AN-X-RAY PHOTOELECTRON SPECTROSCOPY STUDY OF NICKEL
AND NICKEL-BASE ALLOY SURFACE ALTERATIONS
IN SIMULATED HOT CORROSION CONDITIONS WITH EMPHASIS
ON EVENTUAL APPLICATION TO TURBINE BLADE CORROSION

SECOND
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Introduction

The present report accounts for research performed during the period December 1974 - June 1975. It includes in an abbreviated form the results mentioned in the interim report (December 1974 - April 1975) and, in detail, results obtained during the months of April, May, and June, 1975. Particularly the progress made in work on pure metals and binary alloys was substantial; also new superalloys have been studied. An important step forward has been done by carrying out the first experiments on samples corroded in the presence of Na_2SO_4. Preliminary quantitative work proved to be very useful in spite of its relatively large degree of approximation.

We are now convinced that continuing the investigations in the same directions, and perhaps with additional techniques such as ion recoil spectroscopy, our results will constitute an important contribution to the understanding of hot corrosion of superalloys; this will help finding better technical solutions for the extension of the lifetime of jet engines.

The cooperation with scientists from NASA was very efficient and is now established in the form of frequent meetings during which information and new ideas are exchanged.

I. Experimental

All samples were examined with a Varian IEE-15 X-ray photoelectron spectrometer equipped with a high intensity magnesium anode (Kα-radiation, 1253.6 eV). The conditions were kept as much as possible the same as in the experiments described in the previous reports i.e.: sweep width, 36 eV; sweep time, 15 s; X-ray source, 8 kV x 80 mA; analyzer energy, 100 V; analyzer pressure 10^{-6} - 10^{-7} torr; sputtering, 5 min at 40-50 millitorr Ar, ~ 2kV x 2-4 mA.

The specimens (11 mm ϕ, 19 mm height, except for superalloy IN 738X whose diameter was ~ 5 mm) were all provided by scientists of NASA, Lewis Research Center. The following samples were studied: a) four ground-surface finished metals (Co, Cr, Nb, and Al); b) four ground-surface finished samples of the superalloy 713C; c) four ground surface finished samples of the super-alloy IN 738X; d) two binary alloys of Ni and Cr; e) a 1500 Å film of Ni deposited on a Ti rod; f) three ground-surface finished samples of B-1900/Hf: 1) coated with 0.69 mg Na_2SO_4/cm^2 2) coated with 0.59 mg Na_2SO_4/cm^2 and oxidized for 0.75 hr; 3) coated with 0.78 mg Na_2SO_4/cm^2 and oxidized for 3.5 hr.

II. Results and discussion

a) Pure metals were examined in order to obtain reference spectra, run in our specific conditions, for the principal elements of the superalloy composition and to clarify the contribution of each element in overlap regions. On the other hand, information was obtained about the extent of surface oxidation of these metals in ordinary storage conditions as compared with effects of oxidizing media at high temperatures.

Under ordinary conditions all metals studied were found to be covered to different extents by oxides. Before sputtering approximately 70-80% oxide coverage was found for Co, Cr, and Al while Nb showed only an oxide peak. While Co appeared to show both a +2 and +3 oxidation state, the others seemed to display only one oxide. After sputtering, Cr and Al exhibited only an oxide peak while Co was essentially in the metallic state and Nb showed approximately 70% oxide.

The spectra of the oxidized samples* revealed complete oxide coverage before sputtering with all elements appearing to be in a single oxidation state. After sputtering, all were still present as oxides with Cr and Al remaining unchanged but Nb and Co appearing to display at least two oxides (Nb - a slight change, Co-a significant change). Obviously these results must be interpreted with

* Co, Cr, Nb, and Al were exposed to 1 atm air at 600° for 30, 10, 5, and 5 min respectively.

reservation imposed by the incomplete knowledge concerning the effects of sputtering (oxido-reduction processes and non-uniform material removal)

b) Superalloy 713C. The composition of superalloy 713C is given in Table I. The procedure for the study of these samples is the general one described in previous reports. We applied in the case of 713C the same quantitative approach. Figures 1-12 show the spectra obtained for 713C oxidized for 64 hr in 1 atm O_2 (Figures 1-10) and oxidized 1 hr (Figures 11-12). The binding energy (E_b) for all metal peaks corresponds to oxidized states of the element. After sputtering, the only significant changes which occur are exemplified by figures 1b (the Ni region) and 6b (the Mo, Ta, W region). As previously mentioned, one of the effects of sputtering may be the reduction of Ni^{+n} to Ni^{o}, but uncertainty still exists regarding a definite explanation for the phenomenon seen in figure 6b. It would seem that Ar replaces the Mo by some unknown mechanism or possibly the Mo, existing as a thin surface oxide layer, is sputtered away. This phenomenon has been observed with all the superalloys and will be given particular attention in future experiments.

Whenever one wishes to attempt quantitative calculations on a complex system such as the superalloys, it is desirable that peaks used for such calculations be well separated from signals of other elements.

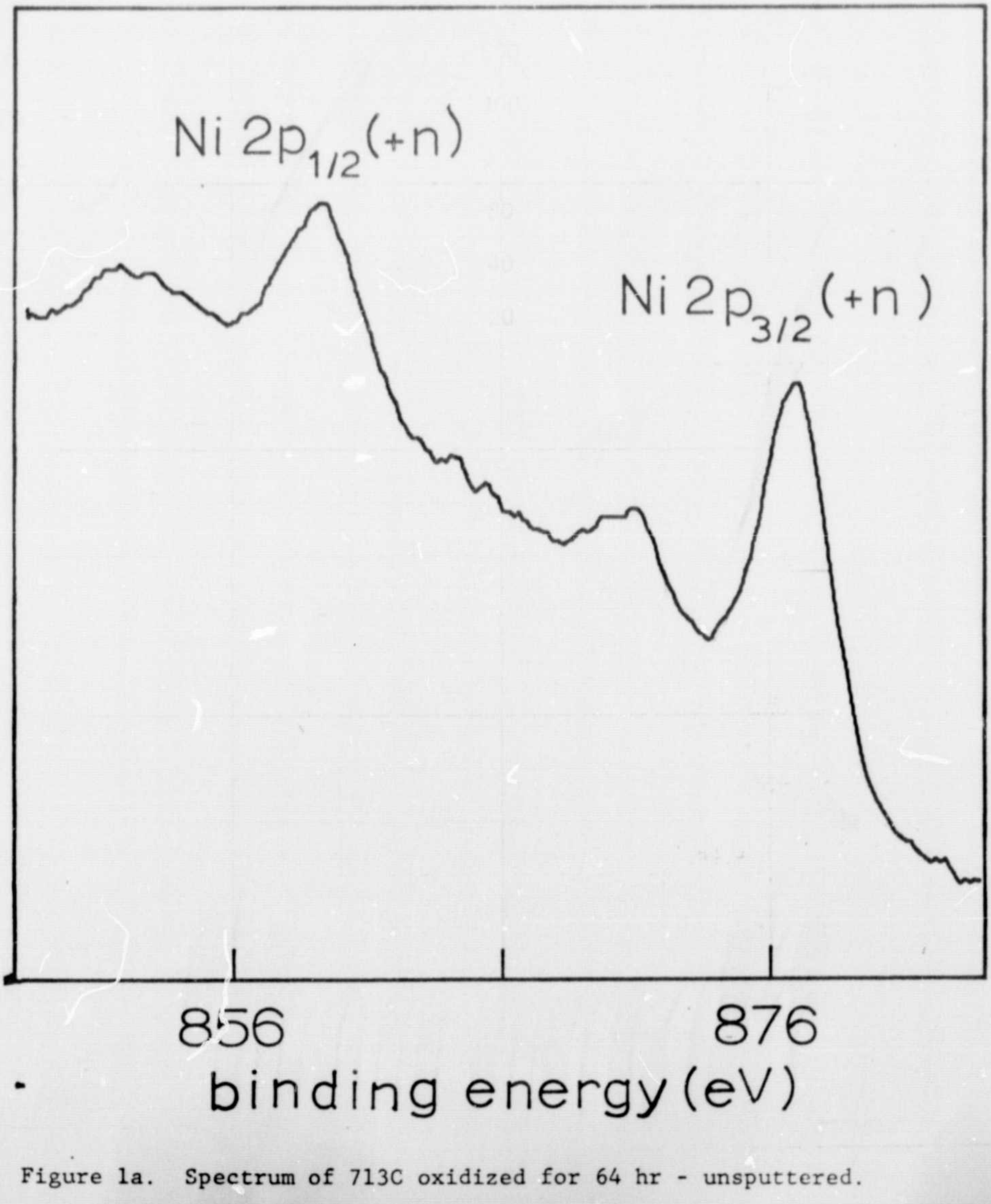

Figure 1a. Spectrum of 713C oxidized for 64 hr - unsputtered.

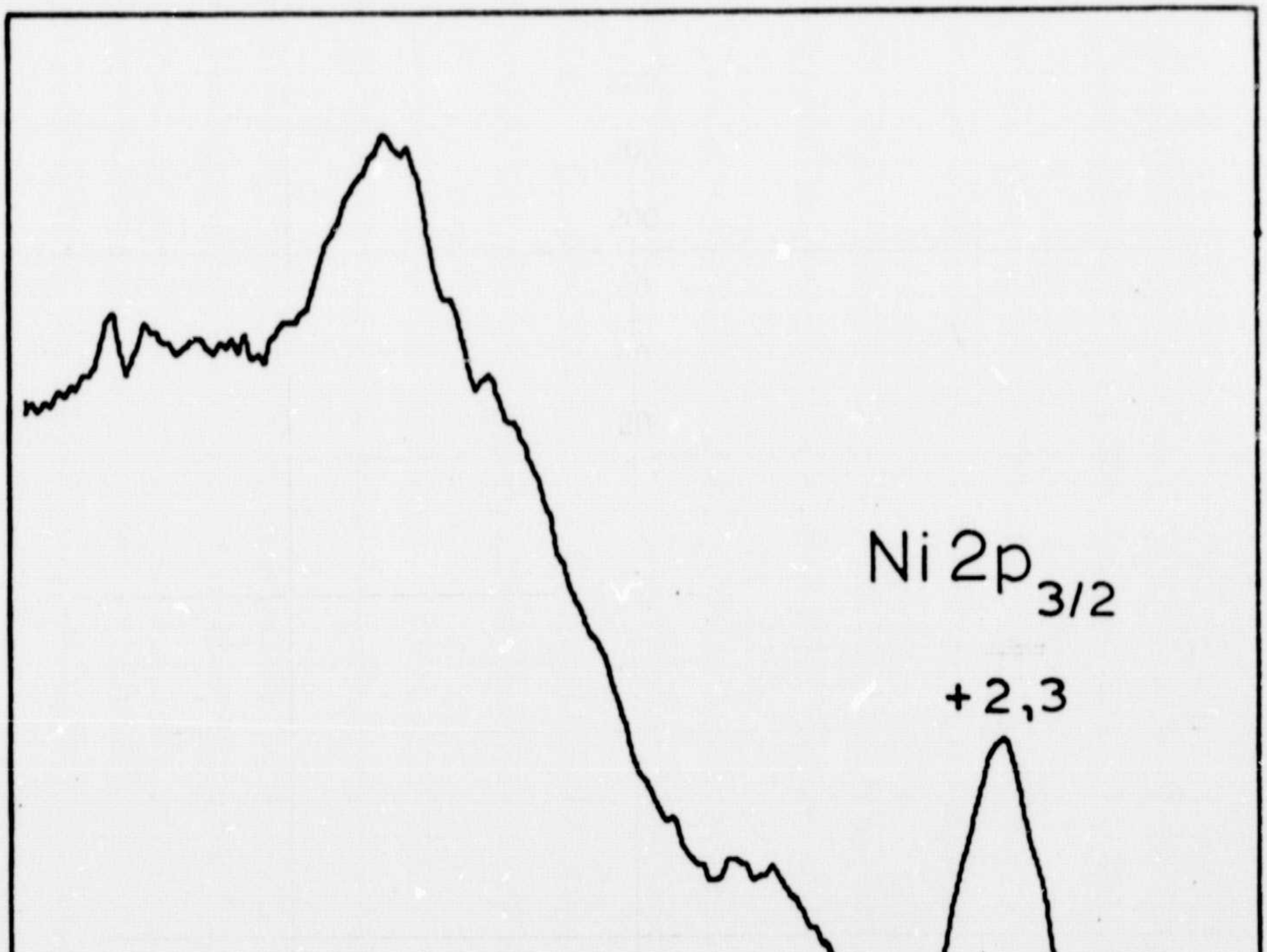

Figure 1b. Spectrum of 713C oxidized for 64 hr - sputtered.

