X-ray residual stress measurements on plasma sprayed molybdenum coatings

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Abstract

Plasma sprayed molybdenum coatings have been applied to friction parts in the automotive field because of their high wear resistance. Clarification concerning the significance of mechanical properties and the residual stress state of the coating is important to improve the performance of the coating. However there are some difficulties in the measurement of mechanical properties of the coating, especially Young's modulus, because it has complex structures including lamella, pores, micro cracks and so on. Young's modulus is required to determine the x-ray stress constant for x-ray residual stress measurements. Strain gauges are often used to measure the strains of a component. If glue is applied to thermal spray coatings to attach a strain gauge, it might be that it penetrates into the pores and becomes solidified, hence incorrect strains will be measured.

In this research, firstly, Young's modulus and x-ray stress constant, *K*, for molybdenum thermal spray coating were determined experimentally by four-point bending tests. The effects of quick-drying glue on strain measurement using a strain gauge were investigated. Secondly, the residual stresses of the coatings were measured using x-ray diffraction. Six types of substrates with a different thermal expansion coefficient (TEC) were prepared. The materials used, in ascending order of TEC, were Super Invar, molybdenum, SCM440, SK5, SUS304 and A6063. Molybdenum powder was sprayed on the substrates in air with various thicknesses.

The following results were obtained. (1) The effect of quick-drying glue on the mechanical strain measurement on the sprayed coating was negligible. (2) The Young's modulus of the coating was lower than that of the commercial molybdenum sheet. (3) Linear strain response against applied mechanical loads was observed in the case of the polished coating surface. (4) The x-ray stress constant *K* of the coating and the bulk were almost the same. (5) Residual stresses on the coating surfaces were of tensile type on all substrates used in this study. (6) Tensile residual stresses of the coatings increased with the decreased thermal expansion coefficient of substrate.

Keywords: x-ray stress measurement, residual stress, plasma spraying, molybdenum coating, thermal expansion coefficient, quick-drying glue, strain response.

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1 Introduction

Thermal sprayed molybdenum coating is one of the surface modification applications improving the wear resistance. Mo coating also has high heat resistance so that Mo coatings are applied to the engines and sliding parts of automobiles [1].

The effect of controlled residual stress on wear resistance has been reported [2]. Evaluation of the residual stress is essential to improve the enabled functions. In this study, firstly, the effects of quick-drying glue on mechanical Young's modulus measurement using strain gauge were considered. Secondly, the effects of thermal expansion coefficient (TEC) of substrates on residual stress were investigated.

2 Experiment procedure

2.1 Specimen preparation

Materials used as substrates, in ascending order of TEC in air, were Super Invar, molybdenum, SCM440, SK5, SUS304 and A6063. Molybdenum powder was used as a spraying material. TEC of all materials used are shown in table 1. A condition "substrate TEC < coating TEC" can be provided when Super Invar is used as substrate in the case of molybdenum coating despite it has low TEC. Two types of substrate were used for mechanical Young's modulus measurement and residual stress measurement. The former was 100 × 15 × 3mm, the later was 15 × 15 × 3mm.

Table 1: Thermal expansion coefficient of materials at the room temperature α, $\times 10^{-6}$.

JIS	Super Invar	Molybdenum	SCM440	SK5	SUS304	A6063
AISI	ASTM F1684	Molybdenum	AISI 4140	SK50H	AISI 304	ISO AlMg0.5Si
	0.5	4.9	11.8	11.8	17.3	24.3

2.2 Spraying condition

For Young's modulus measurement, molybdenum was sprayed with the thickness of 300μm by the Atmospheric Plasma Spraying system. The spraying condition is shown in table 2. There were two surface conditions. One is as-sprayed surface and another is polished with waterproof abrasive paper.

For residual stress measurement, six types of substrate were sprayed with various thicknesses. Spraying was applied with the different number of passes.

Table 2: Plasma spraying conditions.

Spraying material	Mo powder
Method	APS
Current	800 A
Voltage	26 V
Spraying distance	100 mm
Maximum thickness	300 μm

3 Experimental procedure

3.1 Measurements of mechanical Young's modulus *E*

Loads were applied to coating-substrate composite beam by four-point bending. Tensile or compressive stress was generated at coating surface. The range of applying loads was determined in the elastic region (within -1600 × 10^{-6} strain) determined by Acoustic Emission test [3]. In this paper, the elastic region of the coatings was defined below AE increasing point.

