of the coating process. As with laser cladding, powder-based DED has small responsiveness to the base materials because of low overall heat input. It can also create a uniform microstructure without segregation and can be coated locally [14,15]. Due to these advantages, it is expected to be highly utilized for the manufacturing and repairing of sputtering targets, molds and mechanical parts.

In this study, spherical Mo powders were fabricated through electrode induction melting gas atomization (EIGA), and Mo layer was deposited by powder-based DED using this gas-atomized Mo powders. In addition, the porosity and mechanical properties of Mo deposition layer according to the scan speed were investigated.

2. Material and methods

EIGA was carried out to manufacture Mo powder. φ 25 × 500 mm of Mo electrode with 99.95% purity (World induction, Korea) was used for EIGA. The applied power of the upper induction coil and the lower induction coil was set differently to 25 kW and 35 kW, respectively. The feeding speed and gas pressure were set to 1 mm/sec and 70 bar of argon (Ar) gas. The prepared Mo powder was then deposited on the pure Mo substrate by powder-based DED until the thickness of Mo layer was 0.25 mm. Table 1 presents the details of the process parameters for powder-based DED. Ar gas with a purity of 99.99% was used as the carrier for powders and shield gas to prevent oxidization of the deposition layer. The flow rate of Ar gas was set at 10 liter/min

TABLE 1

Process parameters for direct energy deposition

Scan speed [mm/min]	Laser power [W]	Hatch spacing [mm]	Layer thickness [mm]	Energy density [J/mm^3]
900	800	1.0	0.25	355.6
750	800	1.0	0.25	426.7
600	800	1.0	0.25	533.3
450	800	1.0	0.25	711.1
300	800	1.0	0.25	1066.7

The average particle size and the particle size distribution of gas-atomized powders was analyzed by particle size analyzer (PSA, Malvern Panalytical, MS 3000). The qualitative analysis of gas-atomized powders was also conducted by inductively coupled plasma optical emission spectroscopy (ICP-OES, Thermofisher, iCAP 6200). The surface morphologies of gas-atomized powders and the cross section of deposition layer was observed by scanning electron microscopy (SEM, JEOL, JSM-7500F). In addition, qualitative analysis on the deposition layer was conducted using energy-dispersive X-ray spectroscopy (EDS). Hardness measurement of deposition layer was performed by Vickers hardness tester (Future-Tech, FV-810) with an applied load of 10 kgf and dwell time of 3 s, repeated 5 times for different areas. Porosity was measured using image analysis on SEM images.

3. Results and discussion

Figure 1 shows the surface morphologies observed by SEM and particle size distribution of Mo powders manufactured through EIGA. As shown in Figures 1(a) and 1(b), spherical Mo powders with smooth surface were obtained, and several satellite particles were observed on the surface of coarse particles. These satellite particles were formed because the time for solidification varies depending on the size of the powder. The powder with a large size needs a relatively long time for solidification, so the solidified fine powder attached to the surface of coarse powder where liquid phase still exists. The average particle size was also measured at approximately 37 um and the particle size distribution is close to the negatively skewed distribution (Fig. 1(c)). The purity of atomized Mo powder was about 99.92%, and 49.5 ppm of iron, 65.0 ppm of nitrogen, and 696.0 ppm of oxygen were detected by ICP-OES.

Powder-based DED was conducted to form a Mo layer using these gas-atomized Mo powders. Cross-sectional SEM images and result of EDS analysis of Mo layers deposited with different scan speed are shown in Figure 2. In powder-based DED, high-power laser beams produce an instantaneously melt pool on the surface of Mo powders, which results in the densification of Mo powders. Decreasing the scan speed of a laser beam means an increase in energy density defined as the energy delivered to

