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Protective Oxides Formed on CoCrAlY Coatings

by

Louis F. Aprigliano

DTNSRDC/SME-86/52 Protective Oxides Formed on CoCrAlY Coatings

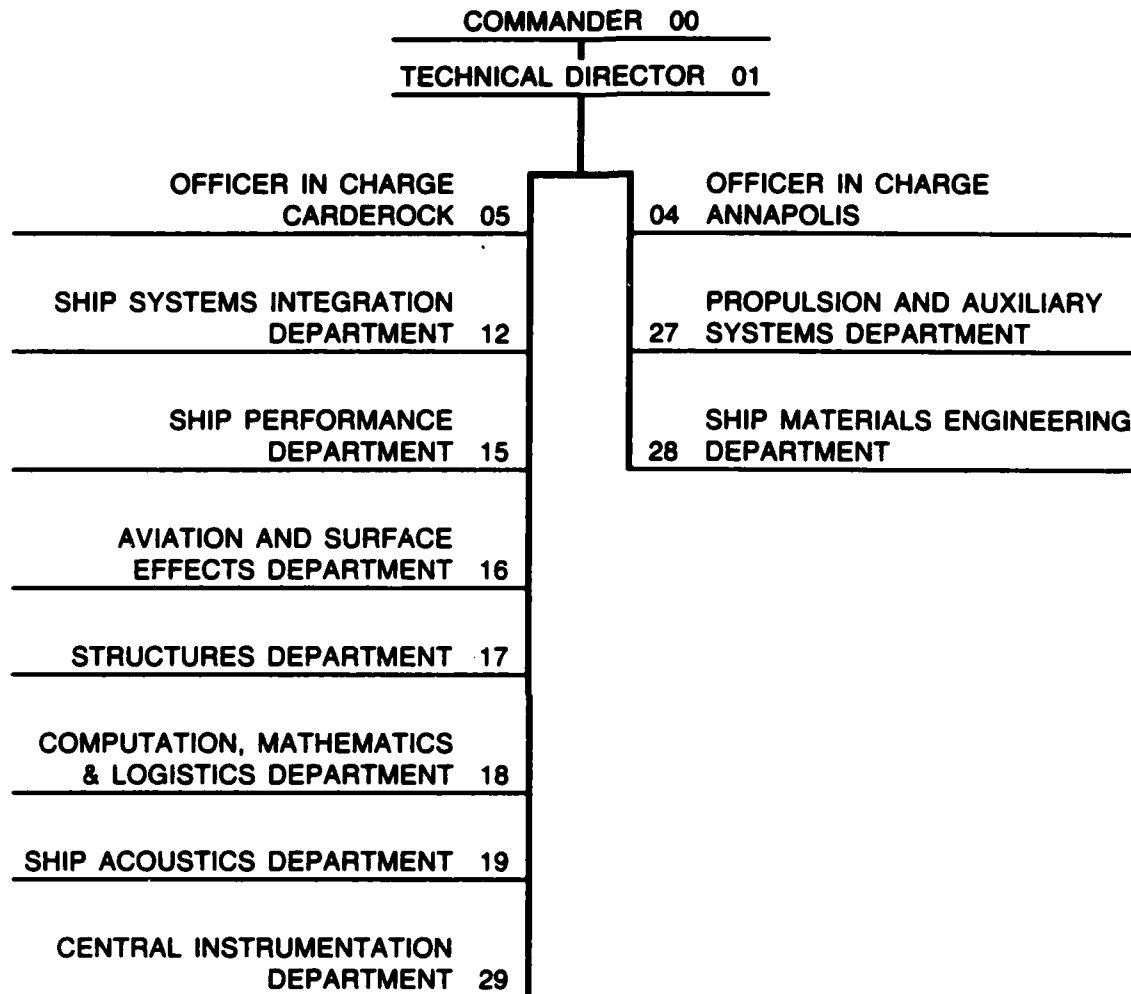
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### ABBREVIATIONS

A	10 <sup>-8</sup> centimeters
at%	Atomic percent
CoCrAlY	A metallic coating containing cobalt, chromium, aluminum, and yttrium
eV	Electron Volt
FAT	Fixed Area Transmission
K $\alpha$	K-alpha
kV	Kilo-volts
PVD	Physical vapor deposition
UHV	Ultra-high vacuum
wt%	Weight percent
$\mu$	Micron, 10 <sup>-6</sup> meters
XPS	X-ray Photoelectron Spectroscopy

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## ABSTRACT

The metallic coatings used to protect the hot-section turbine blades of marine gas turbines are often a mixture of cobalt, chromium, aluminum, and yttrium (CoCrAlY). Using the surface sensitive technique of x-ray photoelectron spectroscopy, the protective oxide scales on CoCrAlY coatings containing nominal levels of 20, 29, and 35wt% chromium were found to be essentially the same and were predominately alumina and a yttrium rich phase that is tentatively identified as yttrium aluminum garnet. As increasing levels of chromium in this coating system are known to improve the coating's hot corrosion resistance, the similarity of the initial scales on all these coatings leads to the conclusion that chromium provides its hot corrosion benefit by slowing the propagation phase of the bulk coating attack.

## ADMINISTRATIVE INFORMATION

This work was supported under Work Unit 1-2813-125, Task Area S0379-SL001 Task 16869 on Materials Development for Second Generation Shipboard Gas Turbines. The program manager was Mr. D. Groghan, Naval Sea Systems Command (SEA 05R33). This work was also supported under Work Unit 2812-017 as part of the DTNSRDC Independent Research Program entitled "Hot Corrosion of Chromium Metallic Coatings". This report satisfies milestones 1-2813-125-21 and 1-2812-017-60.

## INTRODUCTION

Since the mid 1960's, gas turbine engines have been used for ship propulsion. These engines, such as the 20,000 horsepower General Electric LM 2500, undergo a form of high temperature corrosion, called hot corrosion, when used in a marine environment. The parts most severely attacked are the metallic coatings used on the hot-section turbine blades. These coatings are often a mixture of cobalt, chromium, aluminum and yttrium and as a class are identified by the acronym CoCrAlY.\* The

\*Definition of abbreviations are given on page v.

type of hot corrosion most frequently occurring in the Navy's use of these coatings has been designated type 2 hot corrosion. The most destructive part of this corrosion (the propagation phase) takes place when the turbine blade temperatures are in the range of 677° to 732°C (1250° to 1350°F). The macroscopic details of this corrosion process have been described as follows:

- Sulfur in the fuel forms sulfur dioxide and sulfur trioxide during combustion.
- Sulfur dioxide and/or sulfur trioxide reacts with the cobalt in the coating to form cobalt sulfate.
- Sodium sulfate from the ~~fuel~~ ingested by the engine deposits in solid form at 704° (1300°F) on the turbine blades.
- The sodium sulfate and the cobalt sulfate form a low melting point mixed sulfate and in the presence of the sulfur trioxide acidically flux the coating from the turbine blade.

Unpublished data has shown that increasing the chromium content of the coating to 30 or 40wt% from the originally used 20wt% dramatically improved the hot corrosion resistance of these coatings. It has been speculated that in the 20wt% chromium coatings the oxide scales that form on the coatings are a mixture of cobalt oxide, chromium oxide and aluminum oxide, while in the 40wt% chromium coatings the oxide scale is predominately chromium oxide. Thus, it had been hypothesized that in high chromium coatings the formation of cobalt sulfate is impeded by the continuous nature of the chromium oxide.