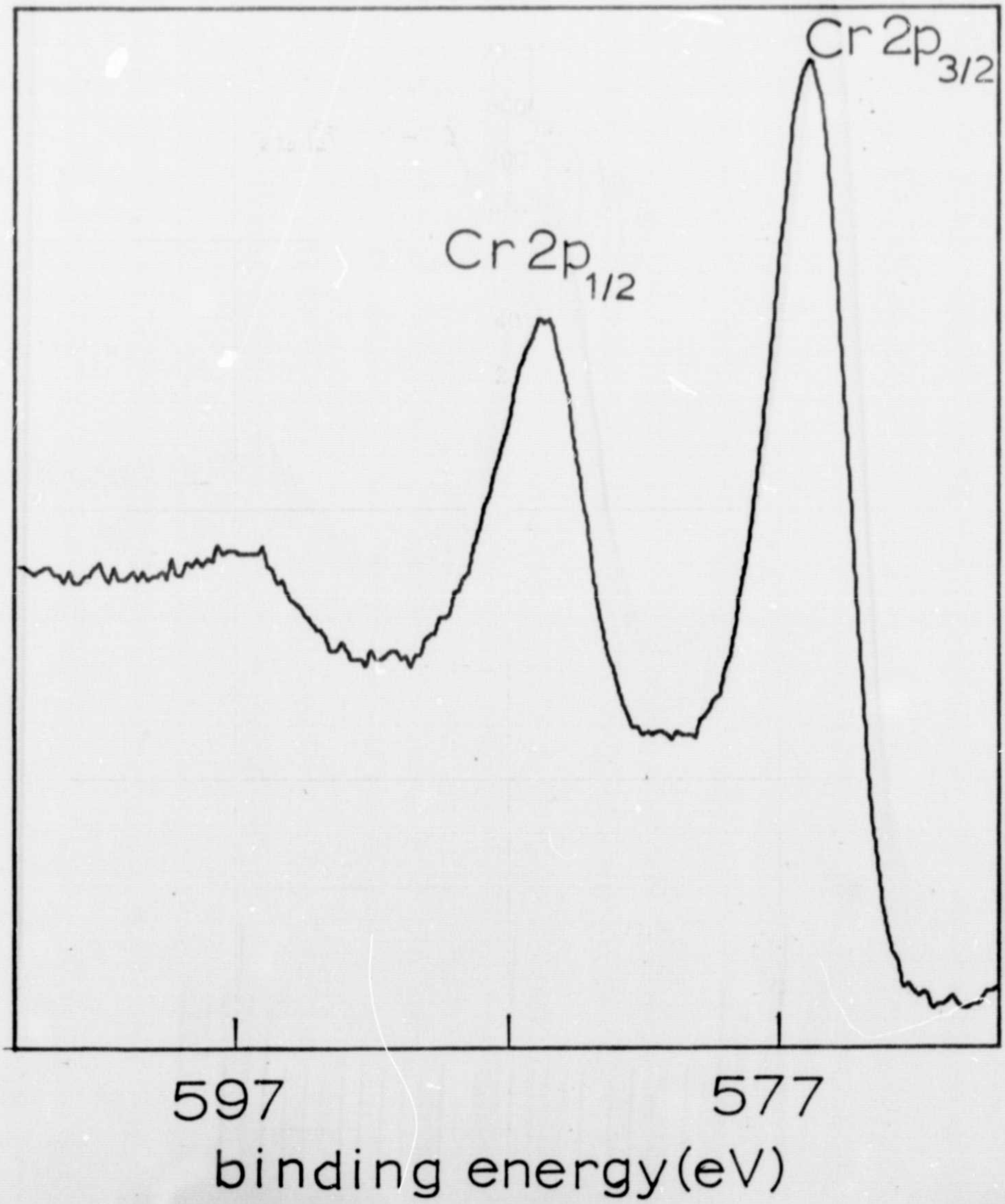

Figure 2. Spectrum of 713C oxidized for 64 hr - unsputtered.

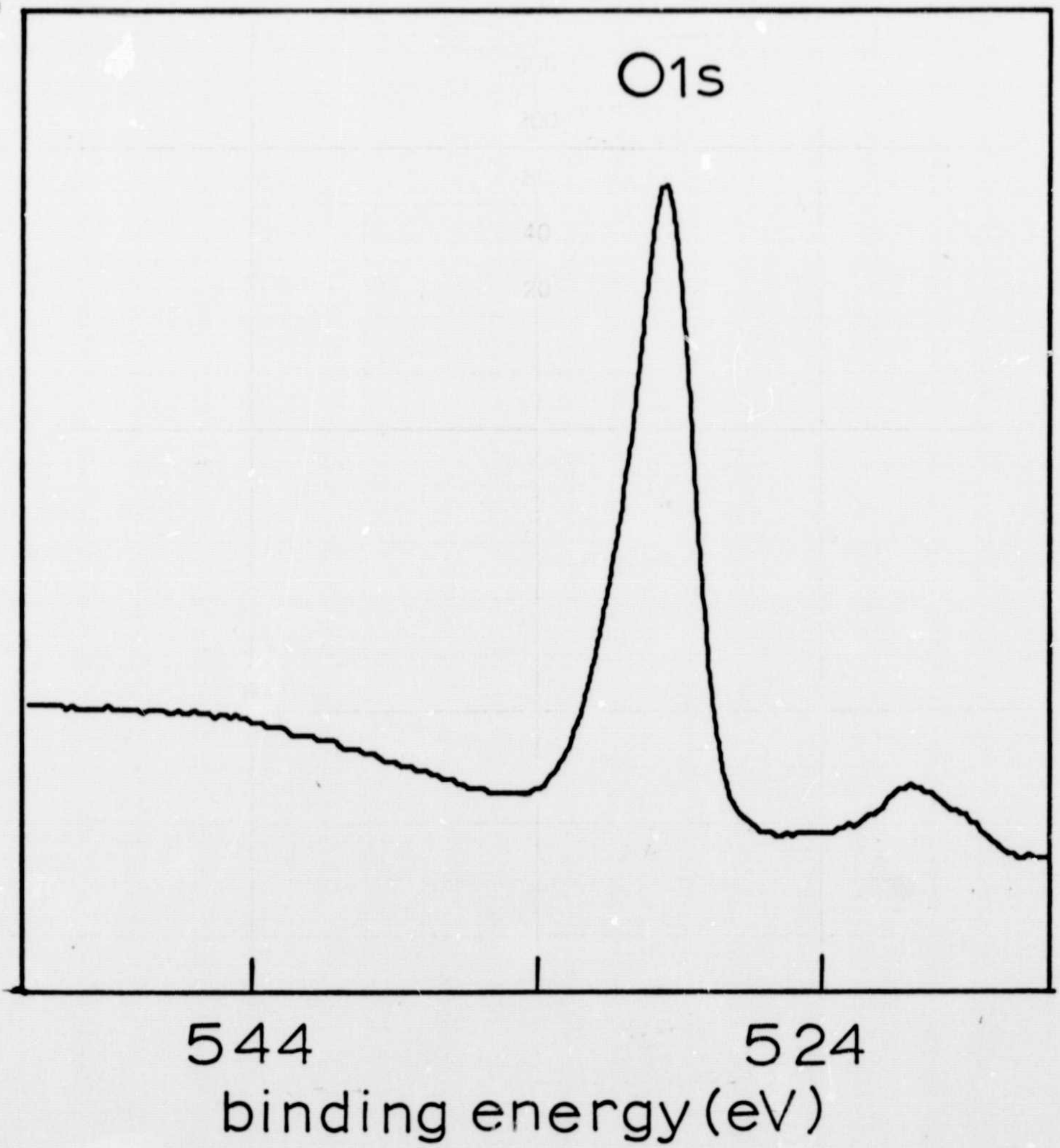

Figure 3. Spectrum of 713C oxidized for 64 hr - unsputtered.

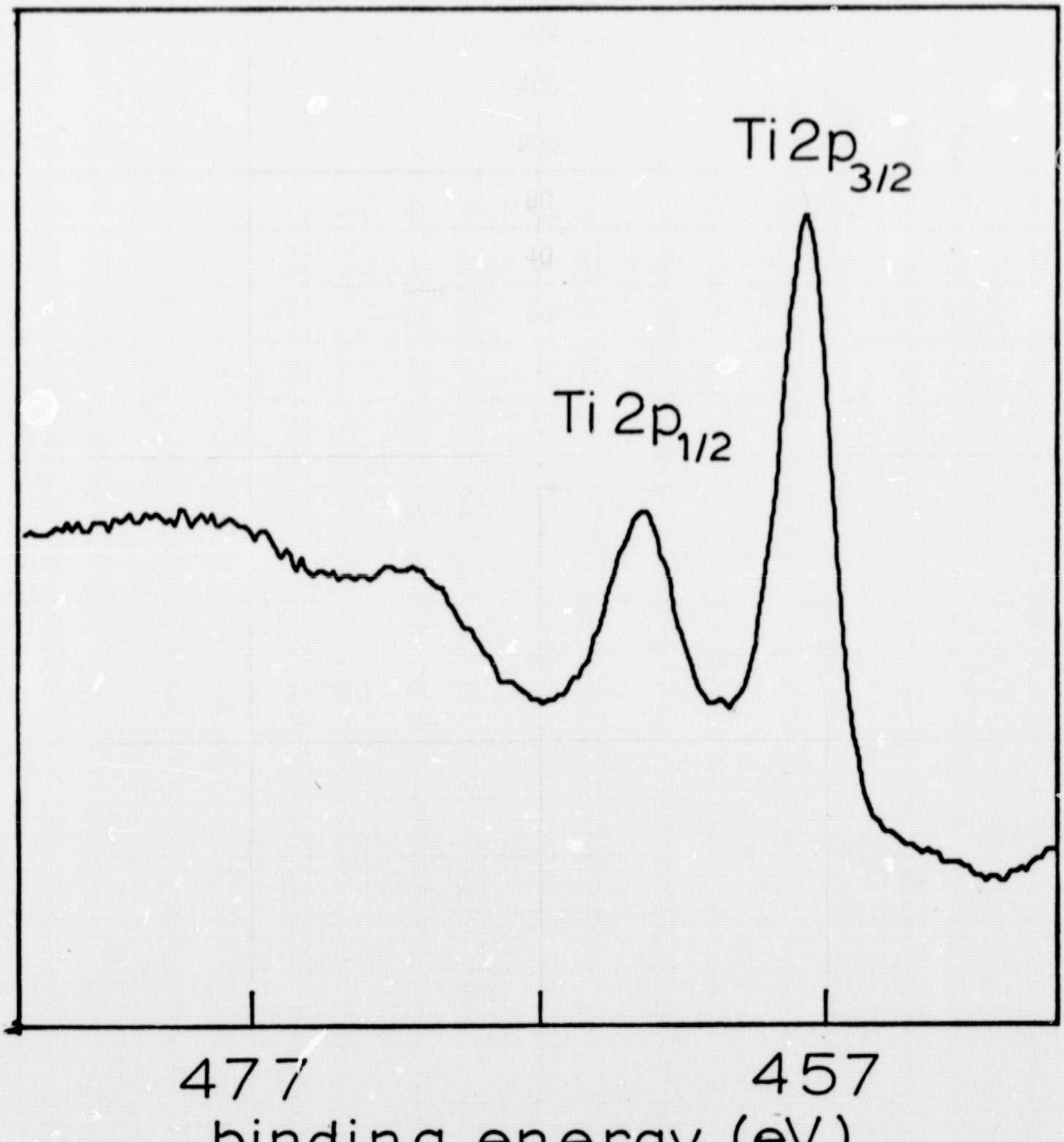

Figure 4. Spectrum of 713C oxidized for 64 hr - unsputtered.

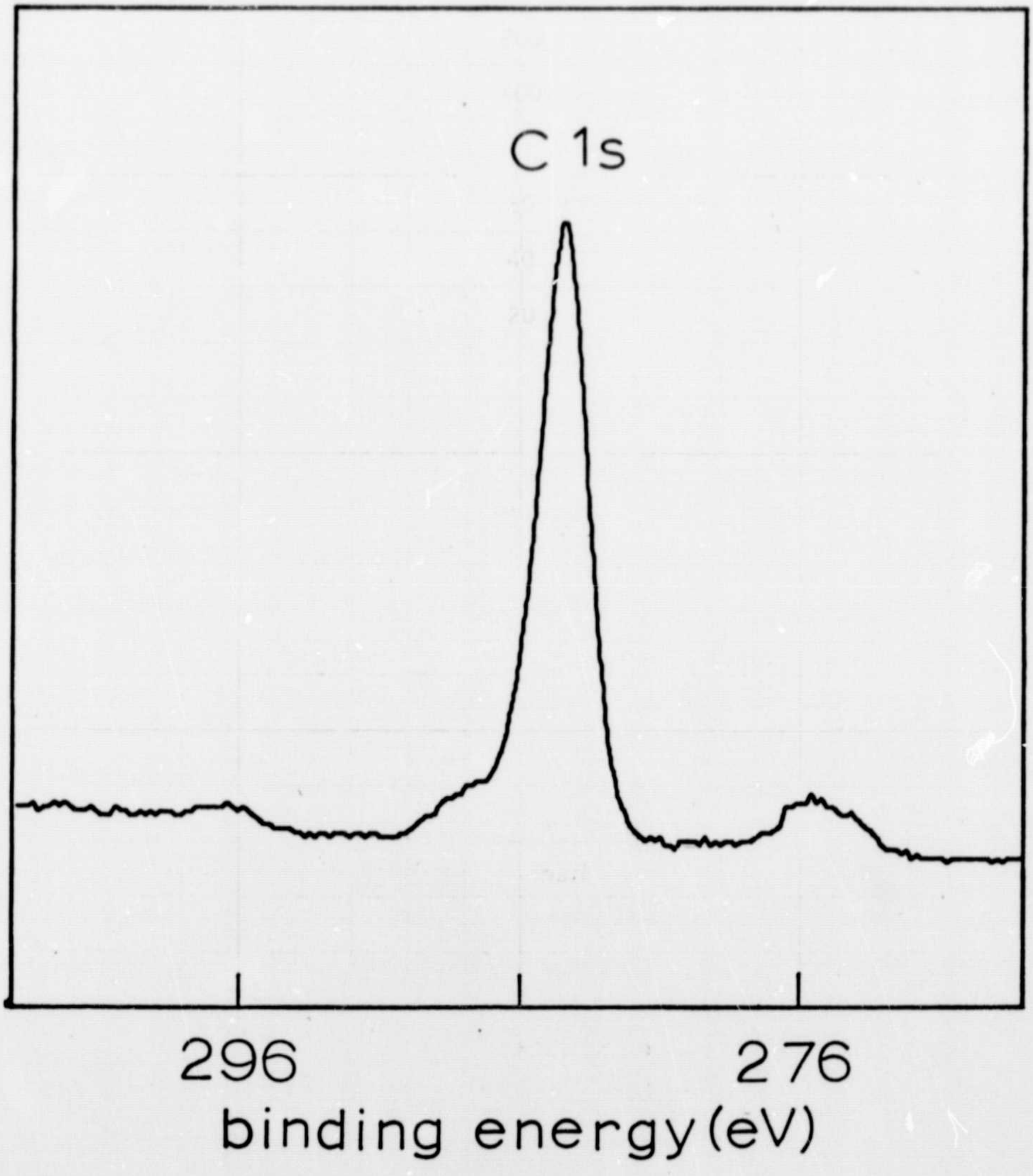

Figure 5. Spectrum of 713C oxidized for 64 hr - unsputtered.

