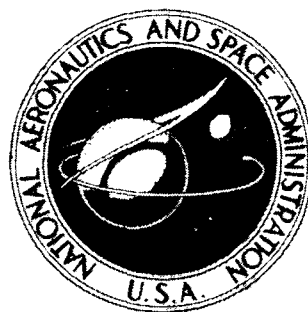


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**ALLOY COMPOSITION EFFECTS ON OXIDATION
PRODUCTS OF VIA, B-1900, 713C, AND 738X -
A HIGH TEMPERATURE DIFFRACTOMETER STUDY**

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1. Report No. NASA TM X-2796		2. Government Accession No.		3. Recipient's Catalog No.	
4. Title and Subtitle ALLOY COMPOSITION EFFECTS ON OXIDATION PRODUCTS OF VIA, B-1900, 713C, AND 738X - A HIGH TEMPERATURE DIFFRACTOMETER STUDY				5. Report Date June 1973	
				6. Performing Organization Code	
7. Author(s) Ralph G. Garlick and Carl E. Lowell				8. Performing Organization Report No. E-7318	
9. Performing Organization Name and Address Lewis Research Center National Aeronautics and Space Administration Cleveland, Ohio 44135				10. Work Unit No. 501-01	
				11. Contract or Grant No.	
12. Sponsoring Agency Name and Address National Aeronautics and Space Administration Washington, D. C. 20546				13. Type of Report and Period Covered Technical Memorandum	
				14. Sponsoring Agency Code	
15. Supplementary Notes					
16. Abstract High-temperature X-ray diffraction studies were performed to investigate isothermal and cyclic oxidation at 1000° and 1100° C of the nickel-base superalloys VIA, B-1900, 713C, and 738X. Oxidation was complex. The major oxides, Al₂O₃, Cr₂O₃, and the spinels, formed in amounts consistent with alloy chemistry. The alloys VIA and B-1900 (high Al, low Cr alloys) tended to form Al₂O₃ and NiAl₂O₄; 738X (high Cr, low Al) formed Cr₂O₃ and NiCr₂O₄. A NiTa₂O₆ type of oxide formed in amounts approximately proportional to the refractory metal content of the alloy. One of the effects of cycling was to increase the amount of spinels formed.					
17. Key Words (Suggested by Author(s)) Oxidation Super alloys High temperature X-ray diffraction				18. Distribution Statement Unclassified - unlimited	
19. Security Classif. (of this report) Unclassified		20. Security Classif. (of this page) Unclassified		21. No. of Pages 24	
				22. Price* \$3.00	

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SUMMARY

High-temperature X-ray diffraction studies were performed during both isothermal and cyclic oxidation at 1000° and 1100° C on the nickel base superalloys VIA, B-1900, 713C, and 738X. These alloys represented ranges in composition with respect to those elements most expected to influence oxidation, chiefly aluminum, chromium, and the refractory metals. The oxidation revealed was complex, with at least five and often seven oxides present. These oxides were aluminum oxide (Al_2O_3), chromium oxide (Cr_2O_3), spinels (usually more than one), tapiolite (a nickel refractory metal oxide with the nominal formula NiTa_2O_6), nickel oxide (NiO), nickel titanium oxide (NiTiO_3), and zirconium oxide (ZrO_2). With respect to the major oxides present (Al_2O_3 , spinels, and Cr_2O_3) the results were consistent with the alloy chemistry.

Those alloys with the least chromium and the highest aluminum (VIA and B-1900) had the greatest tendency for Al_2O_3 and NiAl_2O_4 formation. Conversely, 738X, the alloy with the highest chromium and the lowest aluminum formed the most Cr_2O_3 and NiCr_2O_4 .

The refractory metal content of the alloys apparently affected oxidation chiefly with respect to the tapiolite since the amounts of this phase were approximately proportional to the refractory metal content of the alloy.

The effects of high-temperature cyclic oxidation rather than isothermal were complex, but a major effect was to increase the amount of spinel formed.

INTRODUCTION

Efforts to develop superalloys have been devoted chiefly to improving mechanical properties, especially high-temperature strength. Improved stress-rupture capabilities have been brought about primarily through chemistry changes. These changes mainly

involve lower chromium (Cr), higher aluminum (Al), higher titanium (Ti), and higher refractory metal contents (ref. 1). Such changes have increased high-temperature strength without necessarily increasing oxidation resistance. If proper protection systems are not provided, high-temperature oxidation could lead to shortened component life due to the consumption of the load bearing material. An important consideration in oxidation testing should be the environmental conditions of the test. For example, cyclic service at high gas velocities can yield results far different from those obtained from isothermal testing (ref. 2).

With these factors in mind a program was conducted to investigate the effects of both chemical differences and test parameters on the oxidation behavior of superalloys. The four alloys studied were the commercial cast nickel base superalloys VIA, B-1900, 713C, and 738X. These alloys were chosen because they all contained various amounts of the elements that were expected to most affect oxidation, chromium, aluminum, refractory metals, and titanium. Table I lists the approximate composition of each alloy studied with respect to these elements. Testing of these alloys included isothermal furnace tests, cyclic furnace tests, and exposure to high-velocity combustion products in a simulated gas turbine engine environment.

The overall program was planned so that it would provide

- (1) A comparison of the ranking of the alloys according to the various types of testing and a judgment of these rankings in terms of engine performance
- (2) A description of the oxidation for each alloy in terms of kinetics, scales formed, and alloy microstructural changes
- (3) A better understanding of the role of alloy chemistry in oxidation.

The results of this study are being prepared in separate NASA reports that cover specific portions of the entire study.

This report deals with the high-temperature X-ray diffraction (HTXRD) identification of the oxides that formed during both cyclic and isothermal oxidation. With this technique the course of the reactions can be followed at the oxidation temperature, the sequence of formation of the various oxides can be determined, and the relative amounts of the oxides can be roughly determined. The application of HTXRD to the oxidation of other superalloys is described in references 3 and 4.

Oxidation at 1000^o and 1100^o C was followed for times up to 100 hours at temperature for both isothermal and cyclic tests. These tests were duplicated in another part of the overall program by tests run under similar conditions where parameters such as weight gain and thickness change were measured.

MATERIALS

The alloys were received as cast coupons, 2.5 by 2.5 by 0.625 centimeters. Typical

analyses from the heats used in this work are given in table II. The cast coupons were given the heat treatments they normally receive for commercial use: VIA - 32 hours at 900° C in argon, B-1900 - 4 hours at 1080° C in argon, 713C - no heat treatment, and 738X - 2 hours at 1120° C in argon. Cooling from these treatments was in argon at a rate equivalent to air cooling. Approximately 0.025 centimeter was then machined from each of the coupon surfaces, and each coupon was glass bead blasted. Samples 1.27 by 0.95 by 0.025 centimeters were then cut from these coupons. All samples of each alloy were cut from one coupon.

The microstructures of the as-cast materials are shown in figure 1. The major portion of each alloy includes a mixture of gamma prime ($\gamma' = \text{Ni}_3(\text{Al}, \text{Ti})$) in gamma ($\gamma = \text{Ni}$ solid solution). This is typical of most advanced nickel-base superalloys. In all of the alloys studied massive particles of primary γ' and $(\text{Ti}(\text{C}, \text{N}))$ were observed at the grain boundaries (ref. 5).

PROCEDURES

The HTXRD setup has been described in reference 3. Briefly, the alloy sample (fig. 2) rests on a platinum - 13-percent-rhodium heater with a platinum/platinum - 13-percent-rhodium thermocouple that was spot-welded to the surface struck by the X-ray beam. The sample is heated to the oxidation temperature in static air. In these studies heat up took less than 5 minutes, and temperature overshoot was less than 3° C. Every cycle of a cyclic oxidation test involved 1 hour at temperature followed by natural air cool and 1 hour at room temperature. Diffractograms were taken at intervals throughout the course of the approximately 100 hours at temperature for both the isothermal and the cyclic runs. Data from the diffractograms were plotted at intensities of major diffraction lines of the various oxide phases against time. At the conclusion of each run, a diffractogram was taken at room temperature.