In order to study the validity of this hypothesis, the goal of this research effort was to examine the initial protective oxide scales that form on actual coatings. This was accomplished by using the surface sensitive analytical technique of x-ray photoelectron spectroscopy and will be described in detail below.

## EXPERIMENTAL PROCEDURE

### X-RAY PHOTOELECTRON SPECTROSCOPY

To study the nature of the initial oxides formed on production CoCrAlY coatings, their composition as a function of depth from the surface was studied using x-ray photoelectron spectroscopy (XPS). XPS involves exposing the surface of interest to x-rays of a discrete energy. In the Kratos model XSAM 800 surface analyzer used in these experiments Al K $\alpha$ (1486.6eV) was the radiation source. The interaction of this radiation with the specimen causes the surface to emit electrons with energy characteristic of the atoms from which they were emitted. This process is diagrammatically represented in figure 1. The XPS equipment has an electron energy analyzer which measures the kinetic energy of these emitted electrons. This kinetic energy can be related to the binding energy of the electrons by the relation

$$E_b = E_{x\text{-ray}} - E_{\text{kin}} - \phi_a,$$

- $E_{\text{kin}}$  = kinetic energy of electrons as passed by spectrometer
- $\phi_a$  = work function of entrance to spectrometer lens
- $E_b$  = Binding energy of emitted photoelectrons.

As kinetic energy of electrons are being measured, ultra-high vacuum (UHV) conditions are required in the sample analysis chamber. Without the UHV conditions the electrons would be scattered by gas molecules. The surface sensitivity of the XPS method arises from the fact that it measures the energy of emitted electrons. These electrons have a very short mean free path in solid matter. Typically, this distance is on the order of 5 to 10 angstroms (See figure 2). Therefore, these emitted electrons represent elements present in the outer layer or several atomic layers below the surface.

### XPS QUANTIFICATION

The concentration of a given element in the surface is represented by the

intensity of electrons (counts/second) emitted at a given characteristic energy. A typical spectrum of intensity of electrons versus electron binding energy is shown in figure 3. This spectrum can be expanded with the computer used to acquire the data and the intensity of any peak can be measured. The computer does this by performing a background subtraction around the peak of interest and calculating the area under the peak. If there are partially overlapping peaks, a peak synthesis routine is used to extract the peak of interest. For example, the peaks synthesis routine was used to separate the yttrium 3d5/2 and 3d3/2 peaks. All intensities are then corrected by a multiplication factor which represents the spectrometer efficiency and the probability of emission from a particular electron energy level in a given atom. These correction factors have been determined by the manufacturer of the analyzer. These factors are given in table 1. The equation<sup>1,2</sup> used to calculate the results in atomic percent is

$$C_x = \frac{I_x}{Q_x} / \sum_i \frac{I_i}{Q_i}$$

$Q_x$  = quantification factor for a given element and electron orbital  
 $I_x$  = peak intensity for a given element.

The details of the analysis parameters used to acquire the XPS data are:

- Al excitation (1486.6eV)
- Low magnification
- Low resolution
- FAT mode
- Start Energy of Scan, 1000eV
- Channels, 4000
- True time averaging
- Step Size, 0.25eV
- Dwell, 0.4 sec.

All XPS peaks were referenced to the adventitious carbon 1s peak of 284.6eV.

Table 1 - XPS peak binding energy locations and KRATOS quantification factors.

Element	Electron Designation	Approximate Binding Energy Location of the Peak (eV) for Elemental and/or Oxide State	KRATOS Quantification Factor
Cobalt	2p <sub>3/2</sub>	778 - elemental 780 - oxide	2.5
Chromium	2p <sub>3/2</sub>	574 - elemental 576 - oxide	1.5
Aluminum*	2p	73 - elemental 75 - oxide	0.12
Yttrium*	3d <sub>5/2</sub>	156 - oxide	1.05
Oxygen*	1s	532 - oxide Al <sub>2</sub> O <sub>3</sub>	0.61

\*For more detail on aluminum, yttrium, and oxygen peak locations, see Table 2.

The approximate binding energy of the XPS peaks used in the quantitative analyses are given in Table 1. To assist in identifying the chemical state of the yttrium, XPS spectra were made of pure standards of yttrium oxide (Y<sub>2</sub>O<sub>3</sub>) and yttrium aluminum garnet (Y<sub>3</sub>Al<sub>5</sub>O<sub>12</sub>). The yttrium oxide and the yttrium aluminum garnet had purities of 99.999% and 99.995% respectively. These oxides are non-conductive and charge-up during the spectra acquisition. To compensate for this, the adventitious carbon peak in both standards was referenced to the 1s carbon peak of 284.6eV and all other peaks were corrected accordingly. These locations are shown in Table 2. The peaks were acquired by averaging multiple (5) small range (20eV wide) scans around each location of interest. As mentioned before, in the case of partially overlapping peaks, a peak synthesis routine was used to separate and identify these peaks.

Table 2 - Yttrium, aluminum, and oxygen XPS peak identification.

Material		Binding energy (eV) of XPS peaks*						
		Yttrium		Oxygen			Aluminum	
		3d5/2	3d3/2	1s			2p	
Yttrium Oxide (Y <sub>2</sub> O <sub>3</sub> )		156.35--	160.7	529.25	--	--	--	
Yttrium Aluminum Garnet (Y <sub>3</sub> Al <sub>5</sub> O <sub>12</sub> )		-- 157.1	160.6	--	530.8	--	73.7	--
Aluminum Oxide† (Al <sub>2</sub> O <sub>3</sub> )		--	--	--	--	531.6	--	74.7
CoCrAlY Coatings#	20Cr	--158.1	160.1	--	531.35 Minor	532.1 Major	74.35 Minor	75.1 Major
	29Cr	--157.8	158.5	--	530.8 Minor	531.85 Major	73.85 Minor	74.85 Major
	35Cr	--158.35	160.35	--	531.1 Minor	531.85 Major	73.85 Minor	74.6 Major

\* All peaks are calibrated to 284.6eV, all values ± 0.25eV  
 † Values obtained from reference 3.  
 # All CoCrAlY coatings are in the heat treated condition followed by 1 minute of argon sputter cleaning.

DEPTH PROFILING

To measure the changes in composition of the coating elements as they vary through the protective oxide film on the coatings, the original surface was sputtered off in successive layers while the specimen was in the UHV chamber of the analyzer. This was done with the ion gun attached to the analyzer chamber. The ion gun allows an accelerated ionized beam of argon atoms to impinge on the specimen surface. By a collision process this strips off the surface layers. Typical ion gun parameters used were:

- Beam voltage 4.5kV
- Emission 25 milliamps
- Pressure  $20 \times 10^{-3}$  Pascals
- Beam rastered to cover the entire surface

By using a tantalum oxide standard,  $Ta_2O_5$ , these parameters were found to represent a sputter rate of  $30 \times 10^{-8}$  cm/min for that standard. The standard preparation procedures used are given in the Appendix. After the desired thickness is removed an XPS spectrum is acquired and quantified. This process is continued to the total depth desired. This allows a plot of composition versus depth. Accumulated sputter times at which analyses were made were 0, 1, 3, 15, 47, 79, 159, 191, 231, 247, 263, 287, 303, 319, 343, 351, 367, 391, 407, 455, and 480 minutes.