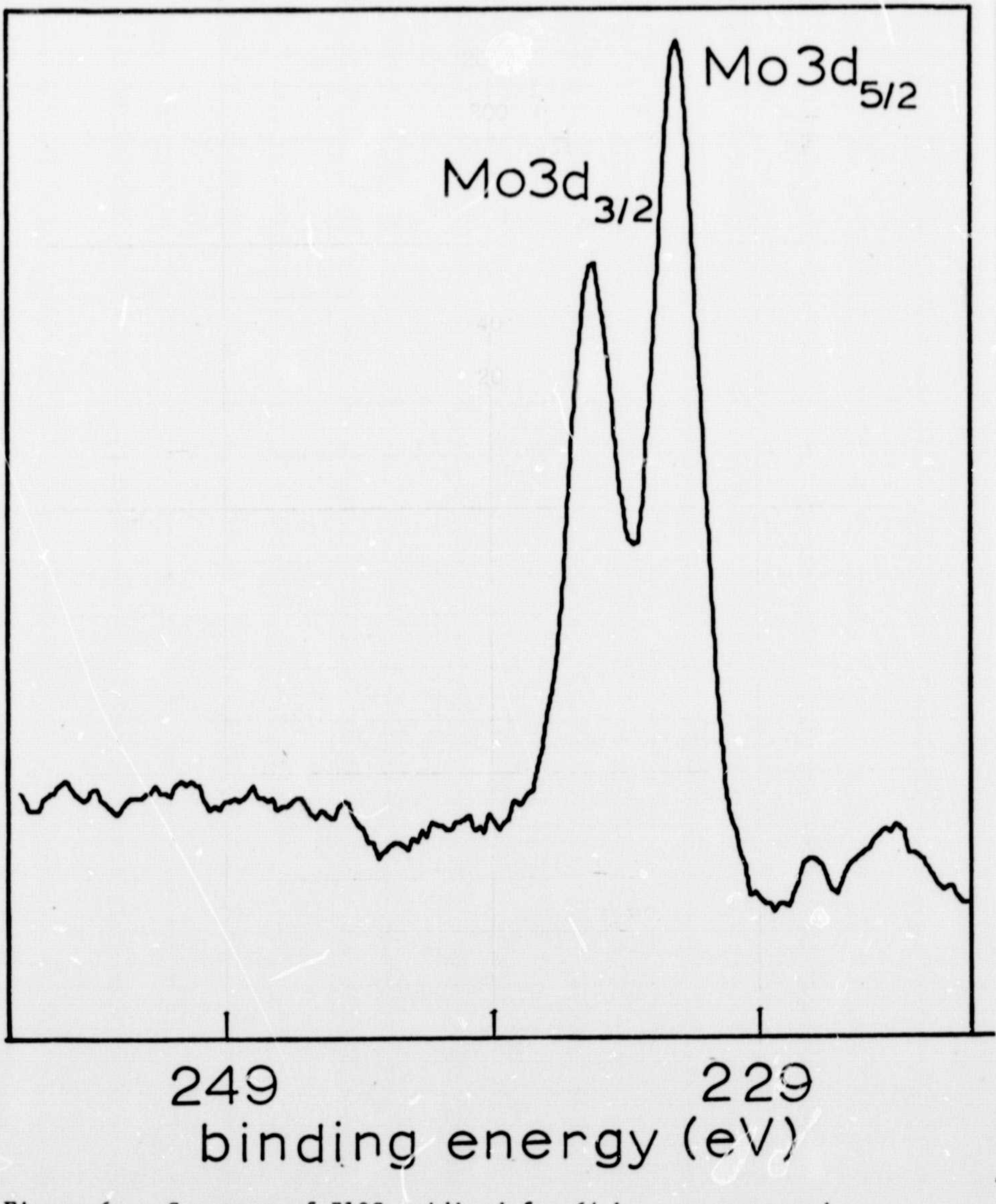

Figure 6a. Spectrum of 713C oxidized for 64 hr - unsputtered.

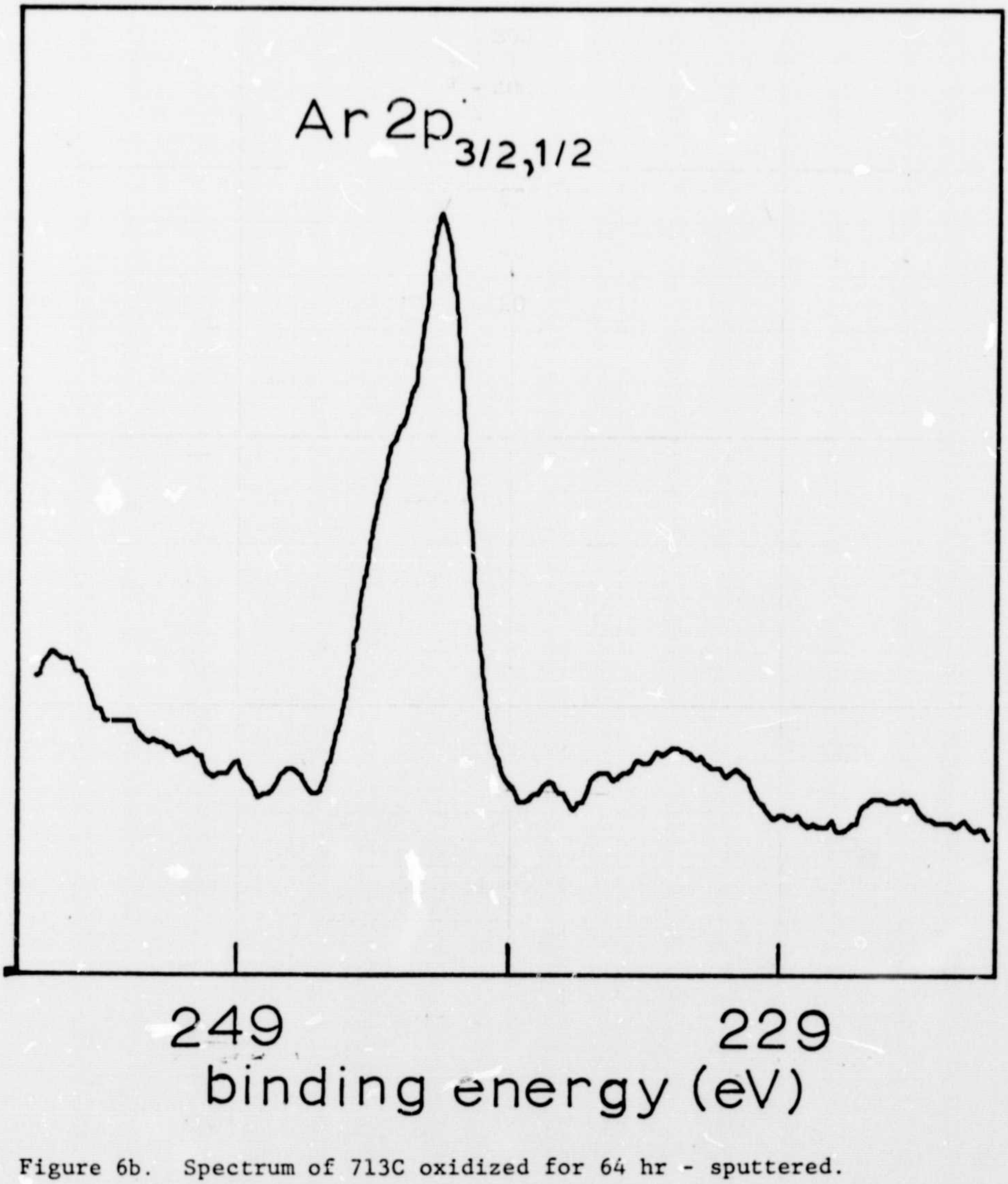

Figure 6b. Spectrum of 713C oxidized for 64 hr - sputtered.

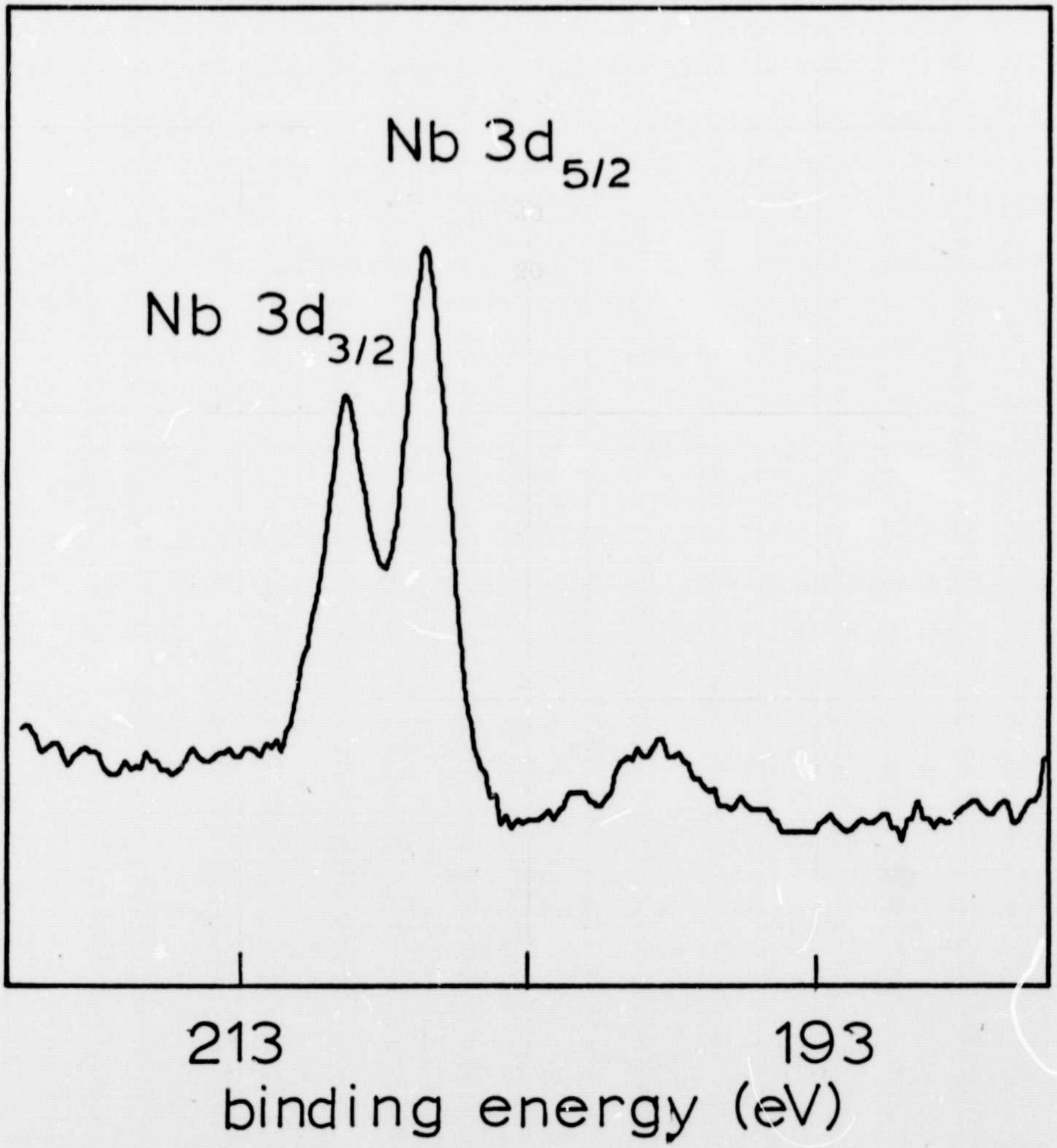

Figure 7. Spectrum of 713C oxidized for 64 hr - unsputtered.