In measuring mechanical strain using the strain gauge, it is said that quick-drying glue penetrates into the pores and solidifies thus making strain measurement ambiguous. In our study, strain gauges were attached using quick-drying glue; Young's modulus of the glue after solidified was 3.2 GPa. With reference to Young's modulus, the coating was measured with various conditions of coating surfaces and substrate thicknesses. All the strain gauges were held for 24 hours after bonding.

Both strains of substrate and coating were measured at the same time. Young's modulus of coating, E_C, was calculated by the following equation (1)

$$E_C = \frac{t_C A_S E_S - \left(\frac{\varepsilon_C}{\varepsilon_S} + 1\right) E_C Z_S}{\left(\frac{\varepsilon_C}{\varepsilon_S} + 1\right) Z_S - t_C A_C} \tag{1}$$

from the theory of composite beam. Where *t* is the thickness, *A* is the cross-section area and *Z* is the geometrical moment of area, respectively. Two suffixes C and S mean coating and substrate. Coating surfaces are postulated as uniaxial stress.

Furthermore the coating was broken by bending just after cooling with liquid nitrogen. The fractured surface was observed by a Scanning Electron Microscope to clarify the penetration depth of quick-drying glue.

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3.2 Measurements of x-ray stress constant *K*

Tensile and compressive stress was applied to coating surfaces within the elastic region described previously. Loads were applied gradually and slope of 2θ-$\sin^2\psi$ diagram [4] *M* was determined in each case under the condition shown in table 3. 2θ-$\sin^2\psi$ diagrams were obtained by averaged diffraction angle in three times continuous measurements. X-ray stress constant *K* was calculated with M-σ_{app} diagram. The equations for *K* and *M* are as follows.

$$K = \frac{\sigma_{app}}{M} \quad , \quad M = \frac{\partial(2\theta_\psi)}{\partial(\sin^2\psi)} \tag{2}$$

Table 3: Conditions of x-ray diffraction.

Characteristic x-ray	V-Kα
X-ray wavelength	0.250483 nm
Diffraction plane	Mo211
Diffraction angle 2θ	154.267 deg
Kβ filter	Ti
Peak determination	Center of FWHM
Stress determination	2θ-$\sin^2\psi$ method
$\sin^2\psi$ range, step	0.0 - 0.6 , 0.1step
Detecter	PSPC
Tube voltage, current	30 kV, 8 mA
Peak count	2048
Diameter of incident x-ray	ϕ3 mm

3.3 Residual stress measurements by x-ray diffraction

A flattened particle had a thickness of about 4μm and x-ray penetration depth was about 0.9μm. This means that the lattice strain of extreme upper part of the coating surface could be measured in this study. Residual stresses were measured on the principle of the Ω-goniometer method

4 Results and discussion

4.1 Penetration depth of quick-drying glue, and Young's modulus

Fig.1 shows the cross-sectional secondary electron images of fractured surface of the free-standing coating. The chemical composition of quick-drying glue provides white image when exposed to the electron beam irradiation. The right image indicates that the glue penetration depth was about 40μm.

Young's modulus of the coating was measured using three specimens with different conditions. Tensile and compressive stresses were applied to as-sprayed or polished surface, and thicknesses of substrates were 3mm and 5mm. As a result measured E_C was about 235 GPa on an average. E_C seems to be lower than that of bulk molybdenum (323 GPa [5]) because of the porosity of the coating.

Then Young's modulus of quick-drying glue was 3.2 GPa. The penetration depth of quick-drying glue was about 10% of the coating thickness, and the Young's modulus of the glue was about 1% of the coating. It means that the effect of quick-drying glue on mechanical strain measurement on the sprayed coating was negligible.

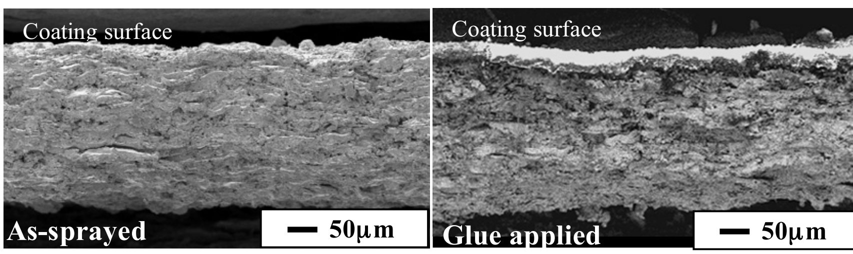

Figure 1: Cross-sectional secondary electron images of fractured surface of the free-standing coating.