#### MATERIAL

The specimen configuration used is as shown in figure 4. This specimen was made of cast Rene 80. This nickel-base alloy is the one used for the first stage hot-section turbine blades of the LM-2500 engine. Prior to machining, the alloy was given a solution heat treatment of:

2225°F (1220°C) - 2 hours in air - air cooled,  
2000°F (1095°C) - 4 hours in air - air cooled.

The machining process removed any oxides formed during the heat treatment. The specimens were then coated by Temescal. This company coats the actual turbine blades for the Navy's LM-2500 engines. Actual production coating procedures were used. The coating was applied by physical vapor deposition to a thickness of 0.126mm (5 mils). Coatings with the compositions shown in table 3 were produced. These compositions were selected to allow for the investigation of the effect of varying the chromium content in the bulk coating on the oxide film composition. After the application of the coating, the specimens were given the following heat treatment:

1925°F (1051°C) - 4 hours in vacuum ( $10^{-4}$  torr) - vacuum cooled,  
 1550°F (845°C) - 16 hours in argon - argon cooled.

This heat treatment is similar to that given to production coatings. Production parts allow for the final step to be done in a vacuum or argon environment. After heat treatment, the coatings are in a configuration that is suitable for direct insertion into the XPS analysis chamber.

Table 3. CoCrAlY coating composition.

Identification Number	Coating Composition* (wt%)			
	Co†	Cr	Al	Y
A	65.77	20.64	13.35	0.24
B	60.15	28.89	10.72	0.23
C	54.03	35.25	10.32	0.40

\* Composition supplied by the manufacturer.  
 † Cobalt composition was done by difference.

## RESULTS AND DISCUSSION

### QUANTITATIVE ANALYSIS

The results of the quantitative analysis are shown in figures 5, 6, and 7 and are listed on tables 4, 5, and 6. The data plots show the quantitative analysis in weight percent on the coordinate axis with the corresponding sputtering time shown on the ordinate axis. For reference purposes the approximate depth of sputtering related to a given sputtering time is also shown. This approximation represents the depth of sputtering as derived from a Ta<sub>2</sub>O<sub>5</sub> standard and should serve as an adequate guide to the depth of sputtering on the coatings. These sputter/quantitative runs

Table 4 - Surface composition of 20Cr CoCrAlY as determined by XPS as a function of accumulated sputter time.

Accumulated Sputter Time (min.)	20Cr CoCrAlY Coating Composition									
	Weight %					Atomic %				
	Co	Cr	Al	Y	O	Co	Cr	Al	Y	O
0	5.0	3.8	47.8	5.4	38.0	1.9	1.7	40.5	1.4	54.5
1	5.4	3.4	48.4	6.0	36.8	2.1	1.5	41.6	1.6	53.2
3	5.3	3.1	48.9	5.9	36.8	2.1	1.4	41.9	1.5	53.1
15	4.0	2.4	49.8	2.8	41.0	1.5	1.0	40.5	0.7	56.3
47	4.7	2.0	52.6	1.6	39.1	1.8	0.8	43.0	0.4	54.0
79	4.3	3.4	52.3	1.3	38.7	1.6	1.5	43.0	0.3	53.6
159	7.8	3.9	49.0	0.4	38.9	3.0	1.7	40.8	0.2	54.3
191	12.0	5.7	47.0	0.2	35.1	4.9	2.6	41.0	0.1	51.4
231	22.0	10.0	39.0	0.3	28.7	9.8	5.0	38.0	0.1	47.1
247	27.0	9.5	35.0	---	28.5	12.4	4.9	34.8	---	47.9
263	29.2	15.3	35.1	---	20.4	14.8	8.7	38.7	---	37.8
287	38.0	18.3	24.3	---	19.4	20.8	11.3	28.9	---	39.0
303	32.7	18.8	33.9	---	14.9	18.0	11.7	40.3	---	30.0
319	38.9	25.3	24.6	---	11.2	23.9	17.6	33.0	---	25.5
343	41.7	19.5	23.0	---	15.8	24.2	12.8	29.2	---	33.8
351	41.3	21.5	24.7	---	12.5	25.0	14.7	32.6	---	27.7
367	40.7	25.1	23.0	---	11.2	25.3	17.7	31.4	---	25.6
383	41.3	21.2	27.0	---	10.5	25.4	14.7	36.2	---	23.7
399	44.1	23.3	23.2	---	9.4	28.3	17.0	32.5	---	22.3
447	45.0	24.5	22.9	---	7.5	30.0	18.4	33.3	---	18.3

Table 5 - Surface composition of 29Cr CoCrAlY as determined by XPS as a function of accumulated sputter time.

Accumulated Sputter Time (min.)	29Cr CoCrAlY Coating Composition									
	Weight %					Atomic %				
	Co	Cr	Al	Y	O	Co	Cr	Al	Y	O
0	6.8	5.5	43.4	6.0	38.3	2.7	2.5	37.5	1.6	55.7
1	7.3	7.4	37.7	5.8	41.8	2.9	3.3	32.2	1.5	60.1
3	6.2	5.5	43.5	6.0	38.8	2.4	2.5	37.4	1.6	56.1
15	2.3	6.4	51.1	3.4	36.8	0.9	2.8	43.0	0.9	52.4
47	6.4	3.3	49.9	2.2	38.2	2.4	1.4	41.8	0.6	53.8
79	5.3	1.0	51.4	1.1	41.2	2.0	0.4	41.4	0.3	55.9
159	5.1	4.3	50.0	0.9	39.7	1.9	1.8	41.0	0.2	55.1
191	6.9	6.5	46.9	0.7	39.0	2.7	2.8	39.2	0.2	55.1
231	14.5	6.5	44.9	0.7	33.3	6.0	3.1	40.3	0.2	50.4
247	18.0	8.4	41.9	0.5	31.2	7.7	4.1	39.1	0.1	49.0
263	24.5	10.6	41.5	---	23.4	11.5	5.6	42.5	---	40.4
287	26.8	13.7	42.5	---	17.0	13.6	7.8	46.8	---	31.8
303	36.6	11.9	31.3	---	20.2	19.2	7.0	35.6	---	38.2
319	39.7	20.7	21.1	---	18.5	22.4	13.2	26.0	---	38.4
343	32.5	19.7	32.0	---	15.6	18.6	8.3	40.2	---	32.9
351	42.1	14.7	28.2	---	15.0	24.0	9.5	35.1	---	31.4
367	43.6	15.2	27.1	---	14.1	25.4	10.0	34.4	---	30.2
391	49.5	19.2	19.6	---	11.7	31.6	13.8	27.2	---	27.4
407	48.8	23.2	17.4	---	10.6	32.1	17.3	25.0	---	25.6
455	49.8	17.9	23.1	---	9.2	32.3	13.1	32.6	---	22.0

Table 6 - Surface composition of 35Cr CoCrAlY as determined by XPS as a function of accumulated sputter time.

