State Analysis of Plasma Sprayed Alumina†

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High temperature materials including ceramics can versatily be coated on the surfaces of substrate materials such as metals and alloys using plasma spraying. Ceramic coatings of alumina and zirconia are widely performed using plasma spraying in order to improve some properties of substrate metals such as heat- and corrosion-resistances. Mechanical properties and porosity of these ceramic coatings have been investigated[1)-4)] but state analysis of plasma-sprayed ceramics has scarcely been reported. In this study, state of aluminum and oxygen in plasma-sprayed alumina were investigated by XPS (X-ray photo-electron spectroscopy) and chemical shift method of Al K_α emission X-ray.

Alumina coating was produced by spraying on mild steel using a spray equipment of METCO 7MB type. The equipment was operated at 500A x 70V. Ar and H_2 gases were used as plasma gas. Binding energies of aluminum and oxygen were measured by a multi-functional spectrometer of HB-50A type (VG Co. Ltd.). Spectra of Al K_α emission X-ray were measured by a spectrometer of 5064P type (Rigaku Denki Kogyo Co. Ltd.).

Binding energies of Al_{2s}, Al_{2p} and O_{1s} in various sprayed aluminas are shown in **Table 1. Figure 1** and **Table 2** show Al K_α emission X-ray spectra and these chemical shifts. Binding energies of Al_{2s} and O_{1s} fairly abruptly shift to higher energies when as-sprayed alumina was annealed at 900°C and decrease with increasing annealing temperature. Compared with the chemical shift of as-sprayed alumina in Al K_α emission X-ray spectra, sprayed-alumina annealed at 900°C shows same value. However, shift of sprayed-alumina annealed becomes larger with increasing annealing temperature in the case of higher temperature than 1000°C.

According to the previous results,[5)-7)] the structure

Table 1 Binding energies of Al_{2s}, Al_{2p} and O_{1s} in various plasma-sprayed aluminas

Heat Treatment	Binding Energy		
	Al_{2s}	Al_{2p}	O_{1s}
as sprayed	121.9 eV	77.1 eV	534.0 eV
900°C,20hr in 10%H_2-Ar	122.2	77.3	534.4
1000°C, 1hr in Ar	122.2	77.3	534.3
1150°C, 0.5hr in Ar	122.0	77.3	534.2

* Reference Ar_{2p}

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Table 2 Chemical shifts of Al K_α emission X-ray in various plasma-sprayed aluminas

Material	2θ (90% height)	2θ (50% height)	Δ°2θ (90% height)	asymmetry degree [2θ(50%)-2θ(90%)]
Al metal	142.708	142.735	0.000	0.027
Sprayed Al_2O_3 (as sprayed)	142.633	142.692	0.075	0.059
Sprayed Al_2O_3 (900°C, 20hr annealed)	142.633	142.692	0.075	0.059
Sprayed Al_2O_3 (1000°C, 1hr annealed)	142.628	142.695	0.080	0.067
Sprayed Al_2O_3 (1150°C, 0.5hr annealed)	142.623	142.703	0.085	0.080
α-Al_2O_3	142.618	142.680	0.090	0.062

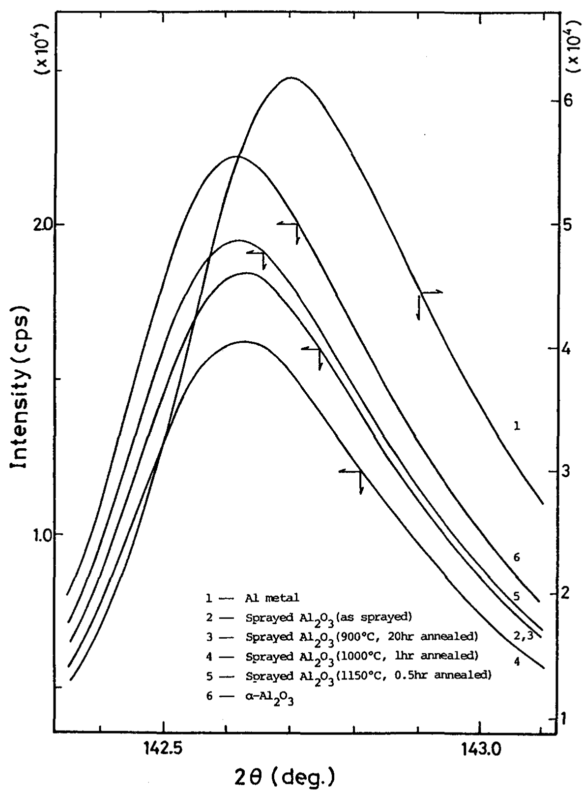

Fig. 1 Spectra of Al K_α emission X-ray in various plasma-sprayed aluminas

of plasma sprayed alumina is γ-Al_2O_3 and it begins to transform to δ-Al_2O_3 when annealing temperature is above 800°C. Further, the transformation of δ-Al_2O_3 to α-Al_2O_3 in plasma sprayed alumina begins near 1000°C. The behavior of chemical shift in Al K_α emission X-ray shows a good agreement to the dependence of the structural change of sprayed alumina on heat treatment. Asymmetric degree of Al K_α X-ray spectrum shows a maximum when sprayed alumina was annealed at 1150°C for 0.5 hr. This may be due to the fact that sprayed alumina is not well-crystallized or consists of more than two phases.

The differences of binding energies of Al_{2p} and O_{1s} between γ-Al_2O_3 and α-Al_2O_3 are not large and they lie between 0.5 and 0.8 eV, so that it is difficult to consider the chemical state of aluminum from the result in Table 2. Conclusively, it is suggested that chemical shift of emission X-ray is more effective to detect the difference of chemical state of aluminum in the isomorphous transition of alumina than XPS method.

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