EVALUATION

From each diffraction pattern, one peak per phase was chosen. In general the peaks chosen were the strongest unambiguous line for each phase. All peaks were then normalized to corundum ($\alpha\text{Al}_2\text{O}_3$) following the procedures of Swanson et al (ref. 6). Their technique consists of comparing diffraction patterns to $\alpha\text{Al}_2\text{O}_3$ by mixing equal amounts of the phase to be compared and $\alpha\text{Al}_2\text{O}_3$. A ratio of the strongest lines of the two phases is used as an indicator of the absolute intensity of each pattern so measured. The main advantage of this technique is that it allows a better evaluation of what major and

minor phases are and of their approximate relative abundance. This still leaves the problem of matrix effects or layering of the oxides (ref. 3) to prevent actual quantitative analysis, but it is a substantial improvement over the use of raw intensities.

The intensities used were peak heights although peak areas were also measured. The peak areas were less precise because of the sharpness of the peaks. The only exception was the spinel patterns in which several spinels were present (see the next section), which prevented the measurement of peaks without overlap. After correction, the intensity of the peaks from each phase were plotted against time at temperature.

RESULTS AND DISCUSSION

General

High-temperature X-ray diffraction studies were performed during both isothermal and cyclic oxidation at 1000° and 1100° C on the nickel-base superalloys VIA, B-1900, 713C, and 738X. The results of these studies are presented in this section.

Metallographic examination of all alloys after testing at all conditions showed γ' depletion zones at the oxide-metal interface (e.g., fig. 3). This transformation of γ' to γ is associated with the consumption of the more reactive metals Al and Ti during oxidation (ref. 7). The extent of γ' depletion depended on the severity of the test.

The major oxides found on the oxidized alloys were Al_2O_3 , Cr_2O_3 , NiO, spinels, NiTiO_3 , ZrO_2 , and a phase whose diffraction pattern corresponded to the ASTM card for a mineral tapiolite $((\text{Fe}, \text{Mn})(\text{Ta}, \text{Nb})_2\text{O}_6)$. The cations in such a compound can vary over wide limits. For example, the ASTM cards for NiTa_2O_6 , CrTa_2O_6 , and CrNb_2O_6 are very similar to that for tapiolite. The phase found, which will be called tapiolite in this report, is probably $(\text{Ni}, \text{Co}, \text{Cr})(\text{Ta}, \text{Nb}, \text{W}, \text{Mo})_2\text{O}_6$. In order to give a rough quantitative estimate of this phase, NiTa_2O_6 was synthesized, and its diffraction pattern compared with that of Al_2O_3 in a mixture of these oxides as described in the MATERIALS and PROCEDURES sections. From these results, an approximate correction factor was calculated. The accuracy of this factor depends somewhat on the nature of the metals in the tapiolite.

The spinels formed in the various alloys ranged in lattice parameter from that corresponding to NiAl_2O_4 ($a_0 \sim 8.05 \times 10^{-10}$ m or 8.05 Å at room temperature) to NiCr_2O_4 ($a_0 = 8.32 \times 10^{-10}$ m or 8.32 Å at room temperature). These spinels will be designated NiAl_2O_4 and NiCr_2O_4 in this report, although it must also be understood that other cations may be present in spinels with these lattice parameters. In cases where both these spinels formed, there were separate, distinct diffraction peaks for the two phases; in others the peak for a reflection also included intensities from the entire range of spinels

intermediate between NiAl_2O_4 and NiCr_2O_4 . In many cases a distinct spinel was often present with a lattice parameter intermediate between NiAl_2O_4 and NiCr_2O_4 . The relative heights of the peaks for these spinels are given in table III. In determining the correction factor for the spinels, an integrated intensity was measured that included the entire range of spinels found. In order to compare this with the peak heights of other phases, it was assumed that the ratio of peak height to integrated intensity for the spinel was the same as the ratio of peak height to integrated intensity for Al_2O_3 and Cr_2O_3 (ref. 8).

Considerable signal was present from the nickel solid-solution substrate for all tests except the isothermal 1100°C 738X test after 25 hours. The presence of this reflection assures that the X-ray beam completely penetrated the scale. Thus all major oxides in the scale should be detected.

The increases observed in peak heights of most oxides with time is mainly due to the increase in oxide scale thickness rather than to phase changes at the expense of other oxides present.

Oxidation of VIA

Plots of the corrected peak height against time for the four test conditions are shown in figure 4. For isothermal oxidation at 1000°C (fig. 4(a)), the predominant oxides were Al_2O_3 and the spinels, with both increasing throughout the test. Note that the spinel intensities are often plotted on a different scale from the other oxides. This was done because the spinel intensities were often much higher than those of the other oxides. The spinel present at the beginning corresponded to NiCr_2O_4 . But as oxidation progressed lower-lattice-parameter spinels appeared and at 100 hours NiAl_2O_4 was predominant, although NiCr_2O_4 was still present. Chromium oxide was present as a minor oxide from the beginning, gradually decreasing from about 10 hours until it was not found at 96 hours. Tapolite was present as a minor oxide at all times.

Isothermal oxidation at 1100°C (fig. 4(b)) showed spinels as the predominant oxides, again increasing in amount to 100 hours. In this case no spinel corresponding to NiCr_2O_4 was found, but NiAl_2O_4 and an intermediate spinel were present from the beginning with NiAl_2O_4 increasing in relative amount and being predominant at the end. Considerable amounts of Al_2O_3 and tapolite were present for the entire run. Small amounts of Cr_2O_3 and NiO were found, Cr_2O_3 being present from the beginning and NiO appearing after 1 hour. The chief difference between the isothermal runs was the higher relative amount of tapolite and lower Al_2O_3 at 1100°C .

Cyclic oxidation at 1000°C (fig. 4(c)) was similar to isothermal oxidation except for the appearance of considerable zirconium oxide (ZrO_2) and an increase in the tapiro-

lite formed. No NiCr_2O_4 spinel was formed. An intermediate spinel and NiAl_2O_4 were present from near the beginning with NiAl_2O_4 again increasing and becoming predominant.

Cyclic oxidation at 1100°C (fig. 4(d)) was similar to isothermal except for an apparent increase in Al_2O_3 after about 50 hours. The NiCr_2O_4 spinel was present only during the first cycle; NiAl_2O_4 again increased relative to an intermediate spinel and became predominant. The effect of increasing temperature from 1000° to 1100°C for cyclic oxidation was similar to that for isothermal oxidation: a higher relative amount of tapiolite and lower Al_2O_3 .

The similarity between the isothermal and cyclic results indicates little spalling during cyclic oxidation.

Oxidation of B-1900

The major oxides formed during isothermal oxidation at 1000°C (fig. 5(a)) were Al_2O_3 and spinels. Both increased gradually over the 100 hours. Tapiolite and ZrO_2 were present in small amounts for the entire test. Chromium oxide was present in small amounts at the beginning but was not detected after 5 hours. The spinels present were both NiAl_2O_3 and NiCr_2O_3 at all times with about three times more NiAl_2O_3 than NiCr_2O_3 .

Spinel were the predominant oxides for isothermal oxidation at 1100°C (fig. 5(b)) reaching much higher levels than at 1000°C . Aluminum oxide is again a major phase and increases with time. When first determined, there were equal amounts of NiAl_2O_4 , NiCr_2O_4 , and an intermediate spinel. As oxidation continued, NiAl_2O_4 became predominant, although all these spinels were present at the end. Tapiolite was again present at all times. Chromium oxide was present in small amounts during the early stages of oxidation but decreased and was not found after 31 hours. Nickel oxide was present after 1 hour. The chief difference between the 1000° and 1100°C isothermal runs was the higher relative amount of spinel at 1100°C .

For cyclic oxidation at 1000°C (fig. 5(c)) spinels and Al_2O_3 are at approximately the same levels during the earliest stages, but the spinels increase more rapidly than the Al_2O_3 and soon become the predominant oxide. When first determined, all three spinels were present in approximately equal amounts, but NiAl_2O_4 became predominant as oxidation progressed. Chromium oxide goes through a maximum at 4 hours. Nickel oxide also was present, reaching a maximum later than the Cr_2O_3 . In this case and in others where Cr_2O_3 and NiO are both present, NiO increases after Cr_2O_3 has begun to decrease. Possibly, NiO is more likely to form after Cr has been depleted from the substrate through the formation of Cr_2O_3 and NiCr_2O_4 . Tapiolite was again present at all times.

