

Title	Characterization on Surface of Plasma-Sprayed CoCrAlY Coatings(Materials, Metallurgy & Weldability)
Author(s)	Iwamoto, Nobuya; Makino, Yukio; Hong, Chen Jian et al.
Citation	Transactions of JWRI. 1985, 14(2), p. 275-278
Version Type	VoR
URL	<a href="https://doi.org/10.18910/8156">https://doi.org/10.18910/8156</a>
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# Characterization on Surface of Plasma-Sprayed CoCrAlY Coatings<sup>†</sup>

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## Abstract

Surface state of CoCrAlY coats plasma-sprayed at low pressures was investigated by XPS method. Only aluminum oxide was detected at outermost surface layer of CoCrAlY Coat II (non-optimized), while the oxide at outermost surface layer of CoCrAlY Coat I (optimized) consists of complex oxides containing aluminum, cobalt and chromium. An impure element which can be assigned to iron enriches near surface layer in Coat II but not in Coat I.

KEY WORDS: (XPS) (Plasma-Spraying) (CoCrAlY)

## 1. Introduction

Various alloys have been developed for improving the properties of metallic materials such as heat- and corrosion-resistances. MCrAl alloys are the important ones for satisfying the above-described requirements and some oxygen-active elements are usually added to these alloys. The effect of these oxygen-active elements on oxidation behaviors of these alloys have been well investigated [1-3].

MCrAl alloys occupy the important position as the bond coat materials in ceramic coating using plasma spraying [4]. In plasma spraying, in most cases, these MCrAl bond coats produced under a low vacuum condition show better properties, compared with those sprayed in air [5]. However, surface of MCrAl coat, especially with oxygen-active elements such as yttrium and zirconium, have scarcely been characterized. In this study, state analysis of

surface of plasma-sprayed CoCrAlY coats was performed by X-ray photoelectron spectroscopy (XPS) method and difference between so-called "optimized" and "non-optimized" CoCrAlY coats was examined.

## 2. Experimentals

Two sorts of plasma-sprayed CoCrAlY coats, which were supplied from Plasma Technik Co. Ltd., were used. Chemical composition of original CoCrAlY powder is shown in Table 1. The conditions producing CoCrAlY coats are given in Table 2. Tank pressure in producing optimized CoCrAlY coat was slightly lower than that in non-optimized coat. X-ray photoelectron spectra of these CoCrAlY coats were measured under a vacuum of  $1 \times 10^{-9}$  torr or higher, operating a spectrometer of ESCA Lab-5 (VG Scientific Ltd.) at 10 kV  $\times$  20 mA. Path energy was fixed to 50 eV. Correction of charging effect

Table 1 Chemical composition of CoCrAlY powder.

Co	Cr	Al	Y	C	O	N	P	S	Total all others
Bal.	28.72	6.33	0.82	0.018	0.05	0.008	0.004	0.002	0.20

Table 2 Plasma spraying conditions

Specimen	Plasma Gas		Current	Voltage	Tank Pressure	Spray Distance	Powder Feed Rate
	Ar (l/min)	H <sub>2</sub> (l/min)					
Coat I (optimized)	50	8.5	620 A	76 V	40 mbar	270 mm	39 g/min
Coat II (non-optimized)	60	8.5	620	77	60	270	39

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were performed using  $C_{1s}$  peak position as the standard (284.6 eV).  $Ar^+$  ion sputtering was conducted under the vacuum of about  $5 \times 10^{-6}$  torr.

### 3. Results

Micrographs of surfaces and cross-sections of two sorts of CoCrAlY coats are shown in Fig. 1. It is found that coarse grains are observed in Coat II (sprayed in "non-optimized" condition), compared with Coat I (sprayed in "optimized" condition). Figure 2 gives XPS spectra of CoCrAlY coats in the energy region from 0 to 100 eV. In the non-optimized CoCrAlY coat, the peaks near 24 and 75 eV are fairly strongly observed before  $Ar^+$  ion sputtering, while the peaks near 45 and 60 eV show very weak intensities. The feature is also observed after  $Ar^+$  ion sputtering for 180 sec. The peaks near 45 and 60 eV appears clearly after sputtering for 600 sec. In the optimized CoCrAlY coat, these peaks (near 45 and 60 eV) are observable in non-sputtered coat though not so remarkable. After  $Ar^+$  ion sputtering, these peaks are clearly observable. The peaks near 24 and 75 eV are always observed and the latter becomes sharper after sputtering while the former remains still broad after  $Ar^+$  ion sputtering for 600 sec.