Accumulated Sputter Time (min.)	35Cr CoCrAlY Coating Composition									
	Weight %					Atomic %				
	Co	Cr	Al	Y	O	Co	Cr	Al	Y	O
0	8.7	5.8	40.2	5.0	40.3	3.4	2.6	34.5	1.3	58.2
1	6.7	3.6	46.1	4.1	39.1	2.6	1.6	39.0	1.0	55.8
3	7.2	4.4	46.7	3.4	38.3	2.8	1.9	39.7	0.9	54.7
7	5.2	5.8	47.0	3.3	38.7	2.0	2.5	39.6	0.8	55.1
15	2.7	6.3	46.3	2.7	42.0	1.0	2.7	37.8	0.7	57.8
31	6.6	3.7	50.6	2.2	36.9	2.6	1.6	42.7	0.6	52.5
63	3.7	4.9	50.7	0.5	40.2	1.4	2.1	41.3	0.1	55.1
169	5.1	4.5	47.5	0	42.9	1.9	1.9	38.2	0	58.0
247	15.3	15.2	42.3	0	27.2	6.9	7.6	41.0	0	44.6
303	22.9	24.7	30.8	0	21.6	11.6	14.2	34.0	0	40.2
351	32.9	23.7	25.5	0	17.9	18.1	14.8	30.7	0	36.4
407	32.2	31.6	23.3	0	12.9	19.3	21.6	30.6	0	28.5
455	34.1	37.6	18.4	0	9.9	22.2	27.7	26.2	0	23.9
480	37.6	30.5	20.6	0	11.3	23.6	21.8	28.3	0	26.3

were made for the 20, 29, and 35wt% chromium containing coatings. They show that the initial oxide scales in all cases are essentially rich in aluminum, yttrium, and oxygen with only minor amounts of chromium or cobalt. The significant yttrium in the outer layers of the coatings is interesting in that only 0.2wt% yttrium is added to the bulk coating but approximately 5 to 6wt% is found in the outer protective oxide scale. Preferential segregation of elements to the surface of an alloy has been found to occur in other alloy systems, such as Cu-Ni<sup>4</sup>. With time of sputtering

the composition of coatings, particularly for the 35wt% chromium containing coating, begin to approach the bulk coating composition. Accordingly, the oxygen levels drop from that of the initial layer, but they are not yet zero after the total sputtering time of 480 minutes or approximately 1.3 $\mu$  in depth. This oxygen probably represents coating defects (called leaders) which are common in PVD CoCrAlY coatings. These leaders are typically alumina.

The high concentration of aluminum and yttrium in the outer layers of these coatings, even when the chromium content is at 35wt%, is the most interesting result of this research effort. Unpublished data had shown that increasing the chromium content of these coatings to 30 or 40wt% from the originally used 20wt% dramatically improved the hot corrosion resistance of these coatings. It had been speculated that in the 20wt% chromium containing coatings the oxide scales that form on these coatings are a mixture of cobalt oxide, chromium oxide, and aluminum oxide, while in the 40wt% chromium containing coatings the oxide scale is predominantly chromium oxide. Thus, it had been hypothesized that in high chromium coatings the formation of cobalt sulfate would be impeded by the continuous nature of the chromium oxide. The results of this research effort, however, show that the scales are predominately aluminum and oxygen with a relatively high amount of yttrium, even at the 35wt% chromium level.

The significance of this high amount of yttrium in the surface oxide layers can be appreciated by considering the work of Sprague and of Hwang.<sup>(5,6)</sup> They have shown that the yttrium rich particles in the oxide scale can provide initiation sites common to all of these coatings at which the hot corrosion process can begin. The corrosion of the yttrium rich particles serves to mechanically disrupt the remaining alumina scale and thereby expose the bulk of the coating to the hot corrosion process.

Due to the similiarity of the starting scale in all of these coatings, a logical conclusion is that the chromium provides its hot corrosion benefit in slowing the propagation phase of the bulk coating attack. This then leaves unanswered the question of how does increasing the chromium content of these coatings result in improving their hot corrosion resistance. A means by which varying the chromium content of these coatings might slow the propagation of hot corrosion can be envisioned by considering the works of Luthra<sup>(7,8)</sup> on the sulfation of elemental cobalt and chromium. It has been found that it takes lower levels of sulfur dioxide to stabilize a mixed low melting point salt of cobalt sulfate in sodium sulfate than it does for chromium sulfate (or aluminum sulfate) and that the levels of sulfur dioxide that are present in typical marine gas turbines are sufficient to stabilize liquid mixed sulfates with cobalt sulfate but not chromium sulfate (or aluminum sulfate). This solution of the one sulfate in the other is necessary in order to promote and stabilize the formations of low melting point mixed sulfates which result in the rapid dissolution and fluxing of the coatings. Thus as more chromium is added to these types of coatings, it is likely that the formation of cobalt sulfate is suppressed in favor of chromium sulfate. If this is the case, then the formation of low melting point mixed salts that are needed for hot corrosion propagation are also suppressed. This suppression of the formation of cobalt sulfate could be the key to designing coatings with improved resistance to this hot corrosion environment. It will be the subject of a follow on research effort to show if the suppression of cobalt sulfate formation does indeed occur and if the rate and mechanism of the reactions can be correlated to the properties of cobalt or chromium in their unalloyed (elemental) forms.

## OXIDE FORM OF ALUMINUM AND YTTRIUM

An effort was made to determine the oxide form of aluminum and yttrium in the outer surface of the CoCrAlY coatings. The aluminum and yttrium are expected to be present in their oxide form and could also be present as yttrium aluminum garnet. For this reason XPS spectra were acquired of yttrium oxide and yttrium aluminum garnet for purposes of comparison to the XPS spectra of the CoCrAlY's. The peak locations given in reference 3 for aluminum and oxygen, as found in aluminum oxide, were also used for comparison purposes. These peak locations are given in table 2. The oxygen and aluminum peaks on the CoCrAlY specimens were each found to be made up of two overlapping peaks, one major and one minor. A computerized peak synthesis routine allowed the separate identification of these peaks and this data is shown in table 2. Within the experimental accuracy ( $\pm 0.25\text{eV}$ ) of locating the peak positions, the major aluminum and oxygen peaks seem most closely correlated to the aluminum and oxygen peaks of aluminum oxide, whereas the minor peaks of these two elements correlate to aluminum and oxygen as in yttrium aluminum garnet. The yttrium  $3d_{5/2}$  peak in the CoCrAlY's is closer to yttrium as in yttrium aluminum garnet than it is to yttrium oxide, i.e., 0.7 to 1.2eV vs. 1.5 to 2eV respectively. If these values were less than 0.5eV, the confidence in the comparison would be higher. For this reason the yttrium in the CoCrAlY's is tentatively identified as being present in the form of yttrium aluminum garnet. Consequently, the protective oxide on these CoCrAlY's seems to be predominately aluminum oxide with yttrium possibly present as yttrium aluminum garnet. It should be noted that there is also some cobalt and chromium present in analysis of the surface of these CoCrAlY's, however, the amounts are low relative to the bulk coating chemical composition and it was not possible from the data of this work to determine if the cobalt and chromium were present as discrete oxides or were simply contained within the aluminum oxide.