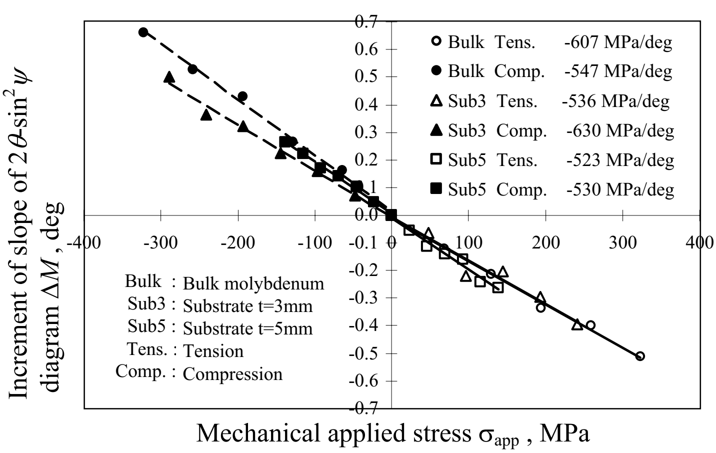

Figure 2: The relationship between slope of 2θ-$\sin^2\psi$ diagram M and mechanical applied stress $\sigma_{app.}$

4.2 X-ray stress constant *K*

In the case of as-sprayed surface slope *M* was not changed regularly. This is the same result with a previous study [6] so that details will be skipped. Fig.2 shows the relationship between M and σ_{app} on polished coating specimens. These specimens had different thicknesses of substrates as t=3mm (Sub3) and t=5mm (Sub5). Bulk molybdenum (Bulk, t=3mm) was also tested. Increment of slope M was evaluated differently depending on applied stress, tension or compression. Applied stresses were calculated based on Young's modulus of coating, E_C. Calculated K values are written in explanatory note in Fig.2.

Considering that the results of bulk molybdenum are criterion, K of thermal sprayed molybdenum coating were almost the same with that, and independent to experimental conditions. This means that the strain response was improved because of polishing the coating surface.

To conclude the averaged K value -563 MPa/deg would be used for residual stress determination.

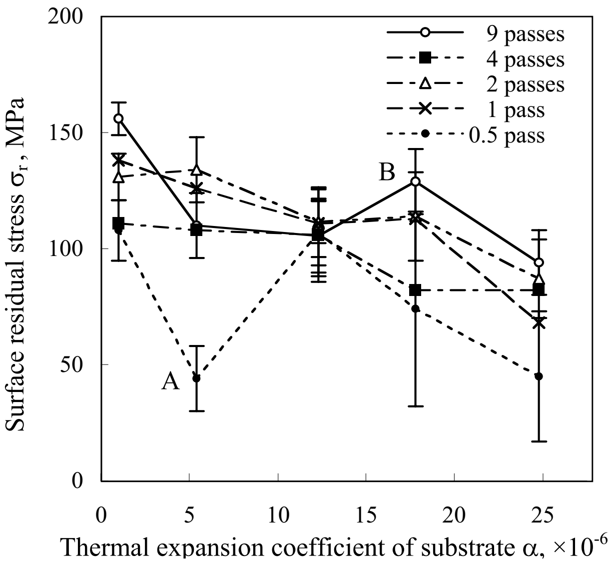

Figure 3: The relationship between TEC of substrates α and surface residual stress σ_r.

4.3 The relationship between TEC and residual stress

Fig.3 shows the relationships between TEC of substrates and surface residual stress of coatings. This result includes the changes of scanning passes of the spraying gun. Residual stresses of all specimens were tension. Here, the melting point of molybdenum is about 2893 K [7]. Therefore the temperature difference was about 2273 K when the molten particles impacted the pre-heated substrate. As a result the temperature difference caused significant shrinkage when the coating began to cool. Therefore the tensile residual stress was generated.

Except for two plots signed A and B in fig.3, residual stresses tend to increase with decreasing the TEC of substrate. It suggested that the shrinkage of substrate contributed to that of lamella in cooling process so-called the bimetal.

5 Conclusion

(1) The effect of quick-drying glue on mechanical strain measurement on the sprayed coating was negligible.
(2) The Young's modulus of the coating was lower than that of the bulk molybdenum.
(3) Linear strain response against applied mechanical loads was observed in the case of polished coating surface.
(4) X-ray stress constant K of the coating and the bulk were almost the same.
(5) Residual stresses on the coating surfaces were of tensile type on all substrates used in this study.
(6) Tensile residual stresses of the coatings increased with decreasing the thermal expansion coefficient of substrate.

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