Cyclic oxidation at 1100°C (fig. 5(d)) shows trends in the oxide curves similar to those at 1000°C . The rates of change are faster, however, and Al_2O_3 decreases during the later states of oxidation.

B-1900 was similar to VIA in that there is a general similarity between the isothermal and cyclic results. The B-1900 did show greater differences between isothermal and cyclic however, especially at 1000°C .

Oxidation of 713C

Isothermal oxidation of 713C at 1000°C (fig. 6(a)) again showed Al_2O_3 and the spinels as the major oxides. Aluminum oxide increased steadily and became the predominant oxide after 10 hours of testing. The spinels leveled off after about 2 hours. The NiAl_2O_4 and NiCr_2O_4 spinels were both present at all times with about twice as much NiCr_2O_4 as NiAl_2O_4 . Chromium oxide and tapiolite were present as minor phases during the entire run. The oxides NiO and NiTiO_3 were present during the later stages.

Isothermal oxidation at 1100°C (fig. 6(b)) was different from that at 1000°C chiefly in that after a short time at 1100°C the spinels increased steadily and became the predominant oxides. At the beginning only NiCr_2O_4 spinel was present. After about 1 hour the NiAl_2O_4 and an intermediate spinel appeared. These were both present in about equal amounts until about 31 hours, after which NiAl_2O_4 increased over the intermediate spinel and was predominant at the end. Aluminum oxide was present in increasing amounts as oxidation progressed. Chromium oxide reached a maximum at about 1 hour then decreased until none was found at 96 hours. Tapiolite was present at all times as a minor oxide, as was NiO after 1 hour.

The cyclic oxidation behavior of 713C at 1000°C (fig. 6(c)) was much different from the isothermal behavior. After a short time spinels became the predominant oxides (compared with isothermal oxidation in which Al_2O_3 predominates). The NiAl_2O_4 and NiCr_2O_4 spinels were present in about equal amounts during the early stages of oxidation. After about 12 hours NiCr_2O_4 was no longer detected but was replaced by the intermediate spinel. This spinel was present in amounts about equal to NiAl_2O_4 until 38 hours, after which NiAl_2O_4 increased and was predominant. Aluminum oxide was a major oxide, increasing steadily during the test. Chromium oxide increased from a minor phase at about 1 hour to become a major oxide, rapidly decreased after 12 hours, and was not found after 70 hours. A considerable amount of NiO was found at 16 hours, but it decreased with further time. Tapiolite was again present as a minor phase at all times.

Cyclic oxidation at 1100°C (fig. 6(d)) showed results similar to that for 1100°C isothermal in many respects. The chief difference is the appearance of appreciable NiO in the range of 2 to 4 hours. The NiO then decreased to become a minor oxide, but in-

creased again after about 40 hours. The spinel also showed somewhat different behavior in that the spinels present after 100 hours were approximately equal amounts of NiAl_2O_4 and intermediate spinel for cyclic oxidation, while NiAl_2O_4 was predominant after isothermal testing.

As with B-1900 and VIA, the chief effect of raising the test temperature from 1000° to 1100° C for 713C was to increase the amount of spinel formed. There were also differences between cyclic and isothermal tests, especially at 1000° C. These differences would be expected to be associated with spalling occurring during the cyclic tests or with cracking of the scale, exposing the substrate to the atmosphere at the crack.

Oxidation of 738X

Isothermal oxidation of 738X at 1000° C (fig. 7(a)) gave results similar to those for 713C except that for 738X the NiAl_2O_4 to NiCr_2O_4 ratio for the entire run was about 1/1 compared with 1/2 for 713C.

The results for the later stages of isothermal oxidation at 1100° C (fig. 7(b)) are more ambiguous than for the other materials, since the diffraction pattern for nickel solid solution was no longer observed after 25 hours, probably because of the increased thickness of the oxide scale. Thus it is also probable that for longer times, reflections from the oxide layers closest to the metal are also absent or much reduced. For example, although tapiolite was found in all stages of 738X oxidation, it was not found in this run after 48 hours. Even with this limitation, it is obvious that the 1100° C oxidation was quite different from that at 1000° C. Chromium oxide was the major oxide in the early stages of oxidation. Its intensity decreased rapidly at about 25 hours, either because of a reduction in its amount or to the reduction of its pattern by the appearance of large amounts of other oxides at this time. The spinels formed were a minor phase until 25 hours when a rapid increase took place; the amount was approximately constant after 48 hours. The spinel was NiAl_2O_4 until 4 hours, when a small amount of NiCr_2O_4 appeared. The dominant spinel was NiCr_2O_4 when the rapid increase took place (at 25 hr), and it was the only spinel after 48 hours. No intermediate spinel was found. Nickel oxide was present as a minor phase during the earliest stages, increasing rapidly after 25 hours. At 25 hours NiTiO_3 appeared and increased rapidly.

Cyclic oxidation at 1000° C (fig. 7(c)) was much different from isothermal in that Cr_2O_3 was a major oxide and much larger amounts of spinels formed. The spinels present at the start of oxidation were NiAl_2O_4 and NiCr_2O_4 in about equal amounts. An intermediate spinel appeared after 3 hours and was present at all later times. The NiAl_2O_4 pattern soon disappeared, the NiCr_2O_4 to intermediate spinel ratio being about 5 for the remainder of the run. Results to be published separately showed considerable

spalling to take place during furnace oxidation. The differences in behavior between the isothermal and cyclic runs are probably associated with this heavy spalling.

Cyclic oxidation at 1100°C (fig. 7(d)) was only conducted for 44 hours because of excessive oxidation, but it gave results similar to isothermal with respect to the major oxides formed. Chromium oxide was again the major oxide during the early stages of oxidation. The spinels and NiO again showed a rapid increase, in this case in the 8- to 12-hour range. During the first hour both NiAl_2O_4 and NiCr_2O_4 were present, with no intermediate spinel. The intermediate spinel first appeared at 12 hours. All three spinels were present during the later stages of oxidation in approximately equal amounts. The decreasing amounts of all the oxides during the later stages of oxidation were probably due to spalling of the heavy scale. (Appreciable spalling was found for these conditions for a similar test run - in another part of the program.) Spalling is the probable cause for the considerable differences between isothermal and cyclic behavior for this alloy.

Comparison of Alloys

Table IV summarizes the results with respect to the relative strengths of the oxide patterns at the completion of the test for all alloys under all conditions. For 1000°C isothermal oxidation all four alloys showed substantially the same behavior with respect to the major oxides present. All showed Al_2O_3 and spinels gradually increasing with time, and all the spinels contained substantial proportions of both NiAl_2O_4 and NiCr_2O_4 during the later stages of oxidation. The discussion of the alloys below will consider only tests under more severe oxidation conditions.

VIA and B-1900 were very similar with respect to most of the oxides and were the low Cr, high Al, high refractory-metal alloys. For both alloys, the spinels and Al_2O_3 were the major oxides, with NiAl_2O_4 the predominant spinel after the early stages of oxidation. Chromium oxide was only a minor oxide for these alloys. The major difference was the presence of larger amounts of tapiolite in VIA. This is consistent with the alloy chemistry since the chief difference in these alloys is the 18-percent refractory metal content in VIA compared with 10 percent for B-1900.

713C differed from VIA and B-1900 in the appearance of considerable Cr_2O_3 during the early stages of oxidation and in the persistence of NiCr_2O_4 spinel until later stages in the oxidation for 713C. 713C is a high Cr, high Al, low refractory-metal alloy. Another difference was that, for cyclic testing, considerable NiO was present during the later stages of oxidation for 713C. 713C was similar to VIA and B-1900 during the later stages of oxidation in that NiAl_2O_4 was the predominant spinel and Al_2O_3 was still a major oxide.