## SUMMARY

Gas turbine engines undergo a form of high temperature corrosion, called type 2 hot corrosion, when used in a marine environment. The parts most severely attacked are the metallic coatings used on the hot-section turbine blades. These coatings are often a mixture of cobalt, chromium, aluminum and yttrium and as a class are identified by the acronym CoCrAlY. In several research efforts it has been found that increasing the chromium content of the coating to 30 or 40wt% from the originally used 20wt% dramatically improved the hot corrosion resistance of these coatings. It had been speculated that in the 20wt% chromium coatings the oxide scales that form on these coatings are a mixture of cobalt oxide, chromium oxide and aluminum oxide, while in the 40wt% chromium coatings the oxide scale was predominantly chromium oxide. This continuous chromia scale was thought to impede the hot corrosion initiation. In order to study the validity of this hypothesis, the goal of this research effort was to examine the critical protective oxide scales that form on actual coatings, as part of determining how chromium improves hot corrosion resistance. Using x-ray photoelectron spectroscopy, it was found that the protective oxide scales for CoCrAlY coatings containing nominal levels of 20, 29, and 35wt% chromium were essentially the same. They were predominately alumina and a yttrium rich phase tentatively identified as yttrium aluminum garnet.

The yttrium in the oxide scale can provide initiation sites common to all these coatings at which the hot corrosion process can begin. This corrosion of the yttrium could serve to mechanically disrupt the remaining alumina and thereby expose the bulk of the coating to the hot corrosion process. In any case, due to the similarity of the starting scale in all of these coatings, a logical conclusion is that the chromium provides its hot corrosion benefit in this coating system by slowing the propagation phase of the bulk coating attack.

#### ACKNOWLEDGEMENTS

The author acknowledges Mr. Richard Stockhausen for his skillful operation of the x-ray photoelectron spectrometer used to gather the experimental data for this research program, and Dr. Wayne Worrell of the University of Pennsylvania for his suggestions regarding the possible presence of yttrium aluminum garnet in the oxides.

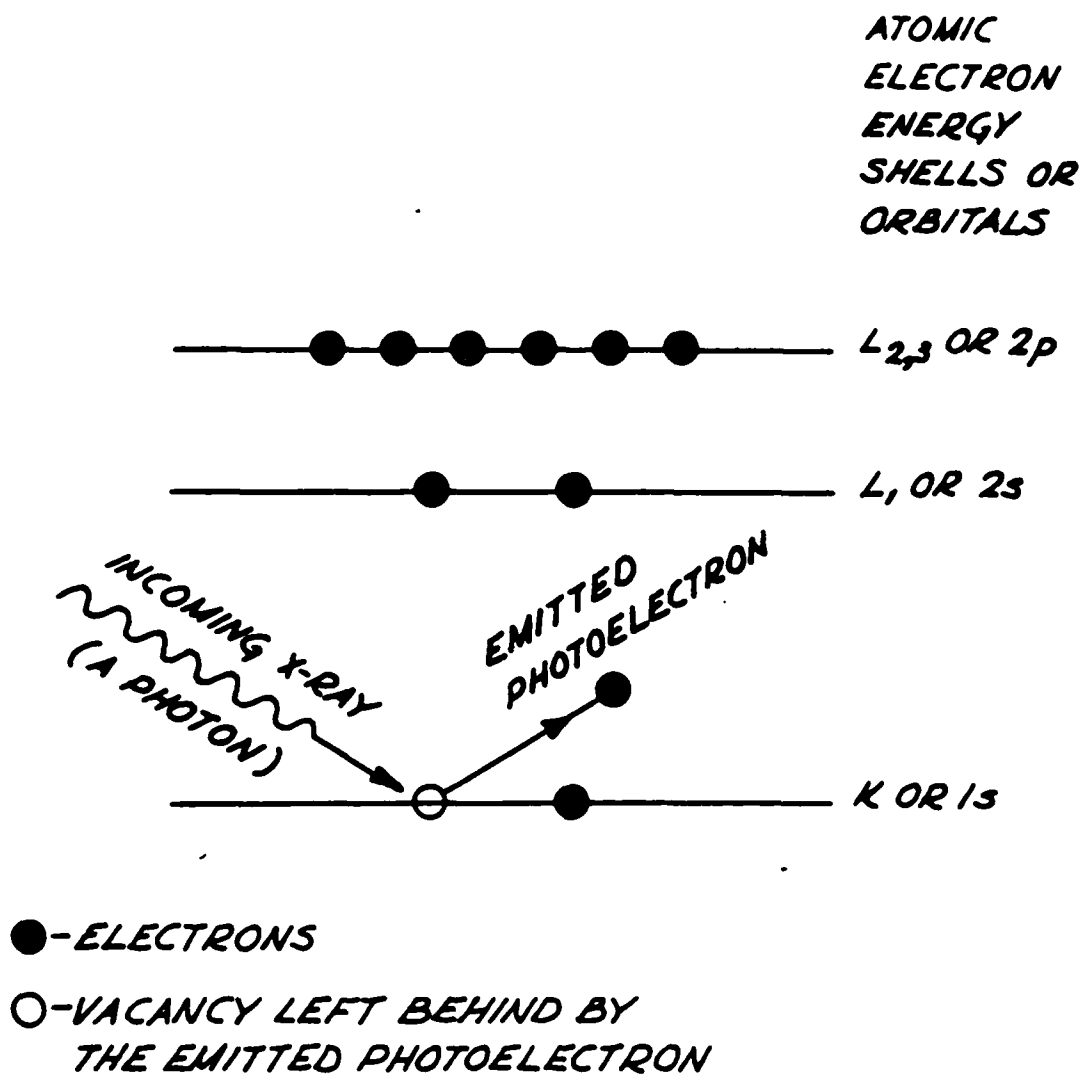


Fig. 1. Schematic representation of x-ray photoelectron emission.