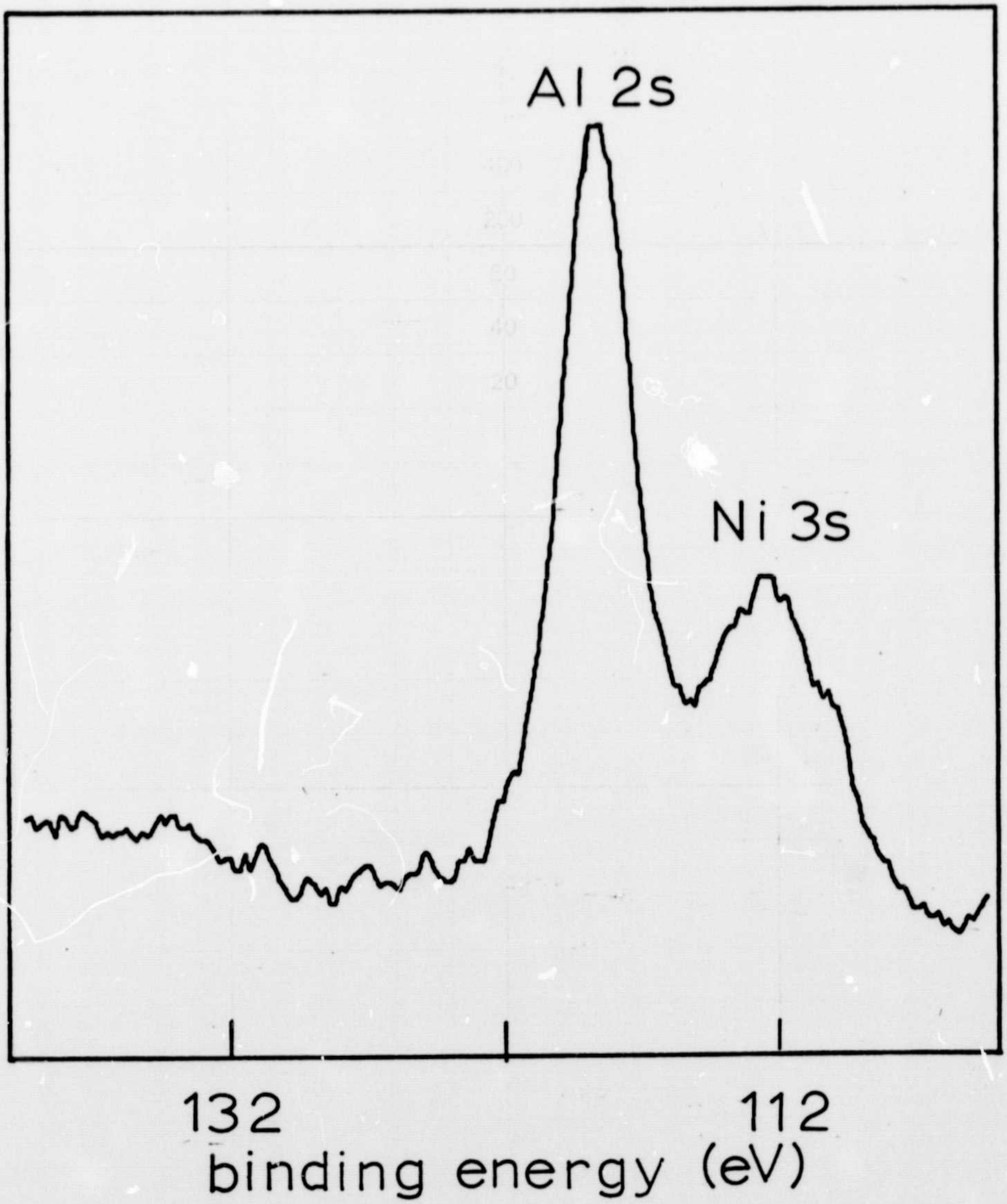

Figure 8. Spectrum of 713C oxidized for 64 hr - unsputtered.

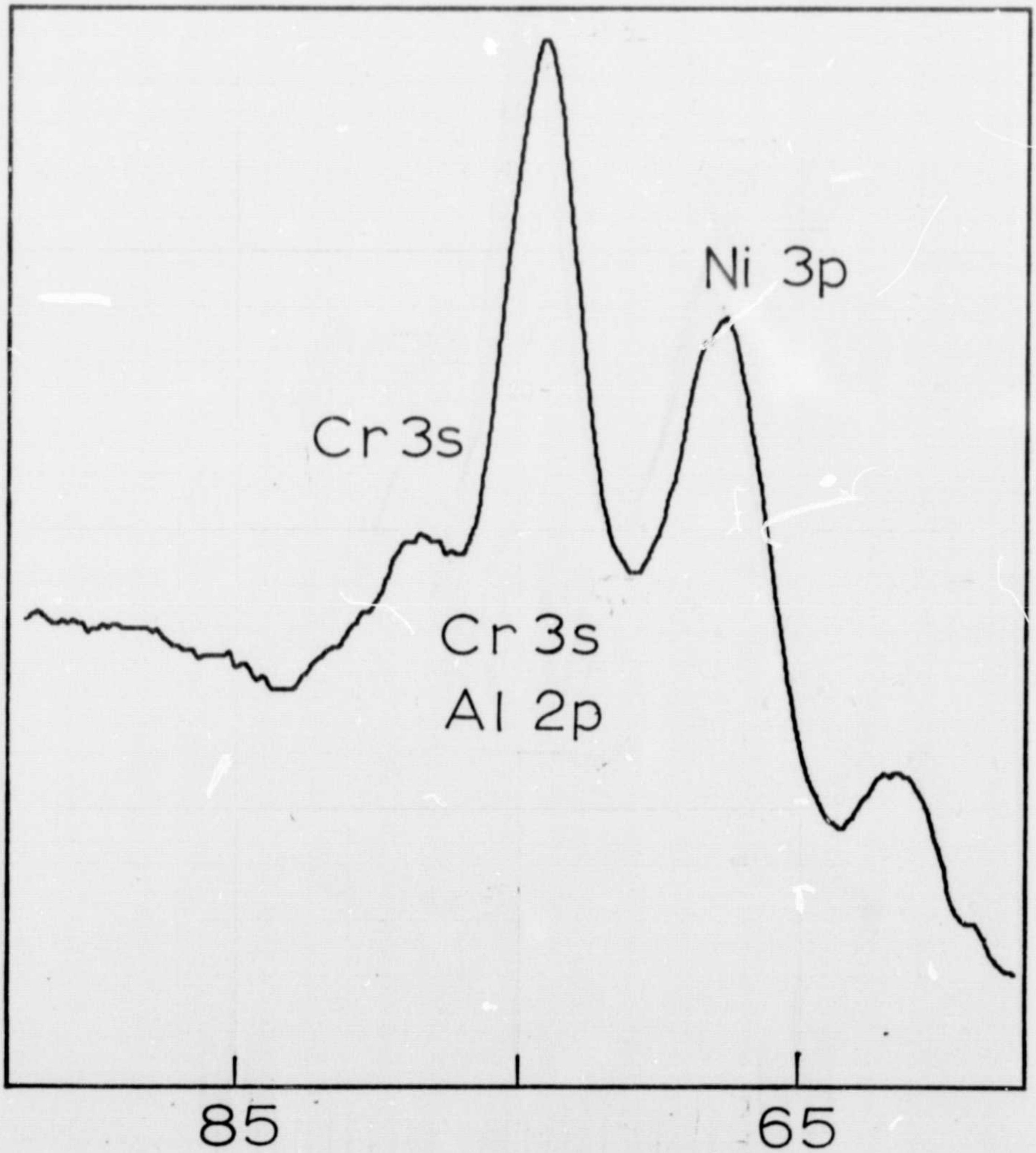

Figure 9. Spectrum of 713C oxidized for 64 hr - unsputtered.

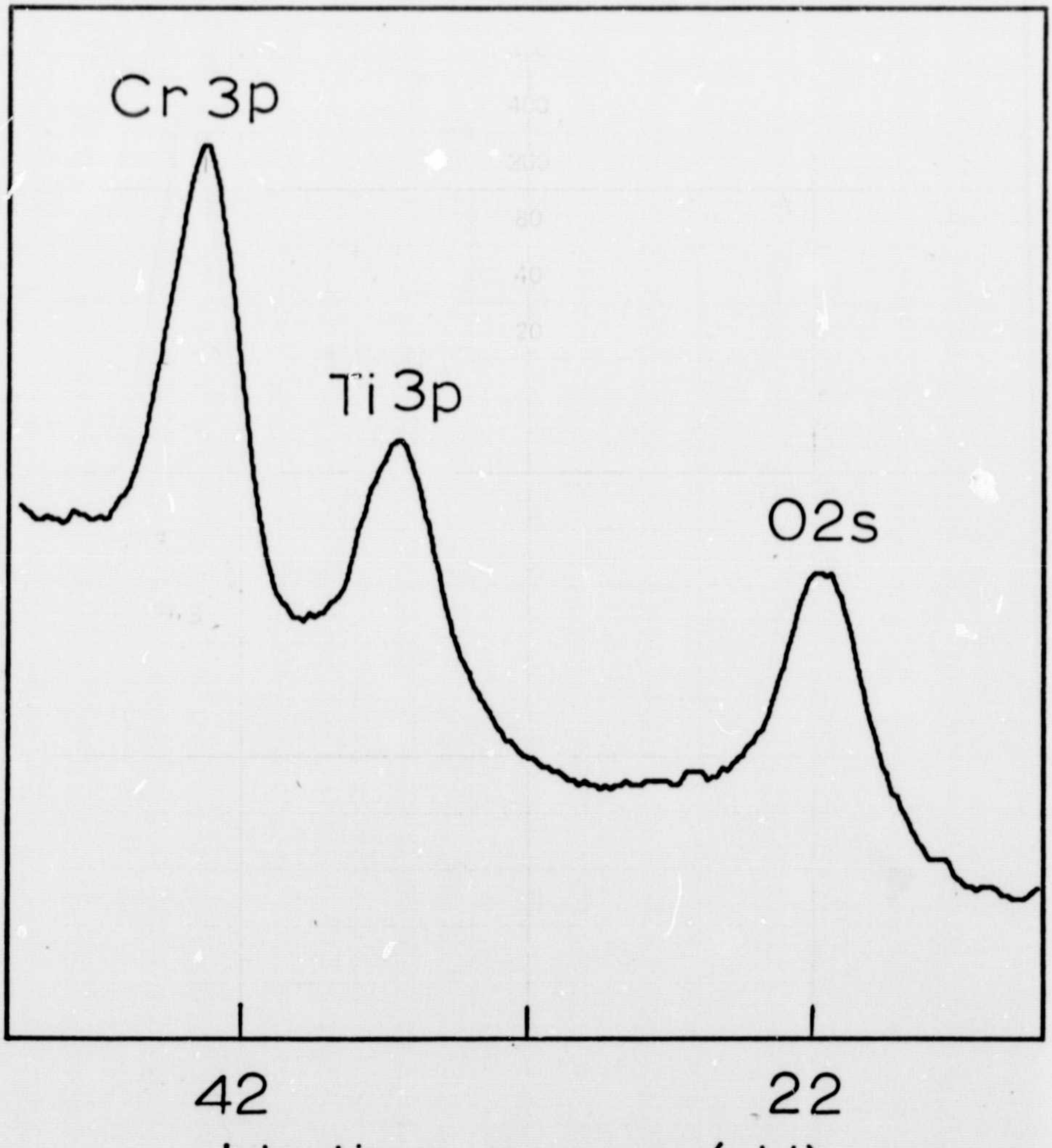

Figure 10. Spectrum of 713C oxidized for 64 hr - unsputtered.

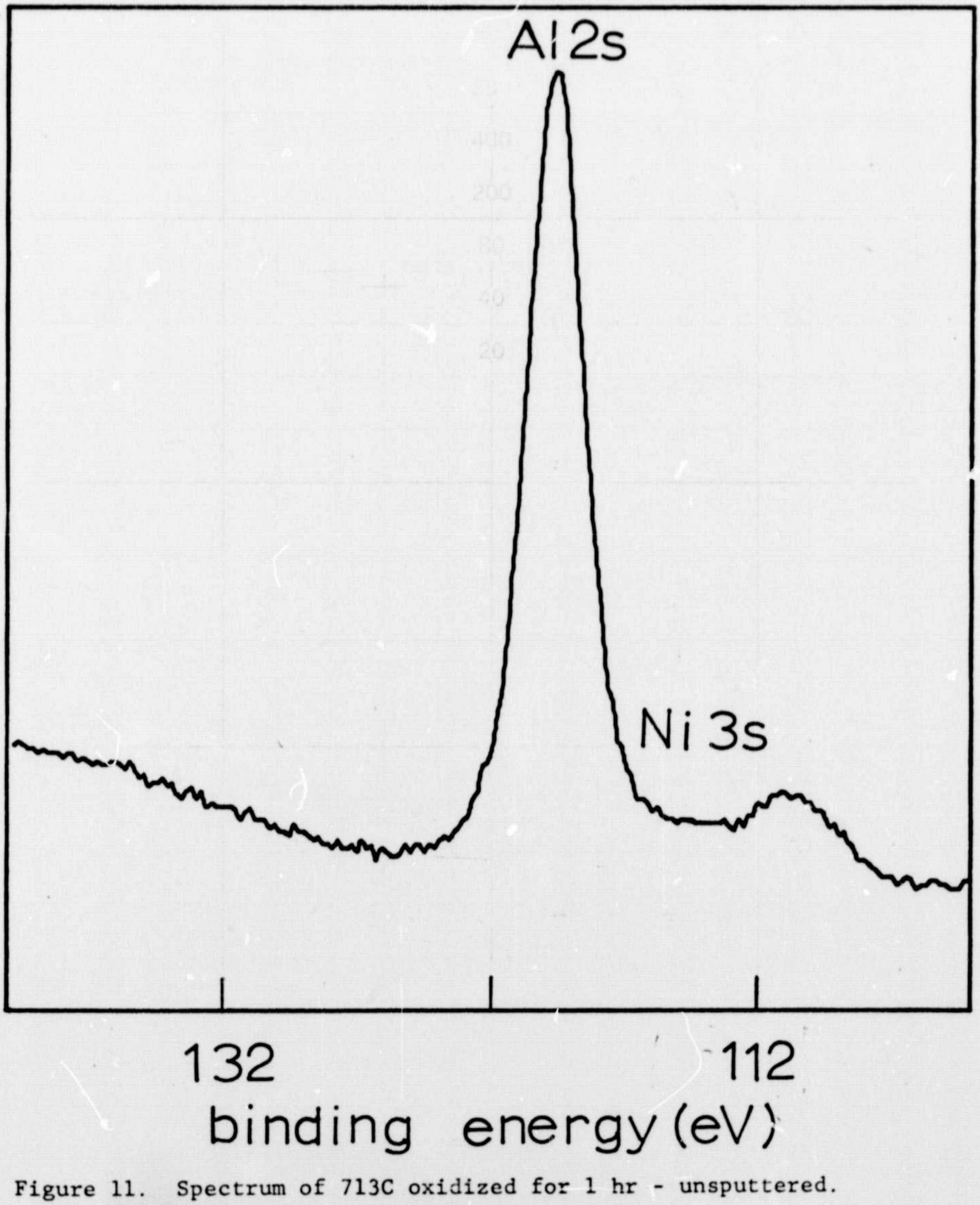

Figure 11. Spectrum of 713C oxidized for 1 hr - unsputtered.