The oxidation behavior of 738X was different from that of the other alloys in many respects. 738X is the high Cr, low Al, low refractory metal alloy. Aluminum oxide was at most a minor oxide in the tests, and Cr_2O_3 was much more evident than for the other alloys. The spinel present during the later stages of oxidation was not NiAl_2O_4 as with the other alloys but was either predominantly NiCr_2O_4 or a mixture of spinels. For cyclic oxidation 738X was similar to 713C in the appearance of considerable quantities of NiO during the later stages of oxidation (only tested 44 hr because of very thick scale formed).

CONCLUDING REMARKS

The patterns obtained from the high-temperature X-ray diffraction study of the oxidation of the nickel-base alloys B-1900, VIA, 713C, and 738X revealed complex oxide relations. Under all conditions at least five, and often seven, oxides were identified. Generalizing such behavior is a difficult task, but some things are clear.

The alloys, B-1900 and VIA, which have shown the best resistance to oxidation in other parts of this program have the greatest tendency to form Al_2O_3 and NiAl_2O_4 . These are also the alloys with the least Cr and highest Al. Conversely, 738X, the alloy that had the least oxidation resistance, formed the most Cr_2O_3 and NiCr_2O_4 . This alloy contained the least Al and most Cr and Ti. 713C, which had good oxidation resistance at 1000°C but less at 1100°C when compared with B-1900 and VIA, formed much Al_2O_3 isothermally at 1000°C but under cyclic conditions and at 1100°C tended to have oxidation products more like 738X. A general effect of cycling was to increase the amount of spinels formed.

While refractory metals and alloys are generally associated with poor oxidation resistance, the alloys with greater refractory metal content had better oxidation resistance. This does not necessarily imply that refractory metals improve the oxidation resistance of these alloys. It does mean that here high refractory metal contents did not impair oxidation resistance. This may be due in part to the formation of tapiolite, a nickel - refractory-metal oxide with the nominal formula of NiTa_2O_6 . This oxide apparently is able to substitute Nb, W, and Mo for the Ta and is therefore capable of tying up much of the refractory metals. Once formed, little seems to happen to this oxide with either time or cycling.

These were the main trends observed. While other oxides, especially NiO and NiTiO_3 , were present from time to time, their roles were apparently minor ones. Thus, the important alloying elements seem to be Cr, Al, and refractory metals. It is

probably their control that offers the best opportunity to change the oxidation process in these advanced nickel-base alloys.

Lewis Research Center,
National Aeronautics and Space Administration,
Cleveland, Ohio, March 14, 1973,
501-01.

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TABLE I. - SIMPLIFIED ALLOY COMPOSITIONS

[All values in weight percent.]

Alloy	Chromium	Aluminum	Refractory metals	Titanium
VIA	6	5.5	18	1
B-1900	8	6	10.5	1
713C	13	6	6.5	.75
738X	16	3.5	7	3.5

TABLE II. - CHEMICAL ANALYSES OF
ALLOYS INVESTIGATED

[All values in weight percent.]

Element	VIA	B-1900	713C	738X
Chromium	5.86	7.99	13.64	15.84
Cobalt	7.24	10.00	.53	8.81
Aluminum	5.27	6.18	6.00	3.57
Titanium	.95	1.11	.87	3.39
Tantalum	9.03	4.14	-----	1.68
Niobium	.45	<.05	-----	.85
Ta + Nb	----	-----	2.10	-----
Molybdenum	2.11	6.05	4.18	1.70
Tungsten	5.96	<.05	-----	2.78
Carbon	.11	.12	.13	.16
Zirconium	.10	.06	.10	.08
Boron	.021	.014	.009	.012
Iron	.08	<.10	.39	<.10
Rhenium	.32	-----	-----	-----
Hafnium	.39	-----	-----	-----
Copper	<.05	-----	<.10	<.08
Manganese	.02	<.02	<.05	<.02
Sulfur	.008	.007	.009	.006
Silicon	<.10	<.05	.17	<.05
Nickel	Bal.	Bal.	Bal.	Bal.

TABLE III. - RELATIVE X-RAY PATTERN STRENGTHS OF SPINELS FORMED DURING OXIDATION

[Key - NiAl_2O_4 ($a_0 = 8.05 \times 10^{-10}$ m): undetermined formula ($a_0 = 8.10 \times 10^{-10}$ m): NiCr_2O_4 ($a_0 = 8.35 \times 10^{-10}$ m).]

Alloy	Isothermal				Cyclic			
	1000° C		1100° C		1000° C		1100° C	
	Start	End	Start	End	Start	End	Start	End
VIA	0:0:1	9:2:3	1:0:0	6:1:0	1:0:0	3:1:0	8:3:6	6:1:0
B-1900	3:0:1	9:1:3	4:3:3	19:3:2	2:2:1	30:0:1	1:1:0	3:1:0
713C	1:0:2	1:0:2	0:0:1	8:0:1	1:0:1	11:3:1	2:1:1	3:2:0
738X	1:0:1	5:0:4	1:0:0	0:0:1	2:0:3	0:1:5	1:0:1	1:2:2

TABLE IV. - RELATIVE STRENGTHS OF MAJOR OXIDE PATTERNS

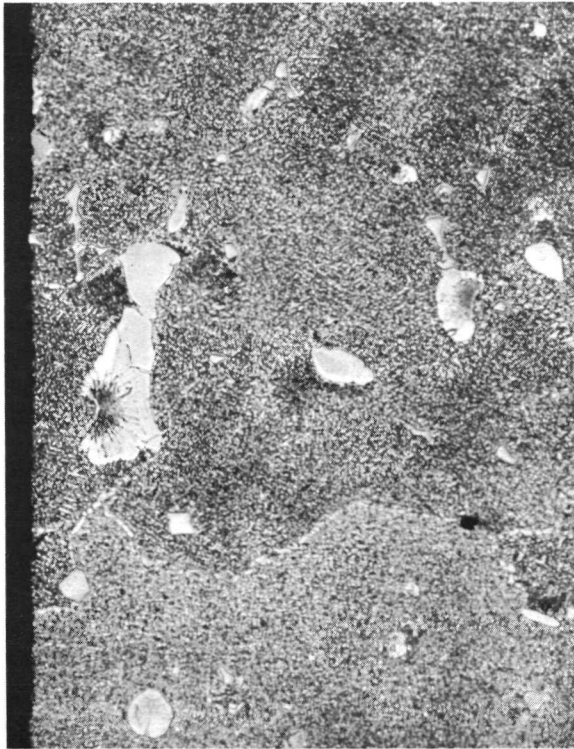
OBTAINED BY HIGH-TEMPERATURE X-RAY DIFFRACTION