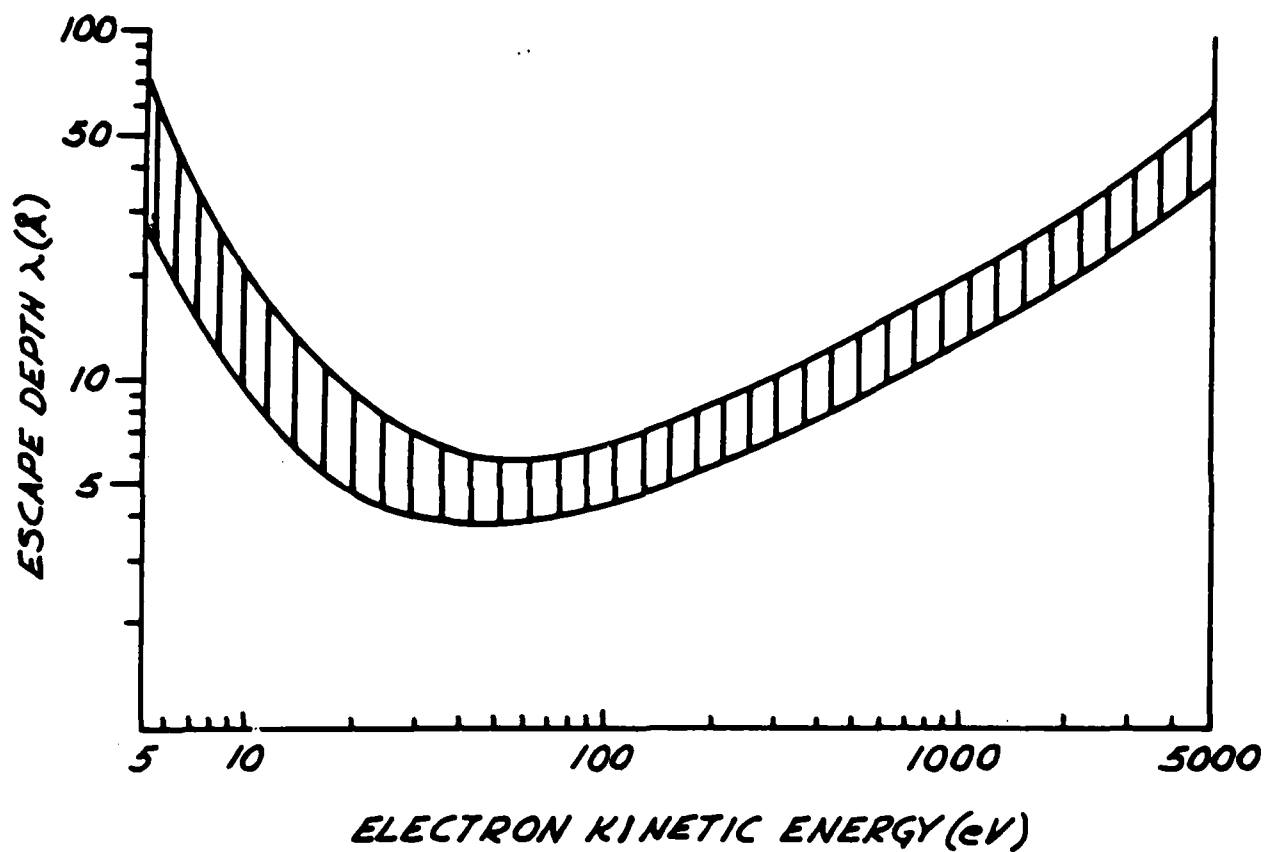


Fig. 2. Sampling depth in XPS as represented by a plot of escape depth against kinetic energy of the escaping electron (ref. 1).

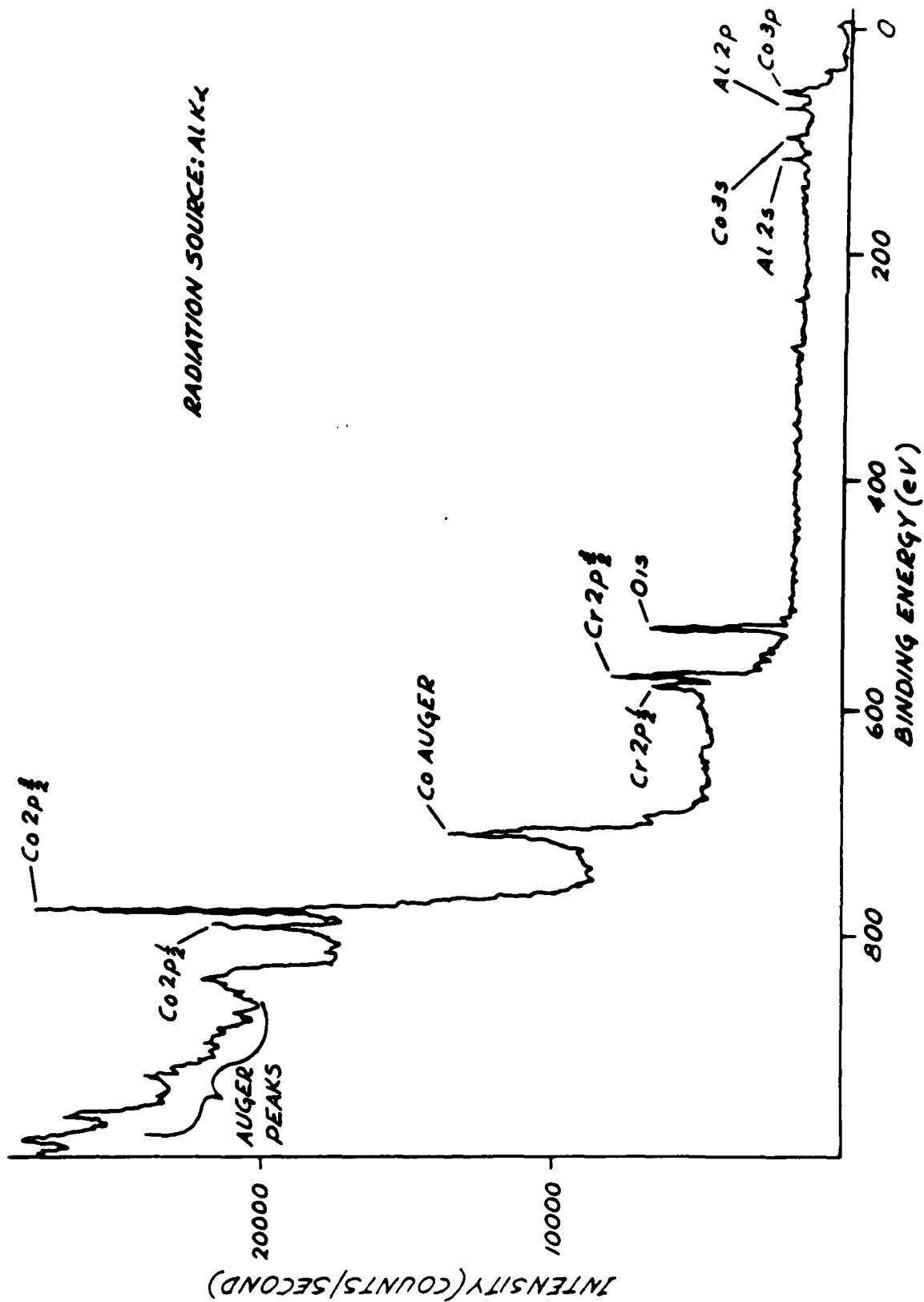


Fig. 3. Typical CoCrAlY XPS spectra after sputtering through initial oxide layer.