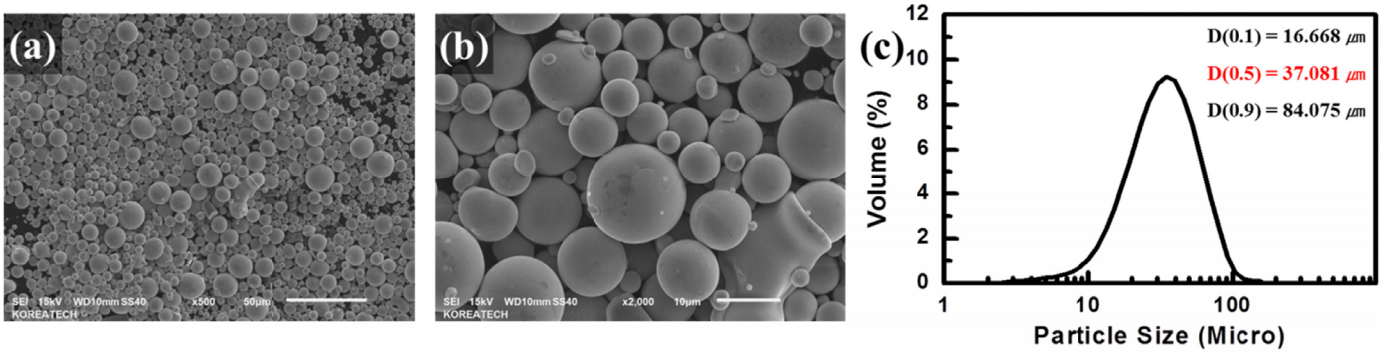

Fig. 1. Surface morphologies and particle size distribution of Mo powder prepared by electrode induction melting gas atomization

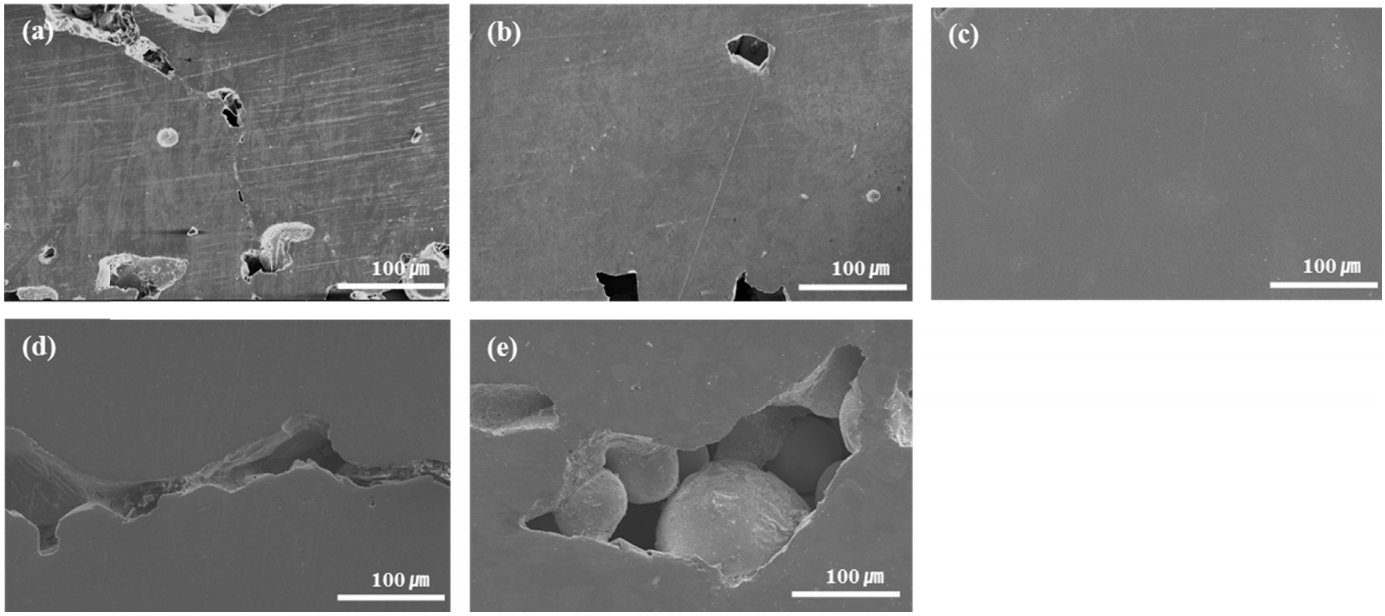

Fig. 2. Cross-sectional SEM images and result of EDS analysis of Mo layer deposited with different scan speeds (mm/min); (a) 900, (b) 750, (c) 600, (d) 450 and (e) 300

