MoO₃ thick film was manufactured by using a thermal spray process (Atmospheric Plasma Spray, or APS) and its microstructure, phase composition and properties of the coating layer were investigated. Initial powder feedstock was composed of an orthorhombic α-MoO₃ phase, and the average powder particle size was 6.7 μm. As a result of the APS coating process, a MoO₃ coating layer with a thickness of about 90 μm was obtained. Phase transformation occurred during the process, and the coating layer consisted of not only α-MoO₃ but also β-MoO₃, MoO₂. Phase transformation could be due to the rapid cooling that occurred during the process. The properties of the coating layer were evaluated using a nano indentation test. Hardness and reduced modulus were obtained as 0.47 GPa and 1.4 GPa, respectively. Based on the above results, the possibility of manufacturing a MoO₃ thick coating layer using thermal spray is presented.

Keywords: MoO₃; Thermal spray; Atmospheric plasma spray; Microstructure; Properties
2. Experimental

This study used MoO$_3$ powder purchased from Nanografi, with a purity of 3N (99.97%). Powder morphology was analyzed using FE-SEM (S-4300SE, Hitachi), and the powder size and distribution were analyzed using a laser particle size analyzer (Mastersizer 3000, Malvern PANalytical). The initial powder had a particle size ranging from a few nm to massive particles larger than 100 μm. An X-ray diffractometer (XRD; X’Pert Pro MRD, PANalytical: Cu-Kα, scan step size: 0.02°, scan rate: 1°/min) was used to identify the feedstock’s phase composition.

The substrate used for the coating was pure Cu. Before performing coating, Al$_2$O$_3$ was used to sandblast the substrate, and a high-pressure air compressor was used to air blow residual particles off the substrate. The plasma spray process was conducted in atmospheric pressure (i.e., atmospheric plasma spray, or APS), and the equipment used was the SG-100 from Praxair. To identify the optimal conditions, various tests were conducted with varying currents and voltages. As a result, all conditions failed to obtain a dense coating layer, and necks were formed through particle surface bonding. The micro-Vickers hardness values of the unsound coating layers measured ranged from 20 Hv to 65 Hv. The reasons for this were analyzed to be i) the size distribution of the feedstock was wide, and ii) the thermal conductivity of MoO$_3$ was low, causing heat to not transfer properly to the particles. Therefore, additional sieving was performed to reduce the powder size distribution. The above powder feedstock was used for the plasma spray process, and the process conditions were voltage of 45 V, current of 600 A, stand-off distance (SoD) of 100 mm, pitch of 3 mm, powder carrier gas of Ar (10 SCFH) and plasma gas of Ar/N$_2$ (105/42 SCFH).

FE-SEM was used to observe the cross-sectional microstructure of the coating layer. Before observation, the mounting sample underwent grinding with SiC paper up to #4000, and mirror polishing using 1 μm diamond suspension was applied. Phase analysis of the coating layer was performed using X-ray diffraction (XRD). To investigate the physical properties of the coating layer, a micro-Vickers hardness tester (HM-200, Mitutoyo) and nano indenter (TI-950, Bruker) were used. Ten tests were conducted on each sample, and the average of outcomes was used. The nano indenter test was used to measure the mean hardness and reduced modulus. A Berkovich-type tip was used, and a load of 3mN was applied. In addition, the loading-holding-unloading times were set as 5 sec, 2 sec and 5 sec, respectively.

3. Results and discussion

Fig. 1(a) is the FE-SEM observation of the powder morphology. The powder had an irregular shape. Fig. 1(b) is the X-ray diffraction phase analysis of the initial powder, and which was composed of α-MoO$_3$ phases with an orthorhombic structure. In addition to the thermally stable orthorhombic α-phase, MoO$_3$ is reported to also have crystalline phases, such as semi-stable
monoclinic β-phase and hexagonal h-phase [15]. Fig. 1(c) shows
the average powder size and size distribution analysis results.
While the initial powder had a relatively narrow distribution,
there were still fine particles of nm units. The powder size dis-
tribution curve has a bi-modal shape, and the average powder
size was 6.7 μm.