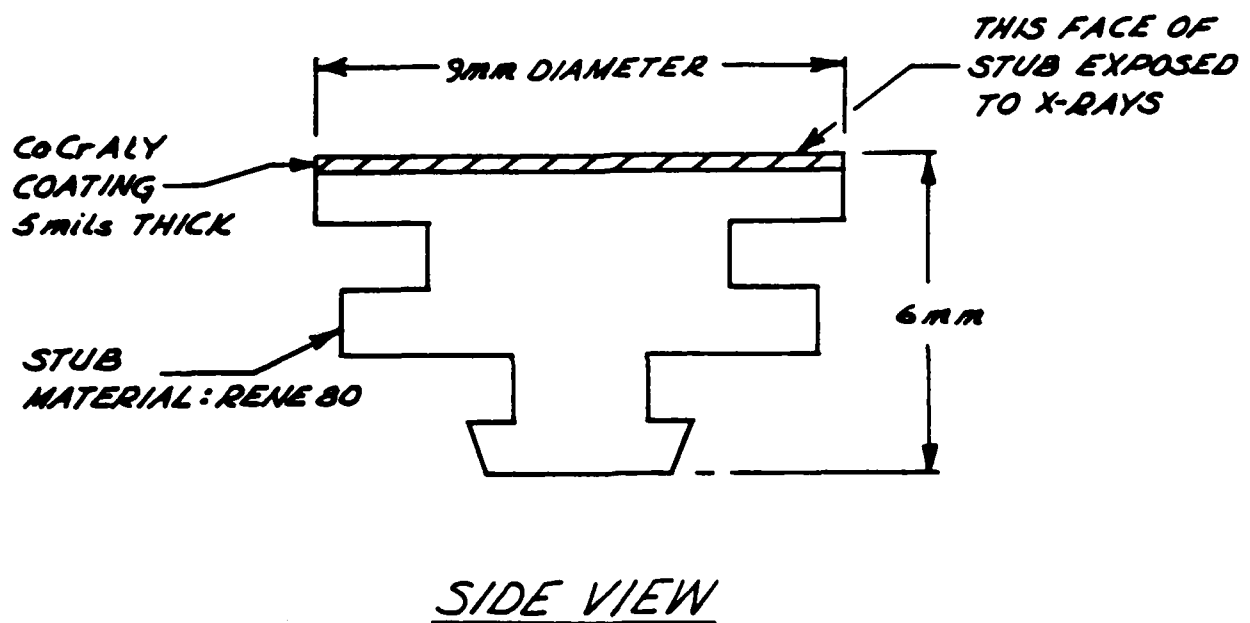


Fig. 4. Specimen configuration.

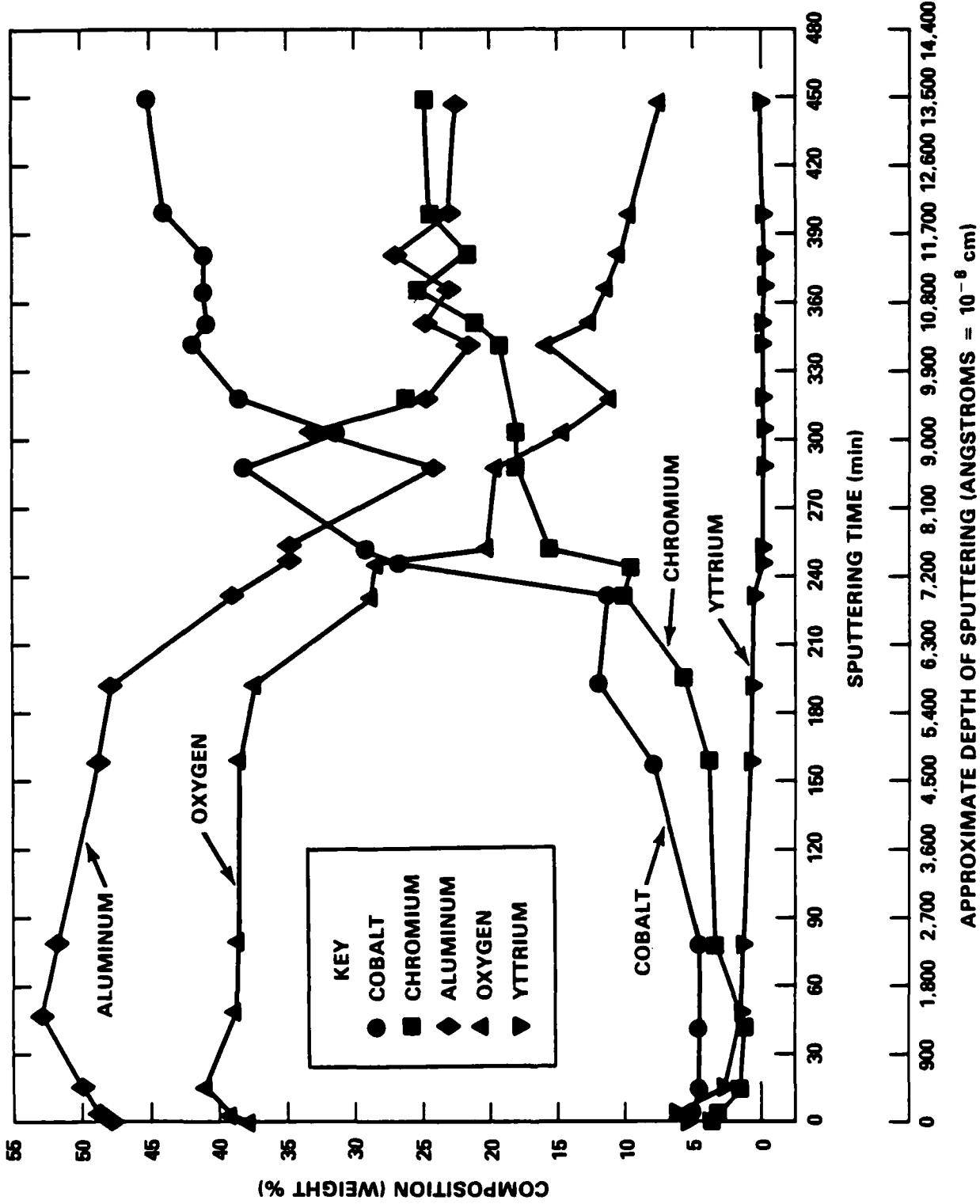


Fig. 5. Surface composition of 20 Cr CoCrAlY as determined by XPS as a function of depth of sputtering.