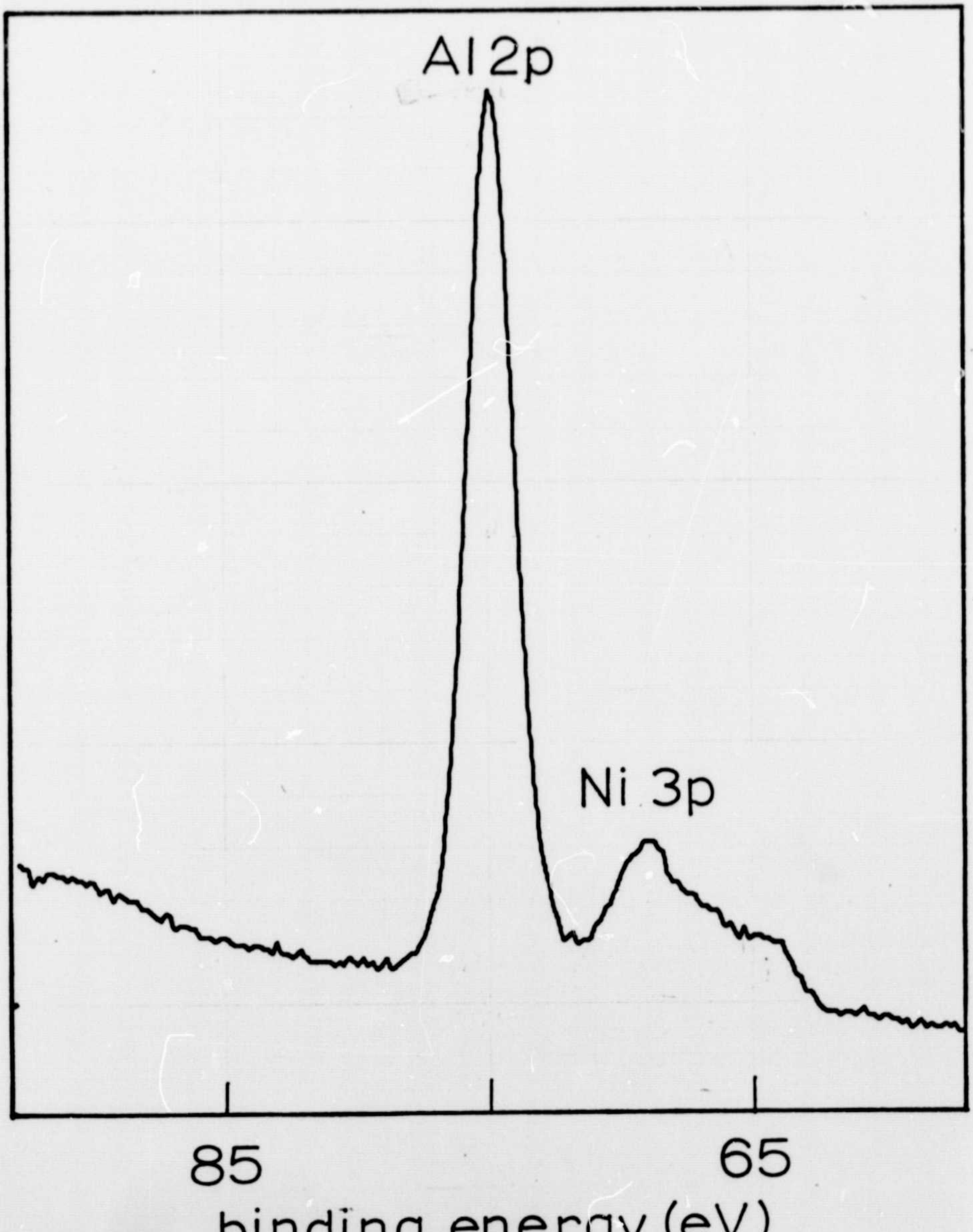

Figure 12. Spectrum of 713C oxidized for 1 hr - unsputtered.

Fortunately this is the case in most of our instances. In overlapping patterns, the uncertainty associated with the necessary deconvolution must be taken into consideration.

One way of avoiding the complications of overlapping peaks is to take the signal of another level as intensity reference. For example, in the case of 713C, the Al 2p signal overlaps with signals of Cr 3s in Figure 9. Therefore, we have chosen Al 2s for intensity reference because, in that region, the overlapping is much less severe (cf Figure 8). The necessity of knowing the position, shape, and relative intensity of peaks obtained from pure metals and their oxides becomes evident here. Although overlapping patterns may present problems, they also provide an opportunity to double check the validity of the calculated data. For instance, calculated values for the 1 hr oxidized sample using the Al 2s level indicates much greater amounts of Al on the surfaces than for Cr or Ni; therefore, as expected, figures 11 and 12 display very weak, if any, signals for Ni and Cr. For the 64 hr sample, Cr was found to be in higher concentration than Al and Ni (both approximately same); thus the Cr and Ni peaks contributed significantly more to the Al 2s and 2p regions.

Table I presents the bulk composition for unoxidized superalloy 713C as found by conventional analytical techniques and the surface composition as calculated

TABLE I

COMPOSITION OF SUPERALLOY 713C

		Atomic % Metal - Unoxodized		
		Before Sputtering		After Sputtering
Element	Symbol	Bulk*	Surface (ESCA)	Surface (ESCA)
Ni and/or Ni^{+n}	■	69.3	38.7(23.8)	61.3
Cr	□	13.2	23.9	21.5
Ti	●	0.9	0.5	0.7
Mo	×	2.4	4.5	3.6
Nb	△	1.1	1.8	1.0
Al	○	12.4	30.6	11.9
Others**	-	0.7	-	-

* Values usually good to ± 0.2 %.

** Fe, C, Ta, Co.

(assuming the metals listed constitute 100% metal composition from the intensities obtained by ESCA). The peaks used for the quantitative calculations are the same as those given in the interim report with the exception of Al for which the 2s peak was chosen. The $3d_{5/2}$ peak (not listed in the interim report) was chosen for niobium. As mentioned in the previous report, other elements such as Co, Mo, and Nb display a metallic peak or a mixture of higher oxidation states, but the values listed in Table I are related to the total intensity of the element concerned, since it was not possible to determine with certainty the contributions of various oxidation states.

From the table, it is apparent that both before and after sputtering, the major constituents of the surface are Ni, Cr, and Al which is also true for the bulk composition. The dramatic change observed for Al after sputtering supports previous results indicating that these superalloys are alumina formers. The composition of the surface after sputtering is similar to the bulk except for the still high Cr content, which remains essentially unchanged.

Although O and C are observed in all samples, the instrument contamination makes it difficult to interpret their effects on our results. This was pointed out in the interim report.

Table II contains the calculated ESCA values of atomic % metal composition for the surface of 713C samples exposed to O_2 atmosphere at 900°C for 1, 19, and 64 hr. The values in parenthesis are those obtained after sputtering; first and second sputterings relate to first and second columns respectively. The data obtained for the various oxidation and unsputtered conditions are best represented by Figure 13 where atomic % metal has been plotted vs time of oxidation on a linear scale. The outstanding feature of the sample oxidized for 1 hr is the extremely high value obtained for Al while Ni is a factor of 13 less than the bulk value; Nb remains about the same; Ti and Mo amounts are 2-3 times greater; Cr is at about 1/2 its bulk value. As seen in Figure 13, Ni, Ti, and Cr increase with increased time of oxidation primarily at the expense of Al. The most dramatic change is seen with Ti which increases by a factor of about 25 in comparison with the bulk composition. Further exposure (64 hr) reveals, within experimental error, essentially no change for Ti, Ni, Mo, and Nb while Cr increases slightly at the expense of Al. The 64 hr results show the surface of 713C to be composed primarily of Cr, Ti, Al, and Ni in the following approximate ratios to the bulk concentration in the unoxidized superalloys: 3:1, 25:1, 1:1, 1:4.

TABLE II

COMPOSITION OF SUPERALLOY 713C

Atomic % Metal-Oxidized*

Time of Oxidation (hours)

Element	Symbol***	1		19		64	
Ni	■	5.1	(8.7 - 6.8)	14.0	(9.2 - 6.2)	15.0	(7.7 - 7.4)
Cr	□	7.7	(10.4 - 11.3)	32.3	(43.1 - 44.7)	40.3	(57.1 - 56.0)
Ti	●	2.8	(3.6 - 4.1)	23.0	(24.7 - 25.3)	23.1	(21.7 - 21.7)
Mo	×	5.3	(0 - 0)	4.2	(0 - 0)	3.6	(0 - 0)
Nb	△	1.0	(1.1 - 1.3)	1.7	(1.3 - 1.3)	2.3	(1.4 - 1.4)
Aℓ	○	78.1	(76.2 - 76.5)	24.6	(21.7 - 22.5)	15.7	(12.1 - 13.5)
Ar**		-	(6.7 - 7.3)		(6.5 - 7.3)	-	(6.1 - 6.4)

* First value in parenthesis was obtained after first sputtering; second value was obtained after second sputtering.

** Values for argon were calculated separately considering Ar as one of the elements making up 100% metal composition.

*** See Figure 13.

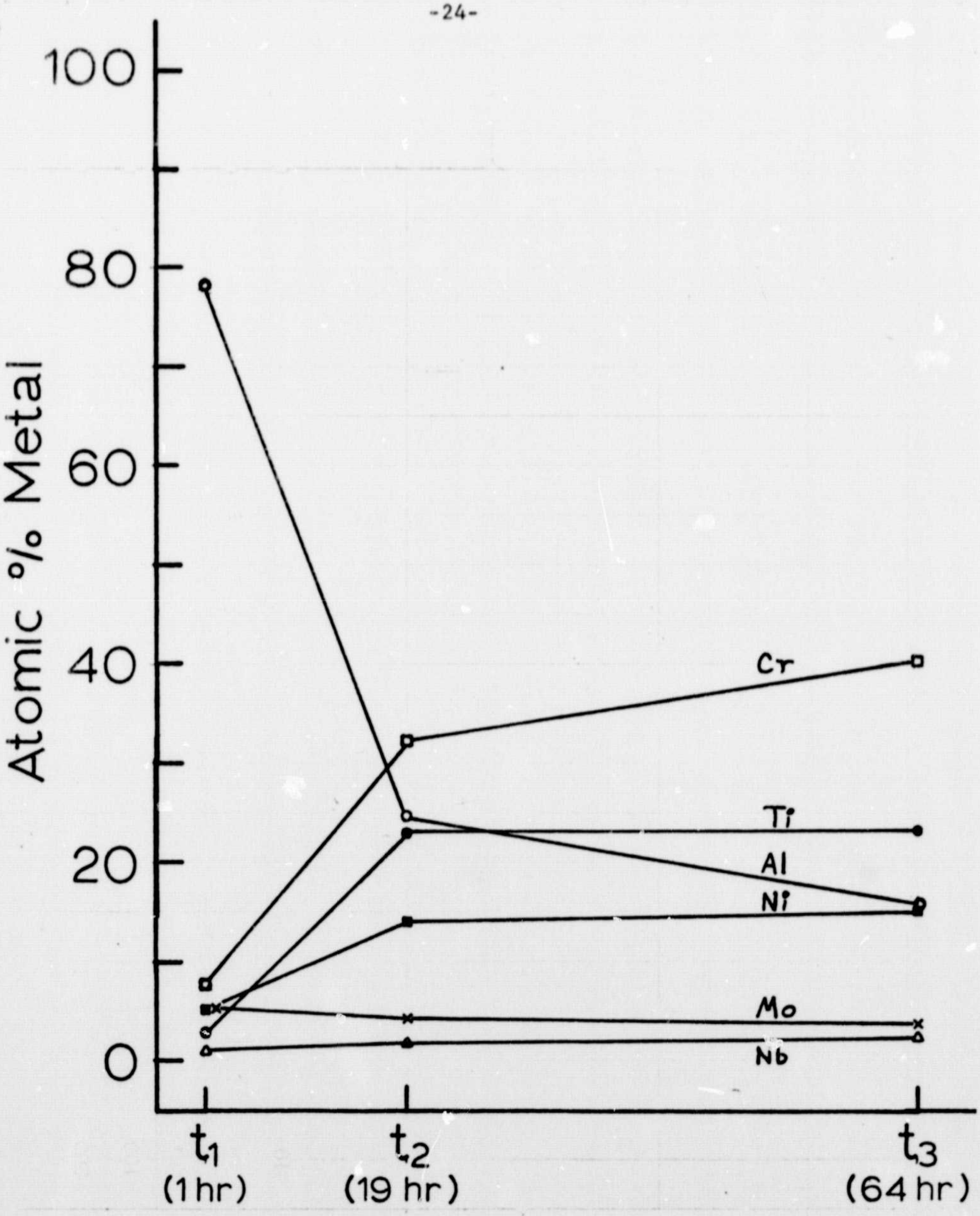

Figure 13. Plot of atomic % metal composition for superalloy 713C oxidized in 1 atm O_2 at 900°C for various periods of time.