AFTER 100 HOURS OF OXIDATION

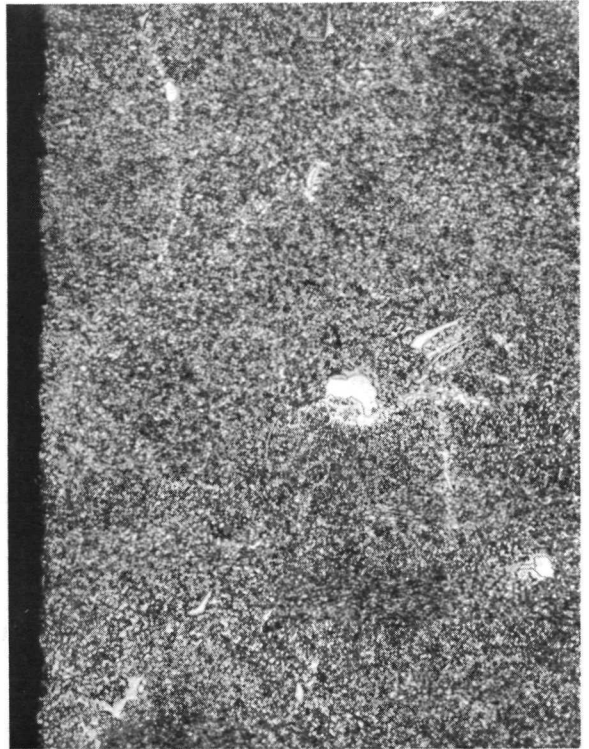
Alloys	Isothermal		Cyclic	
	1000° C	1100° C	1000° C	1100° C
VIA	Spinel - 10 Al_2O_3 - 4 $\text{Cr}_2\text{O}_3 < 1$ Tapiolite < 1	Spinel - 12 Al_2O_3 - 1 Tapiolite - 1 $\text{Cr}_2\text{O}_3 < 1$ $\text{NiO} < 1$	Spinel - 7 Al_2O_3 - 5 ZrO_2 - 3 Tapiolite - 1 $\text{Cr}_2\text{O}_3 < 1$	Spinel - 10 Al_2O_3 - 3 Tapiolite - 2 $\text{NiO} - 1$ $\text{Cr}_2\text{O}_3 < 1$
B-1900	Al_2O_3 - 6 Spinel - 6 Tapiolite < 1	Spinel - 22 Al_2O_3 - 5 Tapiolite - 1 $\text{NiO} < 1$	Spinel - 16 Al_2O_3 - 3 Tapiolite - 1 $\text{NiO} < 1$	Spinel - 20 Al_2O_3 - 2 Tapiolite - 1 $\text{NiO} < 1$
713C	Al_2O_3 - 8 Spinel - 2 Tapiolite < 1	Spinel - 24 Al_2O_3 - 3 Tapiolite - 1 $\text{NiO} - 1$ $\text{Cr}_2\text{O}_3 < 1$	Spinel - 14 Al_2O_3 - 3 $\text{NiO} < 1$ Tapiolite < 1 $\text{Cr}_2\text{O}_3 < 1$	Spinel - 23 $\text{NiO} - 2$ $\text{Al}_2\text{O}_3 - 1$ Tapiolite < 1 $\text{Cr}_2\text{O}_3 < 1$
738X	Al_2O_3 - 6 Spinel - 3 $\text{NiO} < 1$ Tapiolite < 1 $\text{Cr}_2\text{O}_3 < 1$	^a Spinel - 9 $\text{NiO} - 7$ $\text{NiTiO}_3 - 3$	Spinel - 10 $\text{Cr}_2\text{O}_3 - 2$ $\text{NiO} - 2$ Tapiolite - 1	^b Spinel - 4 $\text{NiO} - 3$ $\text{Cr}_2\text{O}_3 < 1$ Tapiolite < 1

^aNo Ni solid solution pattern; some oxide patterns may have been absorbed.

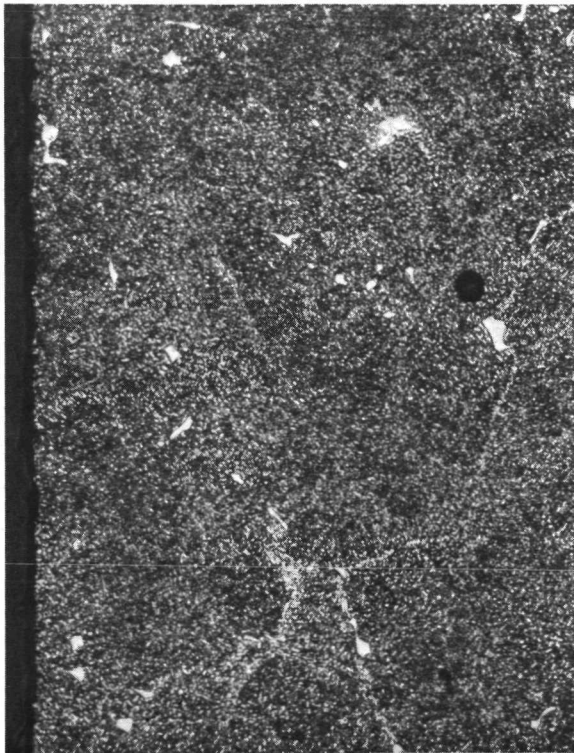
^bData at 44 hr. Test terminated because of excessive oxidation.



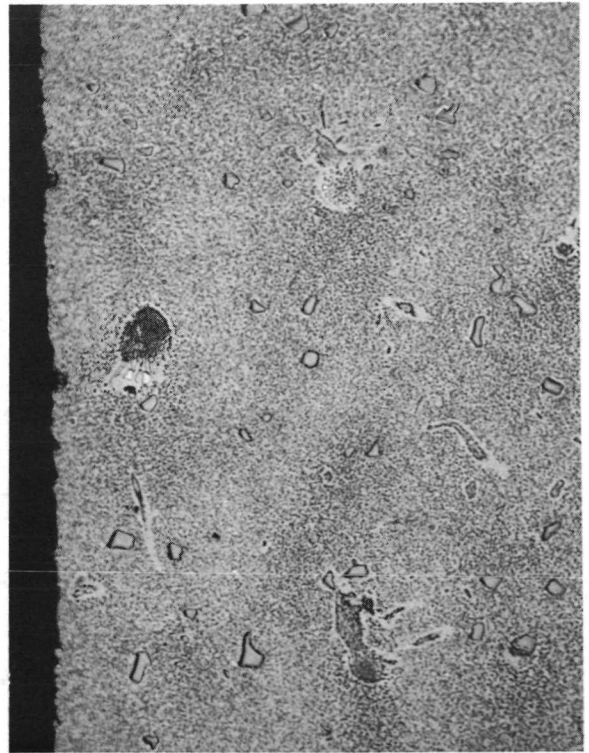
(a) Alloy VIA.



(b) Alloy B1900.



(c) Alloy 713C.



(d) Alloy 738X.

Figure 1. - As-cast microstructures of VIA, B1900, 713C and 738X. Etchant: 33 percent water, 33 percent nitric acid, 33 percent acetic acid, 1 percent hydrofluoric acid. X250.

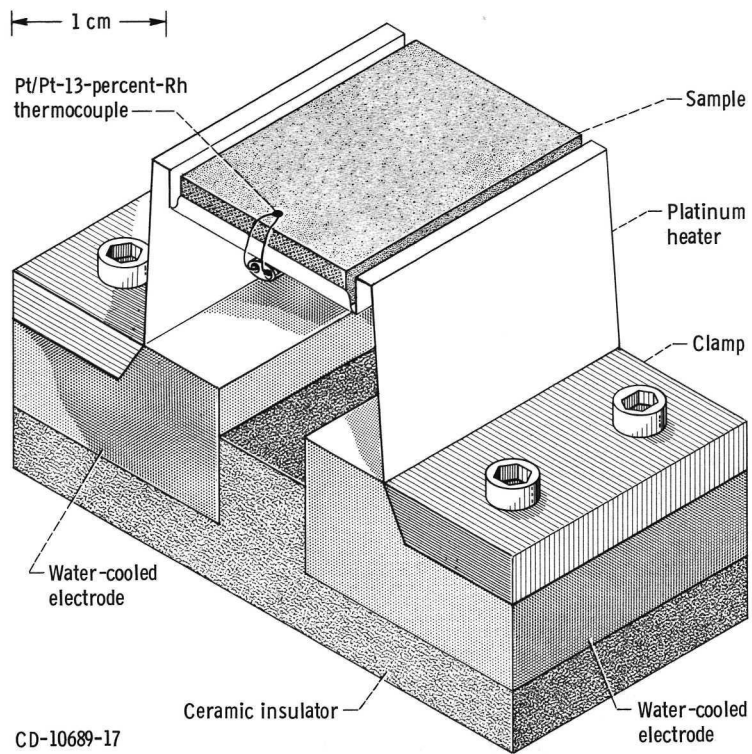


Figure 2. - Heater-sample arrangement for high-temperature X-ray diffraction studies.