a unit area. In the Mo layer deposited with a relatively fast scan speed (i.e. lower energy density) of laser beams, pores were observed as shown in Figure 2(a) and 2(b). This is because the densification of Mo powders is difficult because the molten pool is not sufficiently generated on the surface of the powders. As the scan speed decreased, the pores of the surface gradually increased. In particular, pores were not observed and dense surface was formed in the Mo layer deposited at a scan speed of 600 mm/min (Fig. 2(c)). However, the slow scan speed (i.e. higher energy density) of laser beams causes a volume change during the cooling due to the generation of excessive melt pool on the surface of the powders. For this reason, cracks occurred in the Mo deposition layer as shown in Figure 2(d). In addition, when a large amount of liquid phase was generated on the surface of Mo powder due to high energy density, oxidation that negatively affects the densification occurred severely (Fig. 2(e)). As presented in Table 1, the oxygen content of Mo deposition layer with scan speed of 300 mm/min increased by about three times in atomic percent (at.%) compared to Mo deposition layer with scan speed of 600 and 900 mm/min. Therefore, it is difficult to form a dense Mo deposition layer.

TABLE 2

Results of EDS area analysis on Mo deposition layer with scan speed of 900, 600 and 300 mm/min

Element	900 mm/min		600 mm/min		300 mm/min	
	wt.%	at.%	wt.%	at.%	wt.%	at.%
O K	1.92	10.51	1.41	7.91	7.53	32.80
Mo L	98.08	89.49	98.59	92.09	92.47	67.20
Totals	100.00	100.00	100.00	100.00	100.00	100.00

Figure 3 shows the hardness and porosity of Mo layer deposited with different scan speeds. As expected, the correlation between hardness and porosity in Mo layer was inversely proportional. In particular, Mo layer deposited with scan speed of 600 mm/min (energy density: 533.3 J/mm^3) had the hardness value of 324 Hv with a porosity of approximately 2% or less. Ohser-Wiedemann et al. reported that pure Mo sample fabricated by spark plasma sintering for 3 minutes at 1,600°C with 67 MPa has the hardness value is 209 Hv and the relative density of 95% [16]. Compared to this finding, it was demonstrated that Mo deposition layers with higher relative density and hardness can be formed with less effort by powder-based DED. In future work, we will analyze the sputtering properties of Mo sputtering target through powder-based DED intensively.

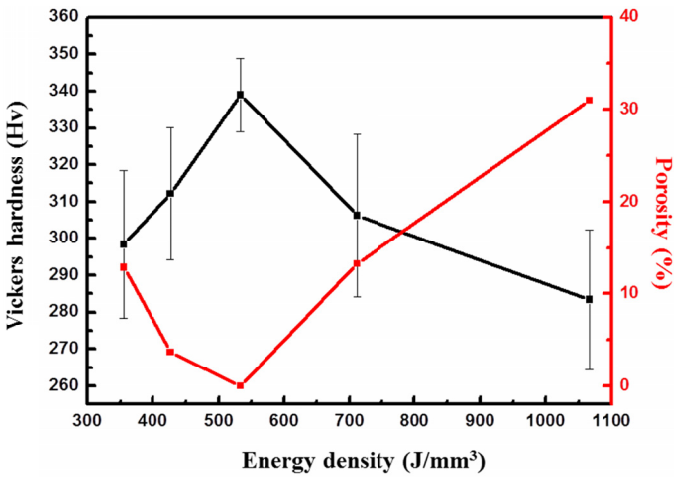

Fig. 3. Hardness and porosity of Mo layer deposited with different energy density

4. Conclusion

In this study, spherical Mo powders with an average particle size of 37 um were prepared by EIGA. Subsequently, powder-based DED with various scan speeds was performed using gas-atomized Mo powder. In the Mo layers deposited with the scan speed of 900 and 750 mm/min, pores were found in the cross section of Mo deposition layer. Mo layer deposited with the scan speed of 600 mm/min had a hardness value of 324 Hv with a porosity of less than 2%. On the other hand, cracks occurred in the Mo layer deposited with a slower scan rate (450 and 300 mm/min), and the Mo powders were not densified due to the oxidation.

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