One real and notable difference between the unsputtered and the sputtered specimens is the complete disappearance of Mo (this phenomenon was mentioned several times previously). There are basically no dramatic changes observable after two sputterings which suggests the oxidation was uniform to a depth of at least 50 Å. The only other changes which might be considered significant are the increase in atomic % Cr after sputtering for all three times of oxidation, the decrease in Ni for 19 and 64 hr, the increase in Ti for 1 hr, and decrease in Nb for 64 hr and possibly 19 hr.

The values found for Ar in Table II were calculated separately such that the atomic % calculation for the metals do not include Ar, but the Ar value was obtained assuming Ar as part of the 100% metal composition. The data for Ar suggest a saturation limit for implantation. The Ar value is ~ 1-2 times that of Mo before sputtering. Possibly, future experiments may reveal a definite correlation between superalloy surface structure and Ar ion implantation.

c) <u>Superalloy IN 738X</u>. Table III presents the bulk atomic % composition of the unoxidized superalloy IN 738X obtained by conventional analytical techniques and the values determined from ESCA for surface composition before and after sputtering. Remarks made concerning the oxidation states for the elements in unoxidized 713C are

TABLE III

COMPOSITION OF SUPERALLOY IN 738X

		Atomic % Metal - Unoxidized		
		Before Sputtering		After Sputtering
Element	Symbol*	Bulk**	Surface (ESCA)	Surface (ESCA)
Ni and/or Ni^{+n}	■	60.1	32.4(21.3)	41.7
Co	▲	8.2	6.2	12.5
Cr	□	17.6	30.5	23.0
Ti	●	4.1	3.6	2.3
Mo	×	1.0	3.9	3.1
W	–	0.8	-	-
Ta	◇	0.5	1.0	-
Nb	△	0.6	0.8	4.2
Al	○	7.2	21.6	13.1

* See Figure 14
** Values usually good to ± 0.2.

applicable also to IN 738X. Much uncertainty exists for the Mo, Ta, and W region. The presence of a W peak was never discernible. Although the peak from which the Ta values were calculated occured at a lower (~2.5 eV) binding energy than normal; no other element could be assigned to this peak. If this is indeed an error, the effect would be an increase of approximately .12% for all other elements (well within the experimental error). Before sputtering the surface appears to be composed primarily of Ni, Cr, and Al with Mo being a factor of 4 higher than its bulk concentration. After sputtering, Ni and Co are seen to increase while Cr and Al decrease. Nb increases by a factor of 7 over its bulk value while Mo and Ti show no significant change. Except for Ti and Nb, all elements appear to better reflect their bulk values after sputtering.

In Table IV are presented the ESCA results, both before and after sputtering, for the surface composition of superalloy IN 738X oxidized for 1, 22, and 100 hr. It is evident that Ti and Cr constitute approximately 90% of all three sample surfaces both before and after sputtering. The results for unsputtered oxidized samples are best represented by Figure 14 in which atomic % metal has been plotted vs time of oxidation. It is immediately apparent

TABLE IV

COMPOSITION OF SUPERALLOY IN 738X

Element	Symbol**	Atomic % Metal-Oxidized*, Time of Oxidation (Hours): 1		22		100	
Ni	■	2.3	(4.4)	2.8	(3.9)	4.9	(4.3)
Co	▲	0.9	(0.8)	1.4	(1.0)	2.6	(0.7)
Cr	◘	27.7	(18.5)	32.7	(22.3)	25.7	(17.4)
Ti	●	59.9	(72.1)	57.5	(70.9)	58.3	(74.9)
Mo	✖	3.0	(0.4)	1.3	(0)	0.8	(0)
W	-	-	-	-	-	-	-
Ta	◇	1.2	(1.1)	0.9	(0.8)	0.7	(0.8)
Nb	△	0.3	(0.5)	0.2	(0.3)	0.2	(0.3)
Al	○	4.7	(2.2)	3.2	(0.8)	6.9	(1.6)

*Values found in parenthesis are those obtained after sputtering the sample at ≈ 50 millitorr Ar, and 2kV x 2 mA for ≈ 8 min.

**See Figure 14.

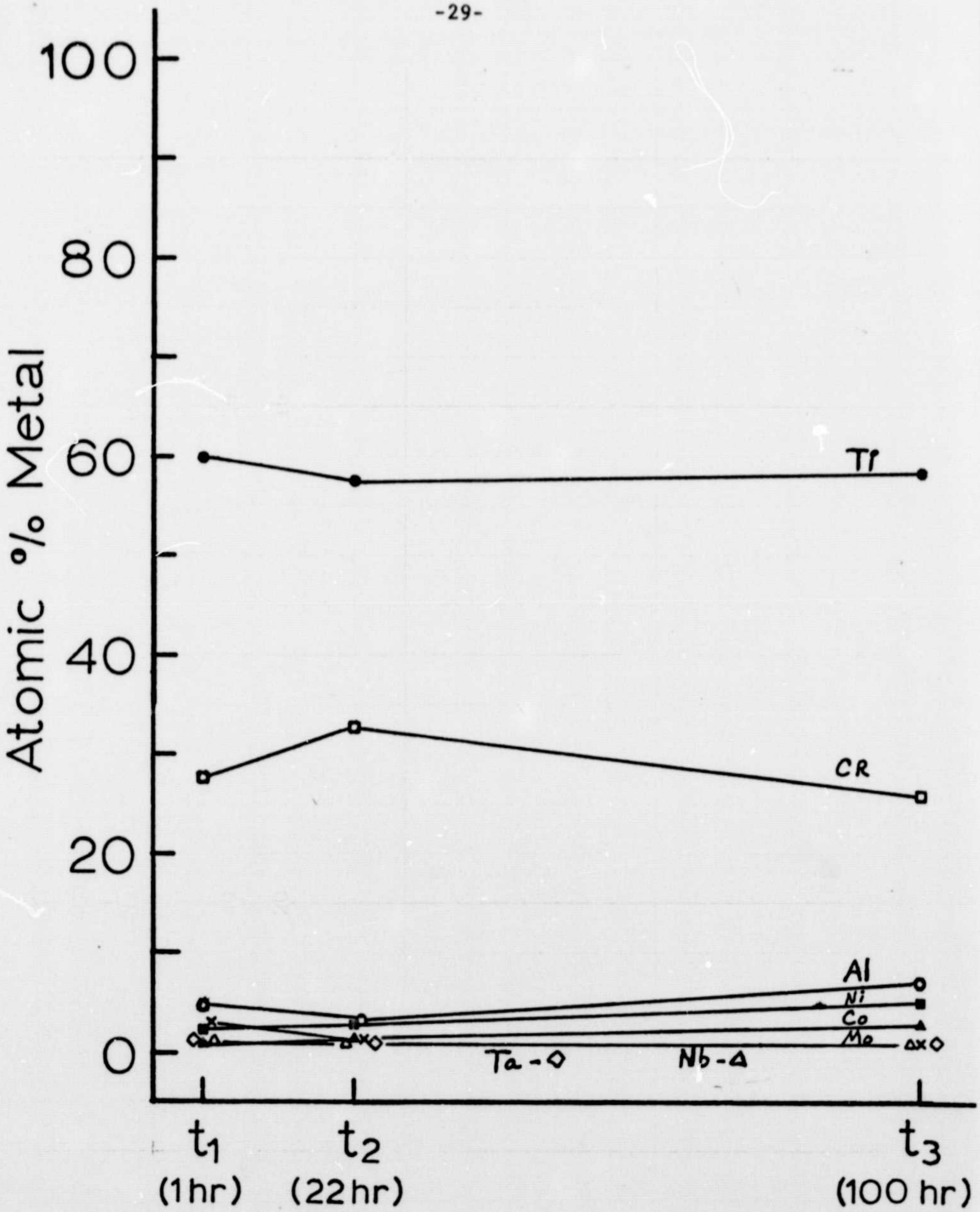

Figure 14. Plot of atomic % metal composition for superalloy IN 738X oxidized in 1 atm O_2 at 900°C for various periods of time.

that Ti and Cr constitute the majority of the surface of all three samples. Within experimental error, there appears to be no significant change in composition with time of oxidation. The values in Table IV for the sputtered samples reveal essentially constant composition for each metal as one goes from 1 hr to 100 hr oxidation. The most outstanding feature is the extremely high value for Ti(it is worth noting that the Ti concentration is four times greater in the bulk of superalloy IN 738X than the other three superalloys which have been examined). At the same time Cr shows a significant decrease after sputtering (its value being close to that found in the bulk for unoxidized samples). For the other elements (Ni, Co, and Al) which are major constituents of the bulk, much lower surface concentrations were found.

d) Two binary alloys of Ni-Cr. A preliminary investigation has been carried out on three samples of a Ni-Cr alloy. Spectra were obtained for an unoxidized sputtered sample of Ni-30Cr, and both a Ni-20Cr and a Ni-30Cr sample oxidized in air at 600° for 5 min. The two oxidized samples were examined before and after sputtering. Qualitative results showed Cr to be essentially in a higher oxidation state (+3) both before and after sputtering in all three samples. The Ni-20Cr sample showed Ni to be essentially in higher oxidation states (+2,+3) before sputtering but after sputtering there was 50% Ni^o. Before sputtering, the oxidized Ni-30Cr appeared to display a slight amount of Ni^o (10-20%) with $Ni^{+2,+3}$ constituting the major portion. After sputtering, Ni^o was ~65%. No Ni^o was observed for the sputtered unoxidized Ni-30Cr alloy.

Table V contains the quantitative results . The data for the unoxidized sample gave (after sputtering) 28% by weight Cr compared to 30% Cr determined by NASA for the bulk. The ESCA results are in good agreement for both determinations (ratio of the $2p_{3/2}$ and 3p peaks were used)*. For both the oxidized samples of the two Ni-Cr

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*The method for calculating the % composition was the same as that described in the interim report. Ni and Cr were assumed to constitute 100% sample composition. The peak ratio of Cr $2p_{3/2}$ to Ni $2p_{3/2}$ was obtained from the ESCA spectra. This value was divided by the theoretical ratio thus giving an atomic ratio of the two elements and therefore atomic % composition, which was then converted to weight % by using the atomic weights of the individual elements. A similar determination was made using the ratio of Cr 3p to Ni 3p which are close in E_b and thus close in kinetic energy for the photoelectrons. Therefore their escape depths are similar and contamination effects will be similar for both.

TABLE V

WEIGHT % OF Ni-Cr ALLOY BASED ON ESCA SPECTRA

Peak Used	Oxidized Ni-20Cr Unsp.*	Oxidized Ni-20Cr Sp.*	Oxidized Ni-30Cr Unsp.*	Oxidized Ni-30Cr Sp.*	Unoxidized Ni-30Cr Unsp.*	Unoxidized Ni-30Cr Sp.*
Ni($2p_{3/2}$)	46	56	8	57	-	72
Cr($2p_{3/2}$)	54	44	92	43	-	28
Ni(3p)	38	53	9	60	-	72
Cr(3p)	62	47	91	40	-	28

*Unsp = Unsputtered; Sp = Sputtered

alloys, the unsputtered samples reveal Cr to be higher in surface concentration than Ni, the 30% Cr sample showing greater than 90% Cr. Although after sputtering, the Cr value is still higher than the bulk value by a significant percentage, both alloys are consistent in yielding the same Ni-Cr content suggesting a uniform oxidation with Cr being more sensitive.

e) <u>B-1900/Hf and 1500 Å Ni/Ti</u>. In an attempt to determine whether Ti migration to the surface of the superalloys was due to thermal diffusion or to affinity for oxygen, an experiment was designed with thin films of Ni deposited on Ti rods. Two Ti samples were covered by sputtering with 1500 Å $\pm$ 100 Å Ni and examined by ESCA as received. The results (as mentioned in the interim report) were essentially identical for both samples. Nickel was present as both metal and oxide (60-70%). There was basically no observable peak for Ti. The B-1900/Hf sample heated in a vacuum revealed a Ti peak consistent with the bulk concentration of an unoxidized sample ($\approx$1%). The Ni region showed both metal and oxide (60-70%) peaks consistent with the Ni spectrum of the unexposed Ni/Ti samples. The 1500 Å Ni/Ti sample, which was also exposed to 900°C in a 10^{-8} torr vacuum, revealed essentially no well defined Ni peak, but Ti was found to be present in a single well-defined higher oxidation state (probably +4). With the assumption that Ni and Ti constitute 100% of the sample composition, calculations based on the ESCA spectra gave a value of 96% for Ti. Thus far, results would seem to indicate thermal diffusion of Ti through a metal such as Ni at high temperatures, but thermal diffusion in the superalloy does not occur or, if so, at a greatly reduced rate. The 1500 Å Ni/Ti sample which was exposed to 1 atm O_2 at 900°C for 10 min revealed Ni to be completely in the oxide state (+2,+3) and Ti in a single oxidation state (probably +4). The calculated intensity ratio for Ni and Ti indicated 74% Ti. However, this value is not reliable for the purpose for which the experiment was intended since the sample surface fell apart. It appeared the Ni deposited scaled off after O_2 exposure. The sample surface examined was non-uniform with irregular scaling. The Ti value would then more likely reflect a combination of Ti migration and direct exposure of the Ti sample surface. Both the vacuum heated B-1900/Hf and Ni/Ti samples showed uniform smooth surfaces indicating that the results obtained could be considered as valid.

f) <u>B-1900/Hf coated with varying amounts of Na_2SO_4 and exposed to conditions of oxidation for different periods of time</u>. Thus far, all ESCA work with the superalloys has been oriented toward the effects of high temperature oxidation. As a preliminary investigation for determining the effects of sulfidation (hot corrosion) NASA scientists prepared the above samples to be examined by ESCA.