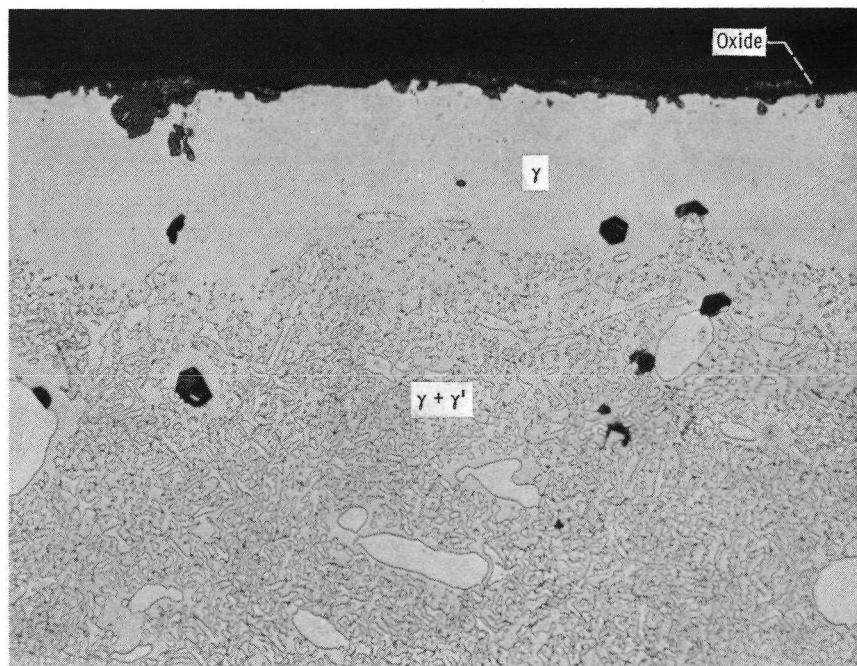


Figure 3. - Microstructure of oxidized VIA. Time, 100 hours; temperature, 1100° C. Etchant: 33 percent water, 33 percent nitric acid, 33 percent acetic acid, 1 percent hydrofluoric acid. X250.

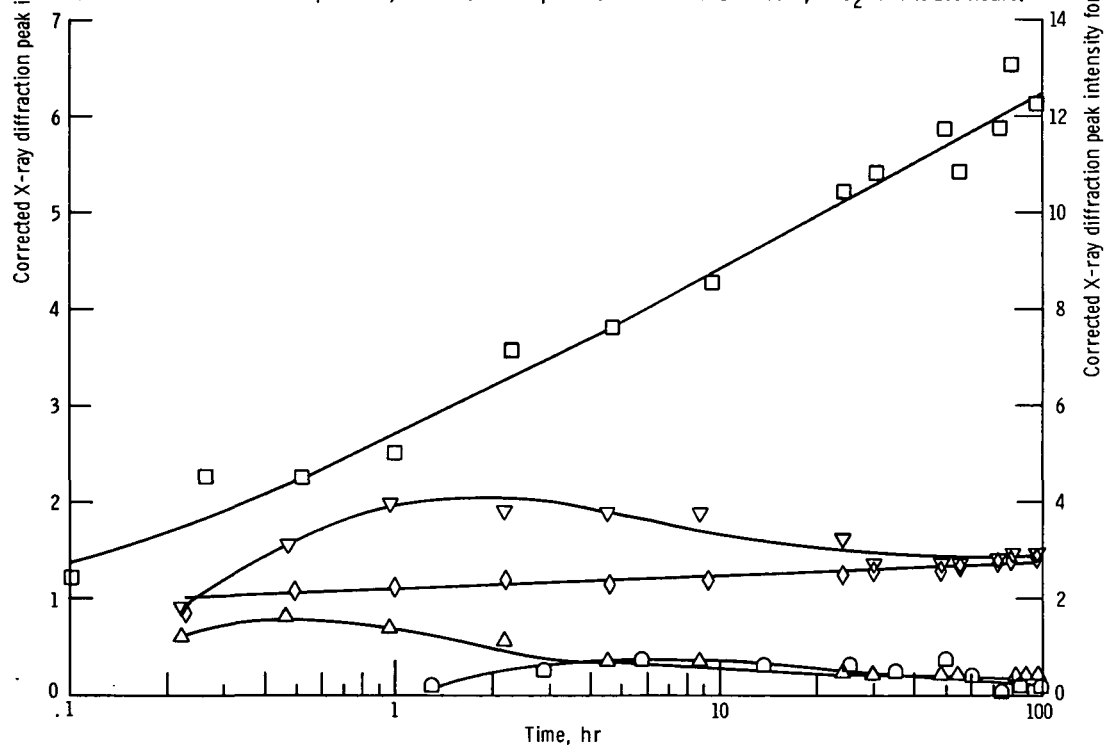
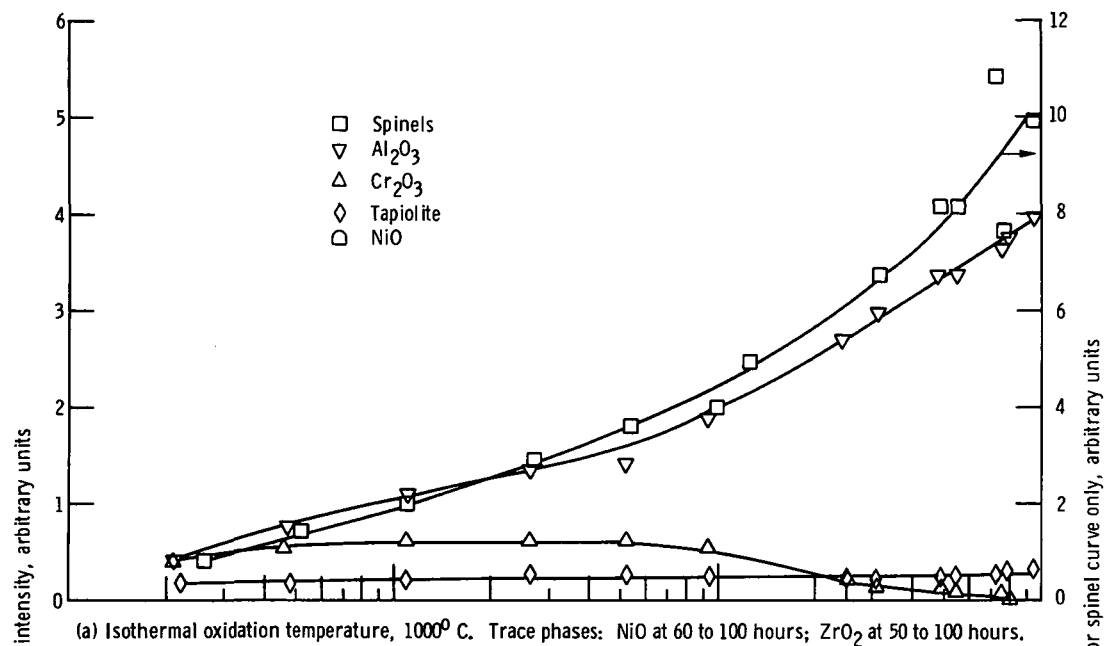


Figure 4. - Oxidation products formed on VIA. Spinel NiAl_2O_4 ($a_0 = 8.05 \times 10^{-10}$) predominant at end of tests.