The melting point and boiling point of MoO₃ are 795°C
and 1155°C, respectively, which are significantly lower than
other oxides with high temperature melting points. As a result,
the powder easily vaporizes when exposed to high-temperature
plasma, so the process was conducted considering that quality
of the coating layer can decrease due to such a characteristic.
When the process was performed with a constant voltage and
different currents during the pre-test, the sample manufactured
with the 600 A, 35V conditions had the highest hardness. In many
studies, pores present on the coating are known to reduce the
hardness of the coating layer as it accepts deformation without
resistance [16-18]. Therefore, it is possible to estimate that the
process condition with the highest hardness value will be able
to manufacture the densest coating layer. Based on the hard-
ness test results of coating layer materials, additional tests were
conducted with current fixed at 600 A and the voltage increased
to 45 V to improve the quality of the coating layer. With the
increased plasma power, the melting level of the powder was
expected to increase. A cross-sectional image of the coating
layer manufactured with the corresponding process condition
was observed using FE-SEM, and the results are presented in
Fig. 2. The coating layer was approximately 90 μm thick, and the
microstructure was composed of lamellae. In general, the
APS process will undergo cooling when melted particles (i.e.,
droplets) collide, and heat transfer to the substrate causes im-
mediate solidification. As the heat transfer to the substrate is
extremely fast, the coating layer undergoes rapid cooling [19],
and it is known that the depositing of droplets forms a coating
layer composed of lamellae. In addition, the cross-sectional
microstructure of the coating layer was confirmed to have de-
fects including inter-lamellar cracks, large pores and unmelted
powder. A hardness test was conducted to identify the densifica-
tion of the coating layer, and the hardness of the coating layer
measured 198.4 Hv. This hardness value is approximately three
times higher than the hardness value measured for the unsound
coating layers formed during pre-tests. This finding confirms
the densification increase in the coating layer.

Fig. 2. Cross-sectional FE-SEM images of coating layer; (a) low magnification and (b) high magnification image

![Cross-sectional FE-SEM images of coating layer](image)

Fig. 3. X-ray diffraction graphs of initial powder and APS coating layer

![X-ray diffraction graphs of initial powder and APS coating layer](image)

These graphs show the phase transformation during the plasma spray process. As the more fully melted powder was used according to SoD, the number of α-Al₂O₃ phases undergoing phase transformation into γ-Al₂O₃ phase increased [20]. This was understood to be the result of rapid cooling that took place when the liquid state shifted to a solid state during the process. Through the findings
of this study, it was estimated that most of the particles fully melted in the corresponding process condition. The occurrence of phase transformation can be explained with the powder particles composed of thermodynamically stable α-MoO₃ phases becoming a liquid state due to the exposure to high temperature plasma and then undergoing rapid cooling as a result of heat transfer to the substrate. And, amorphous phase formation was also suspected to be caused by rapid cooling. In relation to this, Kim et al. reported the possibility of amorphous phase formation in APSed Al₂O₃-ZrO₂ due to rapid cooling [21].

A nano indentation test was conducted to evaluate the properties of the manufactured coating layer (Fig. 4). As pores were present within the coating layer, changes in displacement during holding time were observed in the graph. The test found that the average hardness of the coating layer measured 0.47±0.12 GPa, and the reduced modulus measured 13.4±3.86 GPa. The deviation between hardness values was checked as ~25%, and was considered to be quite high. Further research is needed to manufacture a more uniform coating layer in the future.

![Fig. 4. Nano indentation result curve of APS coating layer](image)

4. Conclusions

This study used the atmospheric plasma spray process to manufacture a MoO₃ coating layer, and presented the microstructure, phase composition, and properties of the manufactured coating layer. A sound MoO₃ coating layer was obtained using the process conditions of 600A, 45V. The cross-sectional microstructure of the coating layer was composed of lamellae, the typical APS process characteristic, and defects such as inter-lamellar cracks, large pores and unmelted powders were observed. Unlike the feedstock composition phase(α-MoO₃), the coating layer was composed of α-MoO₂, β-MoO₂, MoO₃. The phase transformation mechanism was identified to be caused by the rapid cooling that occurred during the process. Based on such findings, the possibility of manufacturing a MoO₃ coating layer using thermal spray was confirmed, and this process is anticipated to make a great to in manufacturing thick MoO₃ films.

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