The results for the sample coated with 0.69 mg Na_2SO_4 /cm^2 and not exposed to oxidation showed well-defined peaks for Na, O, Cl, and S, all four representative of a single oxidation species. The E_b of sulfur was indicative of a sulfate species. The calculated O:S ratio supported the identification of the sulfate species. Na, however, was more abundant (~3x) than could be accounted for. The spectra demonstrated that the Na_2SO_4 coverage was complete (no distinct metal signals were observed). The sample was then washed by suspending it in a beaker of distilled water for 2 hr at 70°C, rinsed with distilled H_2O, and dried in an oven at 90-100°C. The ESCA spectra did not display any S or Na signal.

The sample coated with 0.59 mg Na_2SO_4/cm^2 and corroded for 0.75 hr. showed Na and S (identified only in sulfate form) to be present, but unlike the unexposed sample, most of the metal peaks were identifiable. Peaks observed for Ni, Co, C, O, Mo, Ta, and Al were found to be quite similar in shape and binding energy as those found for previous studies of oxidation. The Ti line displayed asymmetry which might indicate the

the presence of at least 2 different species.

Two definite Cr lines were observed (Figure 15): one for the +3 state (normally seen with oxidized samples) and the other at a higher E_b (closer to the +6 state) which might be due to species such as CrO_3, Na_2CrO_4, and $Cr_2(SO_4)_3$. After washing, essentially no Na or S peak was observable. The metal peaks observed were all slightly broadened.

Two peaks occurred for C(290.1 and 285.9 eV). The 290.1 eV peak is tentatively assigned to a carbonate ion. The two Cr peaks (separated before) now appeared as a single broadened peak (Figure 16) but with a E_b between +3 and +6 (but closer to +3).

The B-1900/Hf sample coated with 0.78 mg Na_2SO_4/cm^2 and corroded for 3.5 hr showed a well-defined Na peak, but the presence of sulfur was questionable. Peaks for all the metals were observed although Ti and Ta gave ill-defined signals. One outstanding observation was the well-defined and intense Co 2p $_{3/2}$ peak (Figure 17). In the past, this region has displayed extreme broadness and poorly defined peaks suggesting a mixture of oxidation states. In contrast to the results obtained in experiments with an oxygen atmosphere, with Na_2SO_4 the great majority of Cr(80-90%) was found in the +6 oxidation state (Figure 18).

After washing the above sample, Na was still present but in a much smaller amount; and no definite S peak was

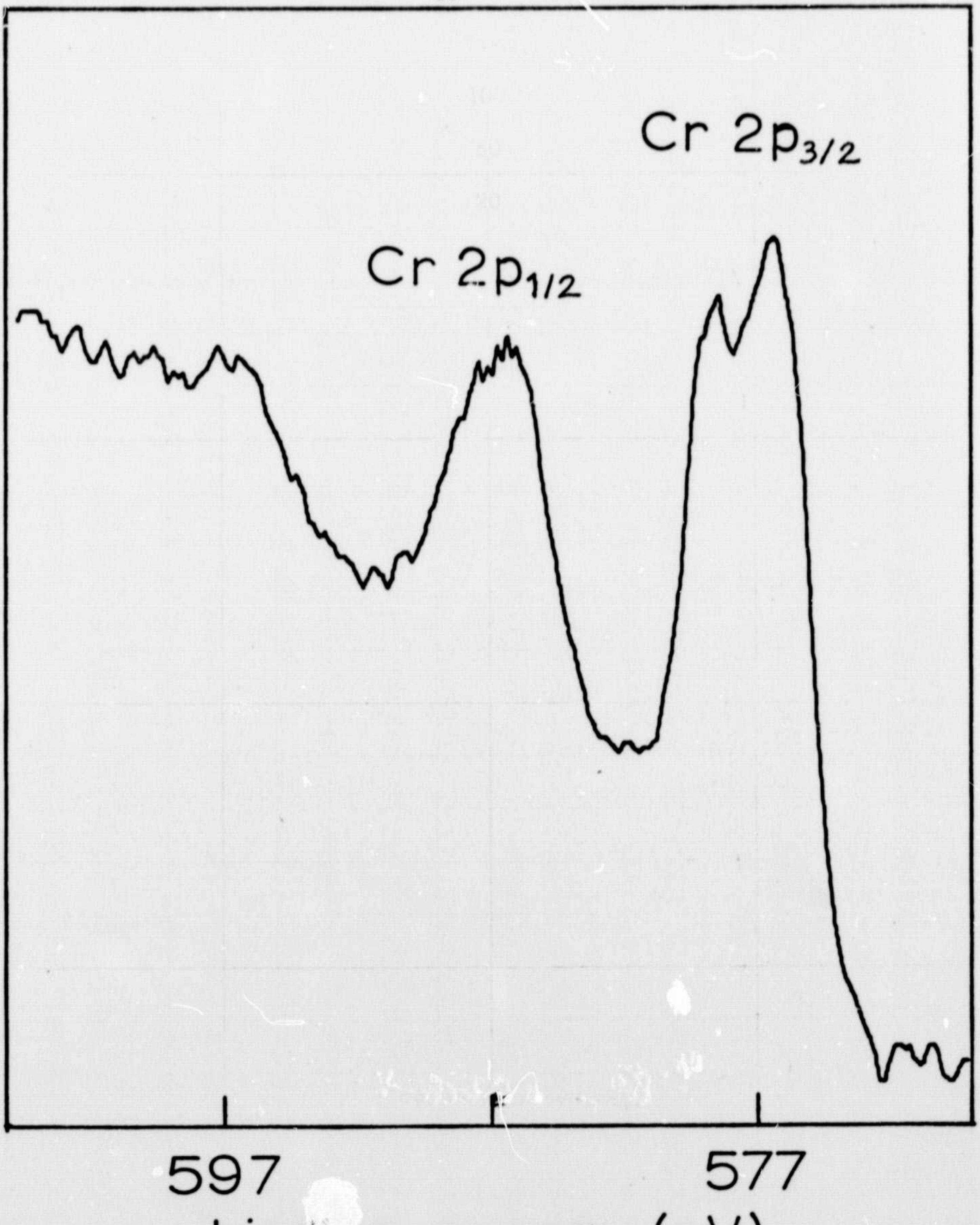

Figure 15. The Cr 2p spectrum of B-1900/Hf coated with 0.59 mg Na_2SO_4/cm^2 and oxidized for 0.75 hr at 900°C (before washing).

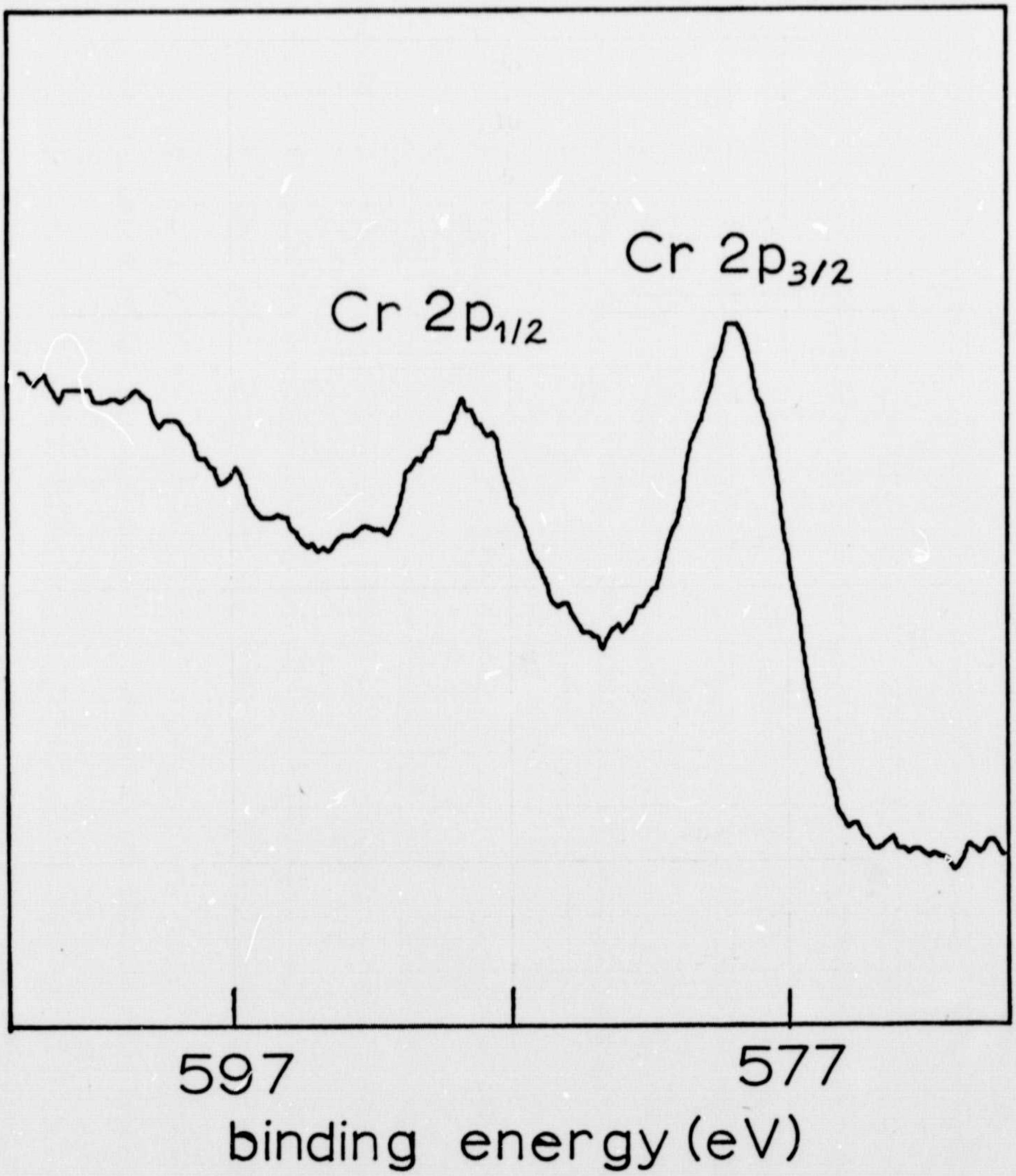

Figure 16. The Cr 2p spectrum of B-1900/Hf coated with 0.59 mg Na_2SO_4/cm^2 and oxidized for 0.75 hr at 900°C (after washing in water).

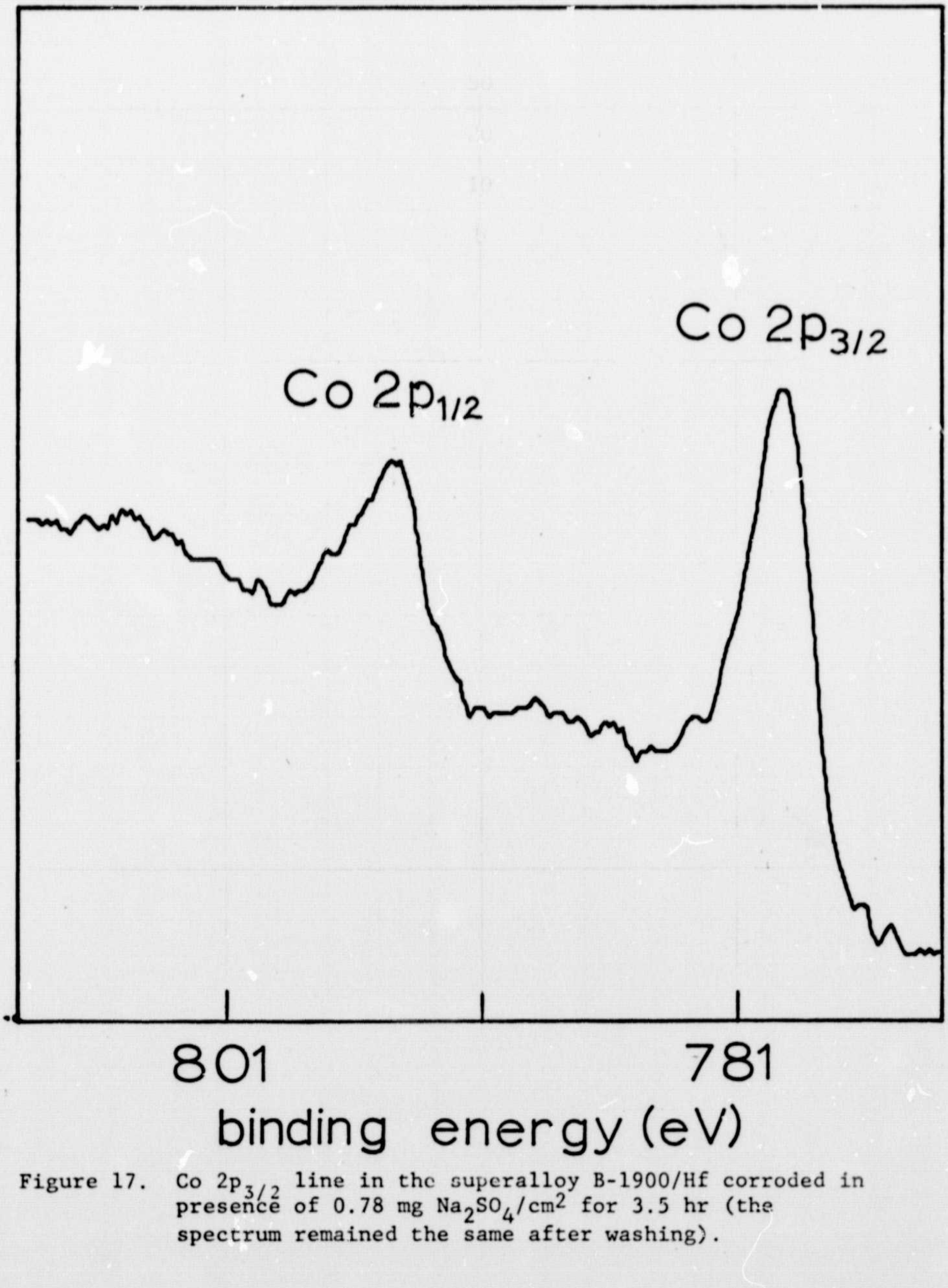

Figure 17. Co $2p_{3/2}$ line in the superalloy B-1900/Hf corroded in presence of 0.78 mg Na_2SO_4/cm^2 for 3.5 hr (the spectrum remained the same after washing).