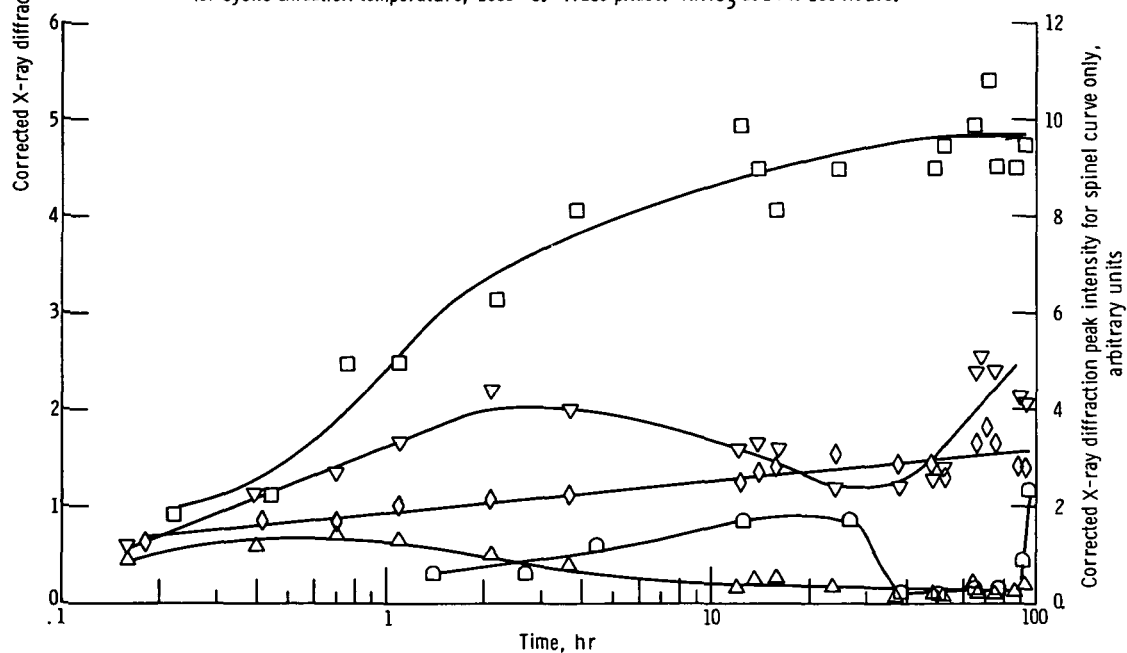
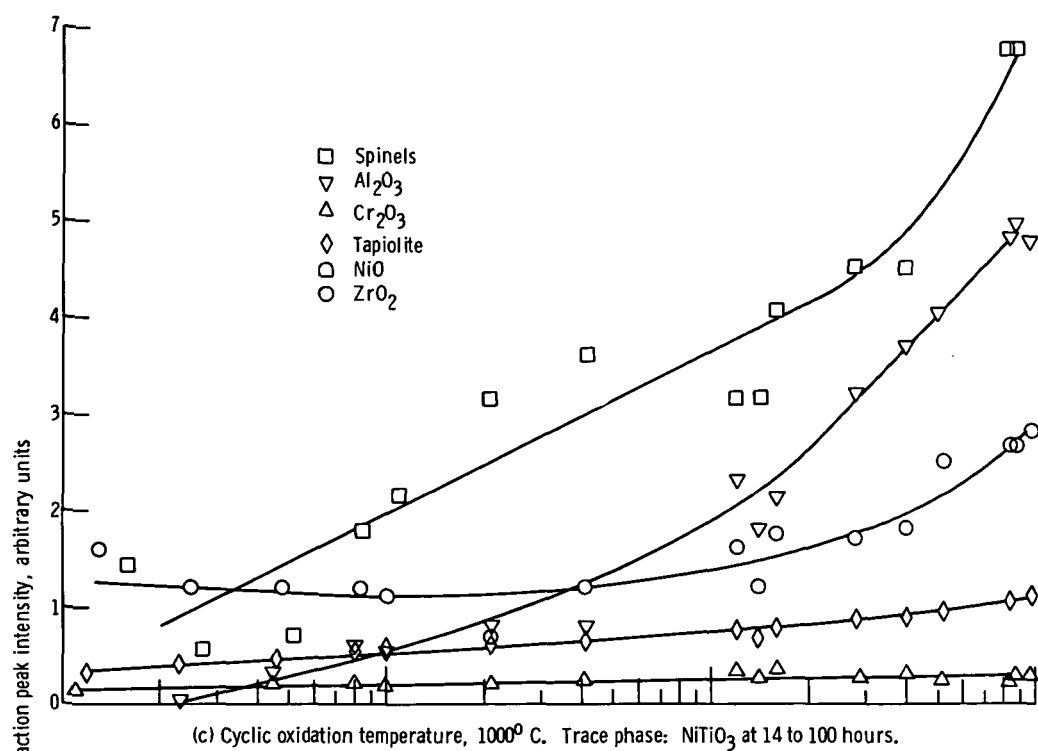
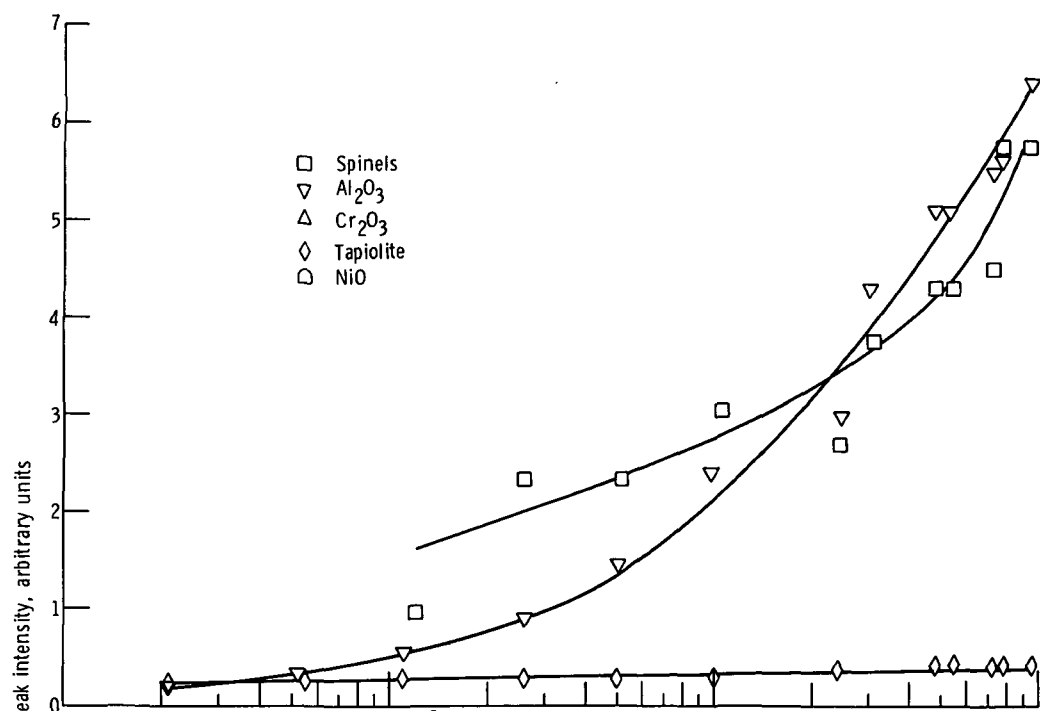
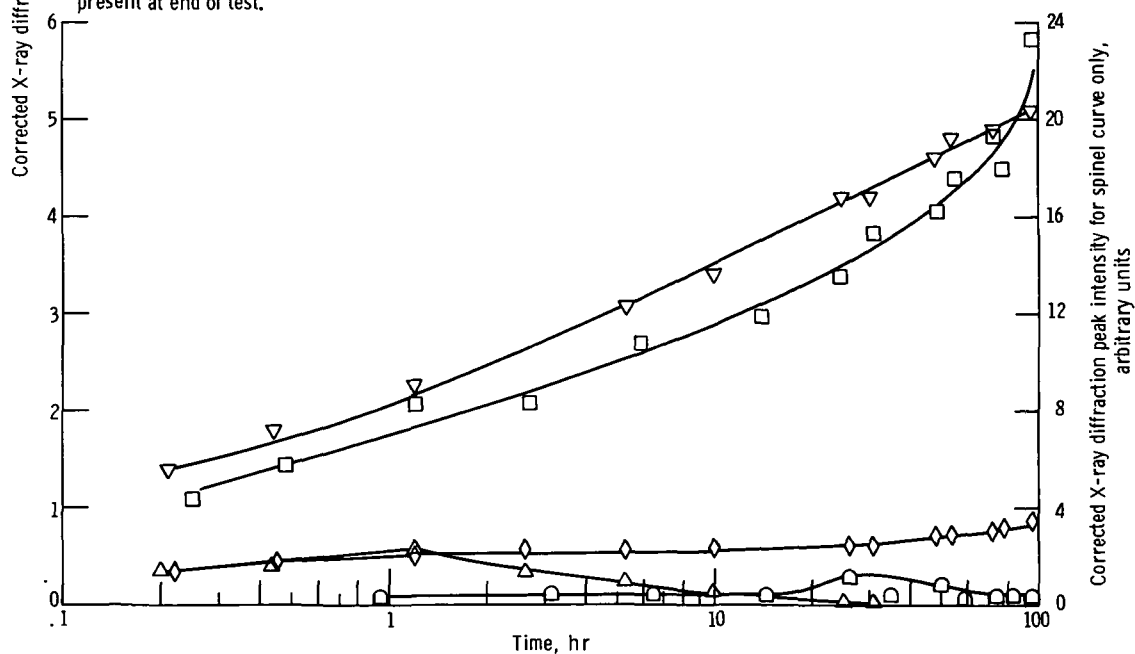


Figure 4. - Concluded.