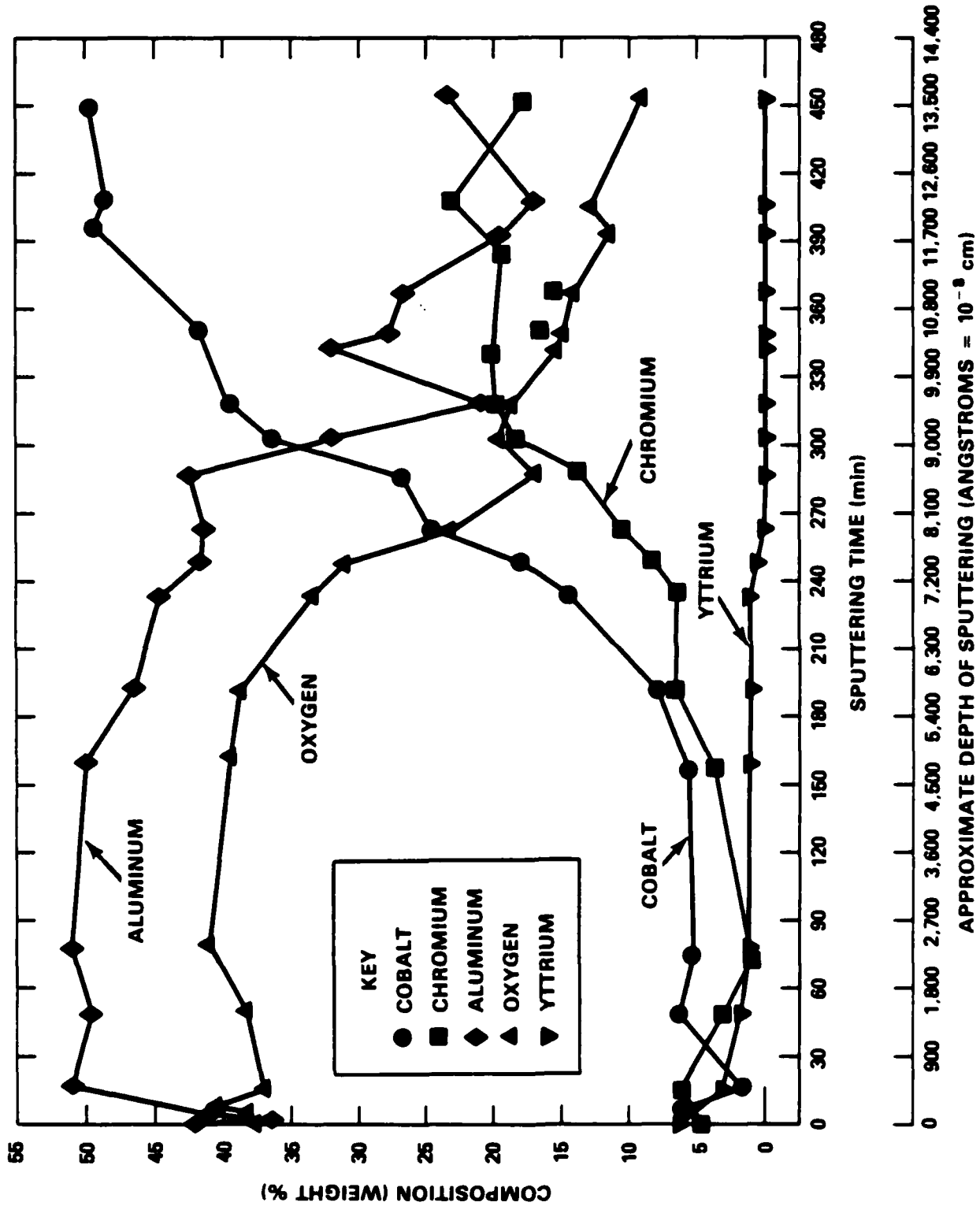


Fig. 6. Surface composition of 29 Cr CoCrAlY as determined by XPS as a function of depth of sputtering.

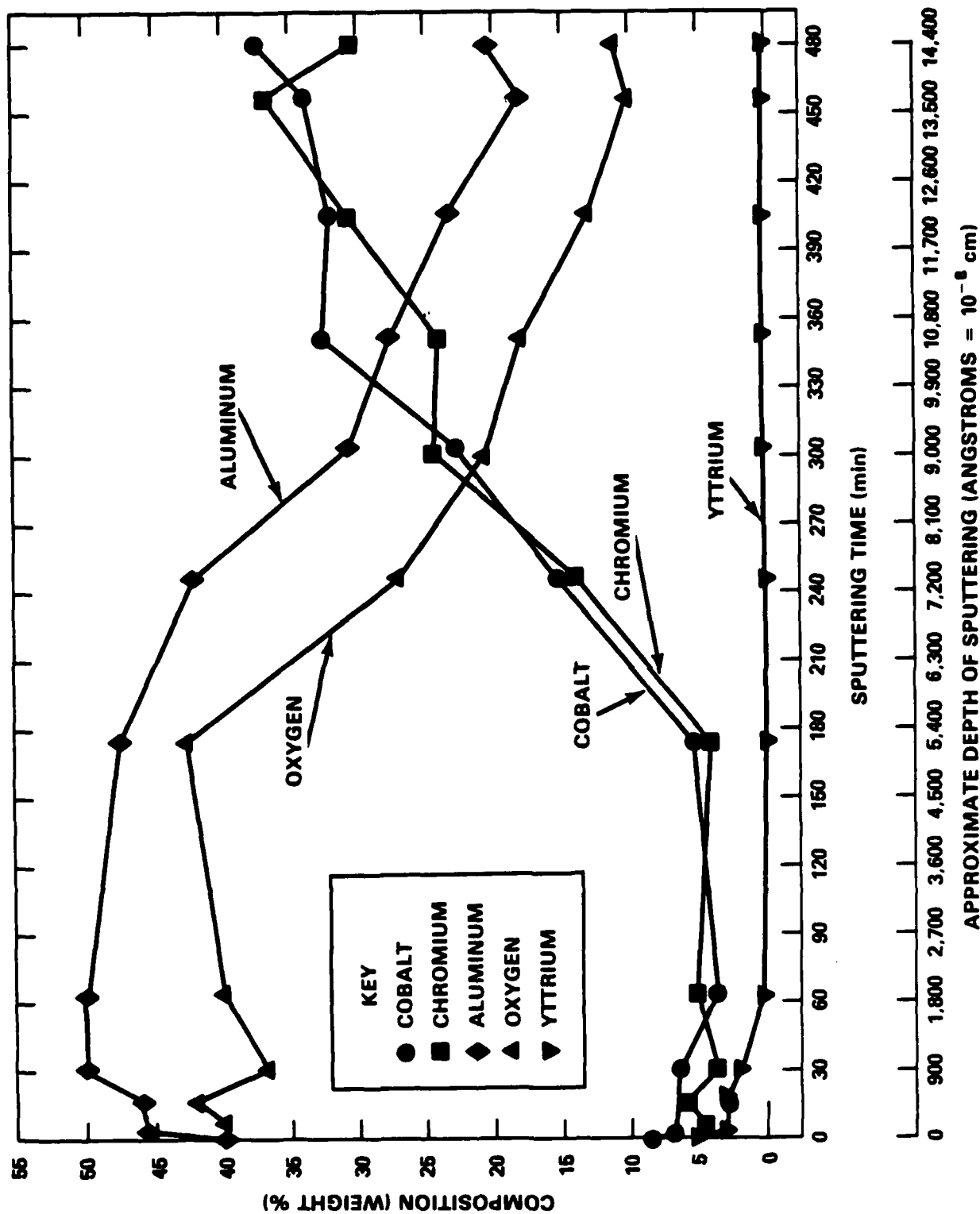


Fig. 7. Surface composition of 35 Cr CoCrAlY as determined by XPS as a function of depth of sputtering.

## APPENDIX

### SPUTTER RATE STANDARD PREPARATION PROCEDURES\*

A 1000Å anodized tantalum specimen may be prepared in the following manner:

- a. "Polish" two .125mm foils of tantalum by dipping them for up to 1 or 2 seconds in an acid solution (59.0% H<sub>2</sub>SO<sub>4</sub>, 17.0% HF, 23.5% HNO<sub>3</sub>).
- b. Pass the samples through two rinses of deionized H<sub>2</sub>O.
- c. Blow them dry with N<sub>2</sub>.
- d. Using one "polished" foil as an anode and another as a cathode, apply 6.66 V DC between them while they are suspended in an electrolyte (94.3% deionized H<sub>2</sub>O, 5.7% HNO<sub>3</sub>). One of these plates is sufficiently anodized when the current drops to zero.
- e. Rinse the "gold" anodized specimen in acetone. The "gold" color indicates 1000 Å of Ta<sub>2</sub>O<sub>5</sub>.
- f. Blow it dry with N<sub>2</sub>.

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\*Procedure obtained from operation manual for the Phi Electronics Sputter Gun.

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