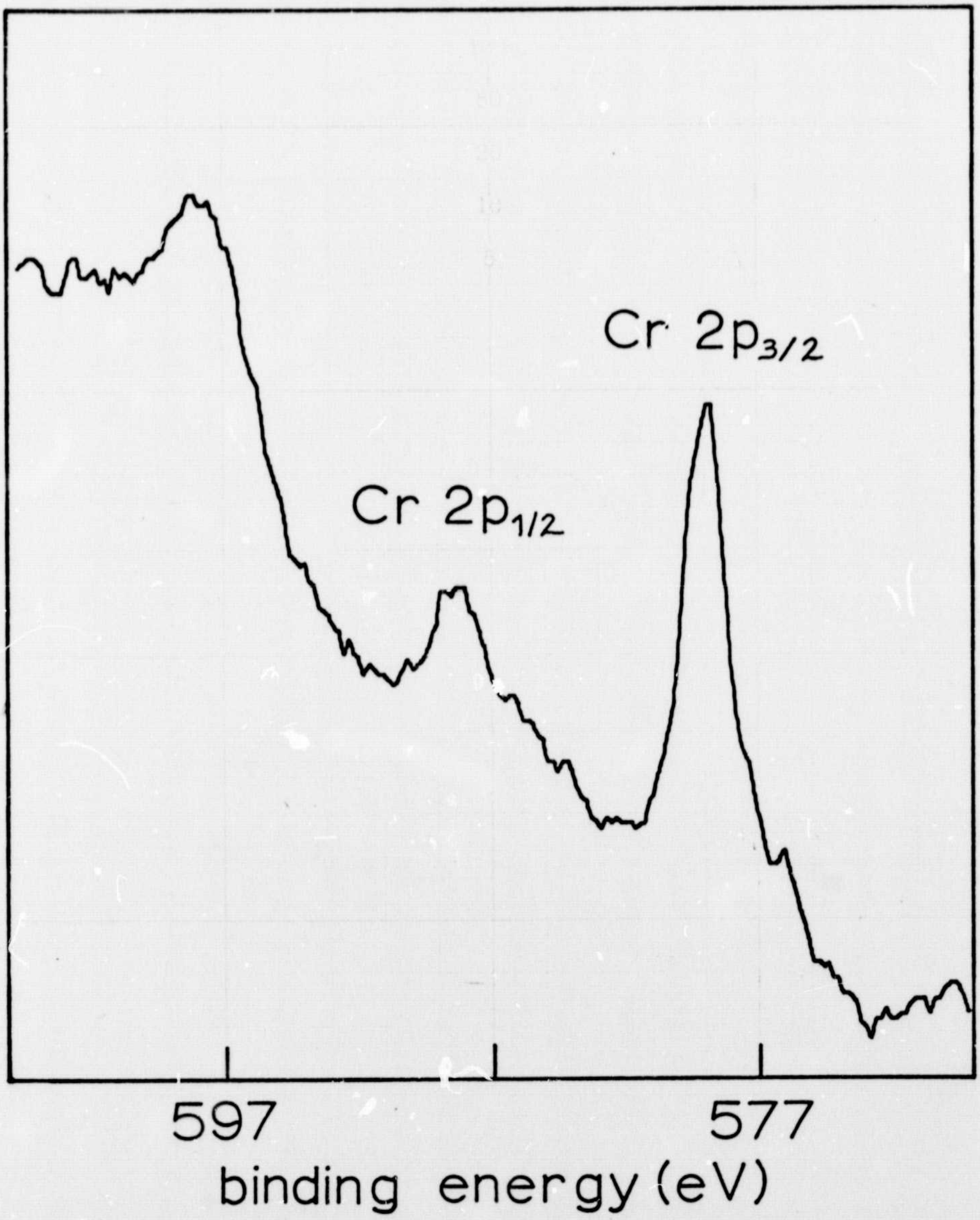

Figure 18. The Cr 2p spectrum of B-1900/Hf coated with 0.78 mg Na_2SO_4/cm^2 and oxidized for 3.5 hr at 900°C (before washing).

observed. The metal peaks (Ni, Co, Al) appeared essentially the same as before washing, and the presence of Ti was certain as well as Mo, although the Mo peak had decreased considerably in intensity and lacked the usual symmetrical shape for a single species. A striking observation was the complete absence of Cr(Figure 19).

Only for the above sample was the washing solution partially examined. A sample of essentially pure graphite was placed in the wash solution which was then evaporated to dryness. The ESCA spectra of the graphite sample revealed the presence of Cr(+6, +3), Mo(+6), S(+6,+2), and Na. The ratio of Mo/Cr signal intensities suggested a 1:1 atom ratio.

Table VI gives the results of calculations performed in order to estimate the extent of formation of water soluble corrosion products for the two Na_2SO_4 corrosion experiments. In the 0.75 hr experiment Ni and Co amounts increase after washing while Cr and Mo decrease. This can be interpreted in terms of formation of Cr and Mo water soluble corrosion products. In the 3.5 hr experiment Ni and Co do not experience further modifications while Cr and Mo practically disappear after washing and the amount of Al doubles. The evolution of Cr signals shows that this element is transformed into a soluble species within the first three hours of Na_2SO_4 corrosion.

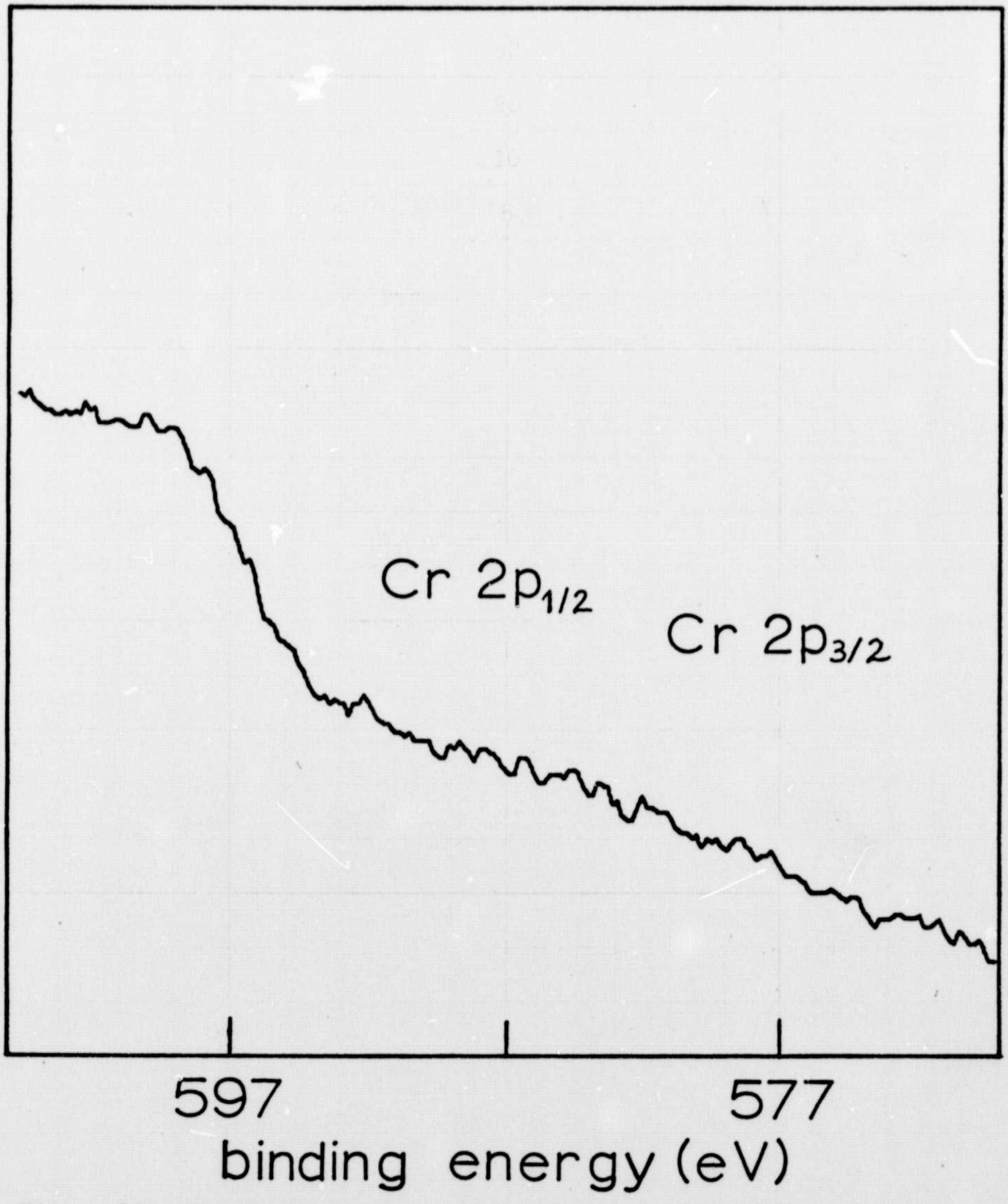

Figure 19. The Cr 2p spectrum of B-1900/Hf coated with 0.78 mg Na_2SO_4/cm^2 and oxidized for 3.5 hr at 900°C (after washing in water).

TABLE VI

SURFACE COMPOSITION OF TWO B-1900/Hf SAMPLES

AFTER EXPOSURE TO CONDITIONS OF HOT CORROSION

	Atomic % Metal* Based on ESCA Spectra			
	0.59 mg/cm^2 - 0.75 hr		0.78 mg/cm^2 - 3.5 hr	
Element	Unwashed	Washed	Unwashed	Washed
Ni	5	16	10	11
Co	4	11	35	33
Cr	36	21	17	0
Ti	2	3	4	3
Mo	9	?	12	1
Ta	1	?	-	-
Al	43	49	25	52

* Values are preliminary and approximate. Only large differences should be considered significant. The metals were taken to represent 100% metal composition although peaks for Na, S, C, O, and Cl were, in some cases, present. Following are values for Na, S, and Cl reported to the Al peak as intensity reference (they can be compared only indirectly with the values for other metals):

1) 0.75 hr - unwashed; Na/Al = 2.9, Cl/Al = 0.15, S/ Al = 0.63
2) 3.5 hr - unwashed; Na/Al = 5.3, Cl/Al = 1.1, S/Al = 0.0
3) 3.5 hr - washed; Na/Al = 0.22, Cl/Al = 0.03, S/Al = 0.0

Co was found to be essentially constant and in high concentration before and after washing. The value for Co seen in Table VI (3.5 hr) is significantly greater than that for Ni. This is in contrast with all previous findings and will be verified in future studies.

III. Conclusions

The spectra of the pure metals and their oxides were quite informative and helpful in analyzing the complex patterns obtained for the superalloys.

The quantitative results for superalloys 713C and 738X complete the proposed study of the effect of oxidation on the four superalloys examined in the first year. The results revealed striking differences between the surface compositions of these two superalloys and their behavior under different conditions of oxidation. The corroboration of results obtained by ESCA and other methods* employed in this study proves to be very useful.

The study of the binary Ni-Cr alloys was helpful not only in the qualitative evaluation of the effects of oxidation on the interacting metals but also in confirming the validity of the quantitative technique used in this study. The need to investigate simpler systems such as binary and ternary alloys is now definitely established.

Although the study of Ni/Ti partially failed, the data obtained suggests that in the superalloy, the observed migration of Ti should be interpreted in terms of dominant chemical reactivity.

The preliminary results on the hot corrosion of B-1900/Hf samples (in presence of Na_2SO_4) are encouraging.

*Elemental analysis, electron microprobe, gravimetry, all executed at the Lewis Research Center.

With experimental conditions kept very close to those employed in the oxidation studies one will be able to derive precious comparative results. Important differences have already been observed. The most significant are: the lack of Ti migration; the strong effects on Cr (at one stage this element is completely transformed into a water soluble species and after washing it simply disappears from the surface); the higher speed of alteration of superalloys in presence of Na_2SO_4.

IV Schedule of Future Investigations

Based on the preliminary results discussed in this report we will carry out detailed studies of binary alloys (Ni-20Cr, Ni-30Cr) exposed to oxygen atmosphere at high temperatures in the presence or absence of Na_2SO_4.

A few experiments with superalloys will be repeated in order to verify their reproducibility and to optimize our research methods. New systems will be investigated in parallel.

At the present stage of our study a theoretical approach in the interpretation of hot corrosion is highly desirable. We will start with model surfaces of binary alloys in which, according to thermodynamic principles, we should find the predominance of the species with the lowest surface free energy.