### 4. Discussions

Micrographs of Fig. 1 support that CoCrAlY particles in producing Coat I were well melted during plasma spraying because metallographs obtained from Coat I show fine structures. There exists some difficulties for assigning each XPS peak because some peaks overlap within 2 eV in such combination as  $O_{2s}$  and  $Y_{4p(3/2)}$ , or  $Cr_{3p}$  and  $Y_{4p(1/2)}$ . Further, broadness due to the existence of each element in various chemical states (for example, in various valence states) produces some ambiguity. Table 3 gives the energies of electronic levels of elements relating to CoCrAlY coat [6]. According to the Table 3, the peaks near 24 and 75 eV are assigned to  $O_{2s}$  and  $Al_{2p}$  peaks, respectively, because 75 eV peak can be observed in non-sputtered coat irrespective of no observation of any peak near 45 eV which corresponds to  $Cr_{3p}$ . The content of yttrium in CoCrAlY powder is very low as shown in Table 1. Accordingly, it is not necessary to be taken into account as far as yttrium is not extremely enriched in sprayed coat. The very low content of yttrium and no appearance of any peak near 157 eV support the assignment of the peak near 24 eV to  $O_{2s}$  peak. Similarly, the peaks near 45 and 60 eV can be assigned to  $Cr_{3p}$  and  $Co_{3p}$  levels. Conclusively, each XPS peak in the energy level from 0 to

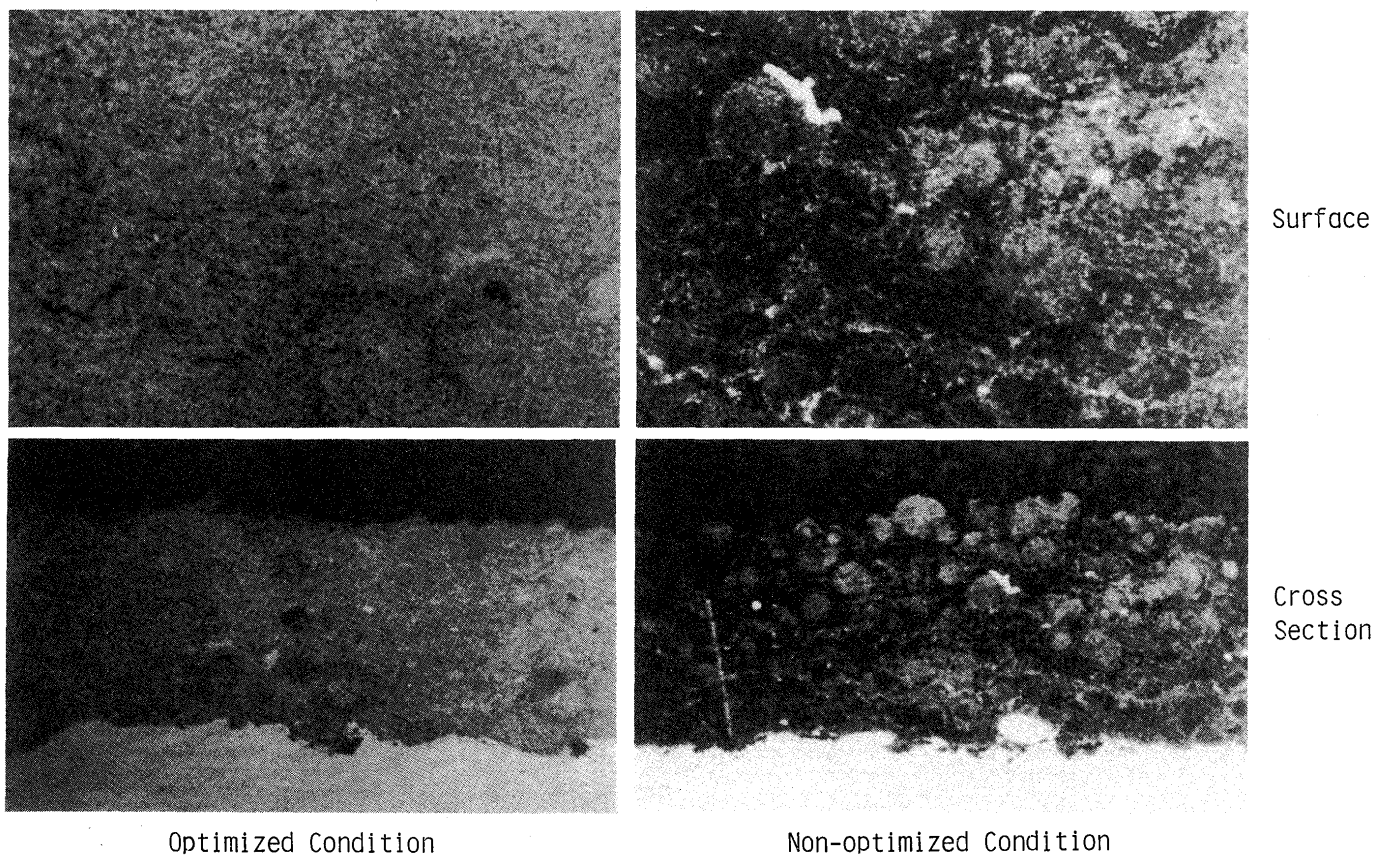


Fig. 1 Optical micrographs of surfaces and cross sections of plasma-sprayed CoCrAlY coats.

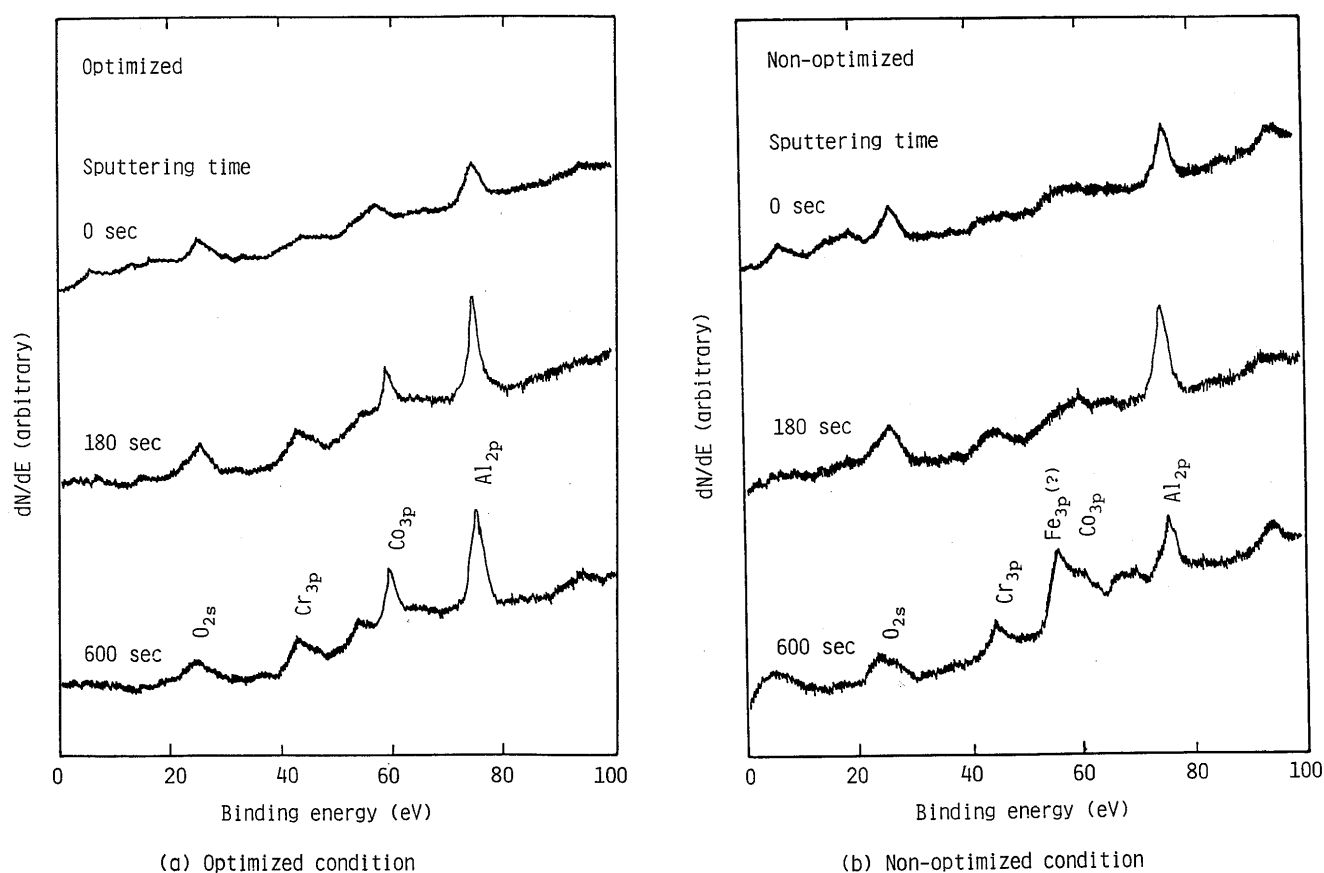


Fig. 2 XPS spectra of plasma-sprayed CoCrAlY coats.

100 eV can be assigned as shown in Fig. 2.

From the clear difference between the spectra obtained after sputtering for 180 sec, it is shown that aluminum is enriched at the outermost surface layer of CoCrAlY Coat II whereas cobalt and chromium are also contained in the outermost surface layer in Coat I. Therefore, it is indicated that oxide layer in the outermost surface of Coat II consists of only aluminum oxide, while the oxide layer in the outermost surface of Coat I consists of complex oxides containing aluminum, cobalt and chromium. The precise crystallographic forms of complex oxides can not be determined by only XPS results though possible oxides are several sorts of spinels containing Al, Co and/or Cr,

$\text{Cr}_2\text{O}_3$ ,  $\text{Al}_2\text{O}_3$ ,  $\text{Co}_2\text{O}_3$ ,  $\text{Co}_3\text{O}_4$  and so on.

The peak near 55 eV remains somewhat unclear. The possible element is iron because  $\text{Fe}_{3p(1/2)}$  and  $\text{Fe}_{3p(3/2)}$  peaks appear at 55 and 56 eV though chemical analysis of powder shows no content of the element. Further, impure iron gives high intense peak in CoCrAlY Coat II after sputtering for 600 sec. The enrichment of iron near surface should be clarified in the further investigation.

Use of ion sputtering sometimes reduces metal oxide to metal or suboxide [7]. The effect can be ignored in aluminum oxide except the broadening of peak width. However, the reduction should be taken into account in the case of transition metal oxide such as  $\text{Co}_2\text{O}_3$  and  $\text{Cr}_2\text{O}_3$ .

Table 3 Line positions from Mg X-rays, by element related to this study\*

Element	1s	2s	2p <sub>1/2</sub>	2p <sub>3/2</sub>	3s	3p <sub>1/2</sub>	3p <sub>3/2</sub>	3d <sub>3/2</sub>	3d <sub>5/2</sub>	4s	4p <sub>1/2</sub>	4p <sub>3/2</sub>
O	531	23										
Al		119	74									
Cr		698	586	577	77	46	45					
Fe		847	723	710	93	56	55					
Co		927	796	781	103	63	61					
Y					395	313	301	160	158	45		25

\* Photoelectron lines are given by eV unit. *Italic* photoelectron lines are related to discussion in this study.

If the appearance of the peak near 55 eV is related to the reduction due to ion sputtering, similar phenomenon should be observed in CoCrAlY Coat I. As shown in Fig. 2, however, such phenomenon was not observed in Coat I. Therefore, the peak near 55 eV is related not to ion sputtering but to enrichment of impure element, as indicated above, which should be attributed to iron.

### 5. Summary

State analysis of surface of CoCrAlY coats plasma-sprayed under low pressure was performed by XPS method. Oxide layer in CoCrAlY Coat I (so-called "optimized") consists of complex oxide containing aluminum, cobalt and chromium, while the oxide layer in CoCrAlY Coat II (so-called "non-optimized") consists of almost aluminum oxide. Further, enrichment of the impure element, which should be assigned to iron, is observed in

non-optimized Coat II. No information on yttrium was obtained on account of very low content.

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