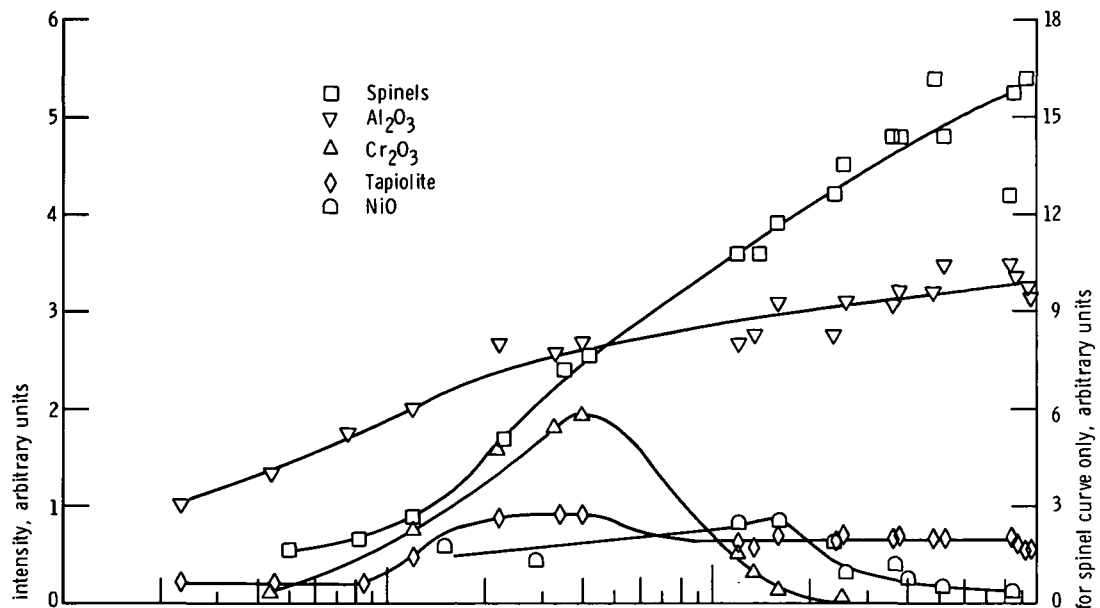


(a) Isothermal oxidation temperature, 1000°C . Trace phases: Cr_2O_3 at 0.1 to 5 hours; ZrO_2 at 0.1 to 100 hours. Spinel NiAl_2O_4 ($a_0 = 8.05 \times 10^{-10}\text{ m}$), intermediate ($a_0 = 8.20 \times 10^{-10}\text{ m}$), and NiCr_2O_4 ($a_0 = 8.35 \times 10^{-10}\text{ m}$) all present at end of test.

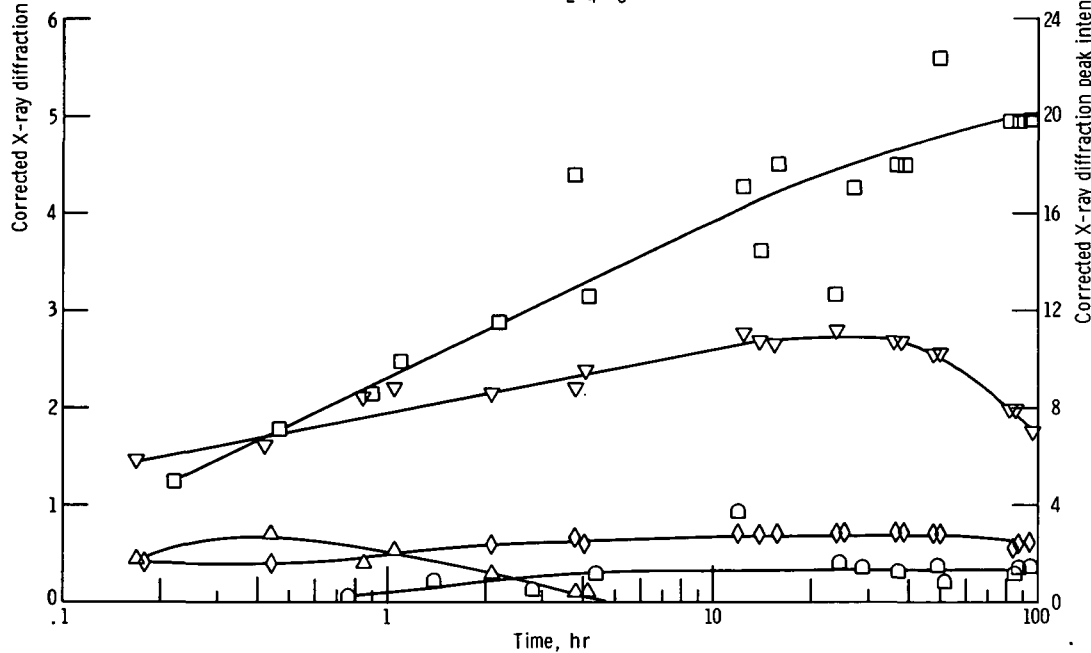


(b) Isothermal oxidation temperature, 1100°C . Spinel NiAl_2O_4 ($a_0 = 8.05 \times 10^{-10}\text{ m}$) predominant at end of test.

Figure 5. - Oxidation products formed on B1900.

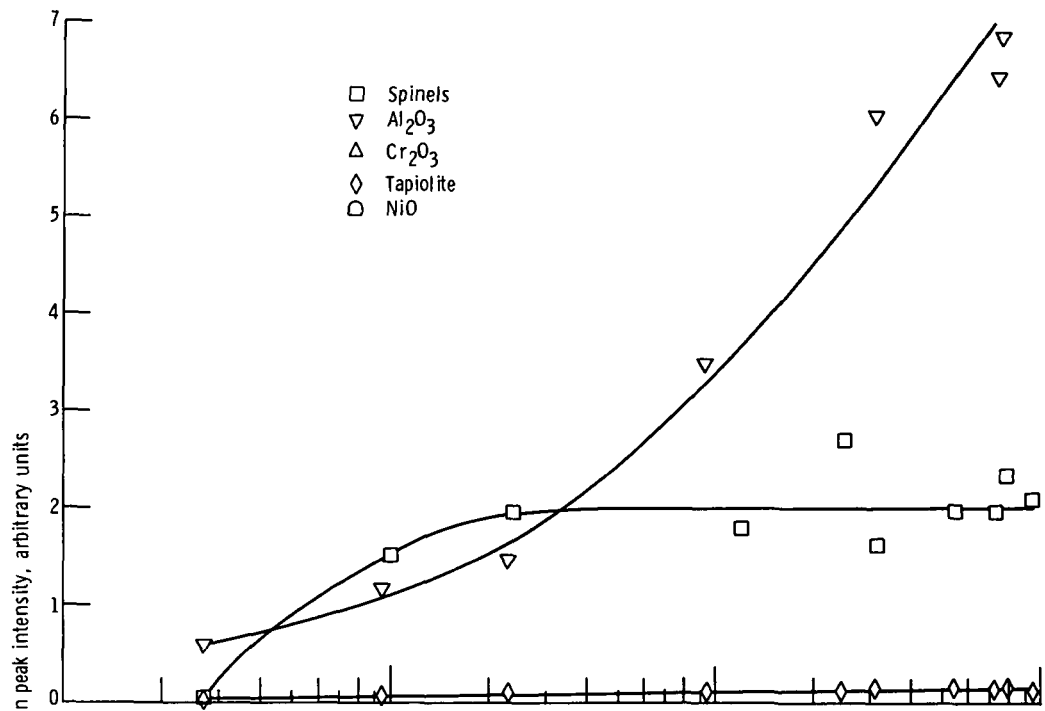


(c) Cyclic oxidation temperature, 1000° C. Spinel NiAl_2O_4 ($a_0 = 8.05 \times 10^{-10}$ m) predominant at end of test.

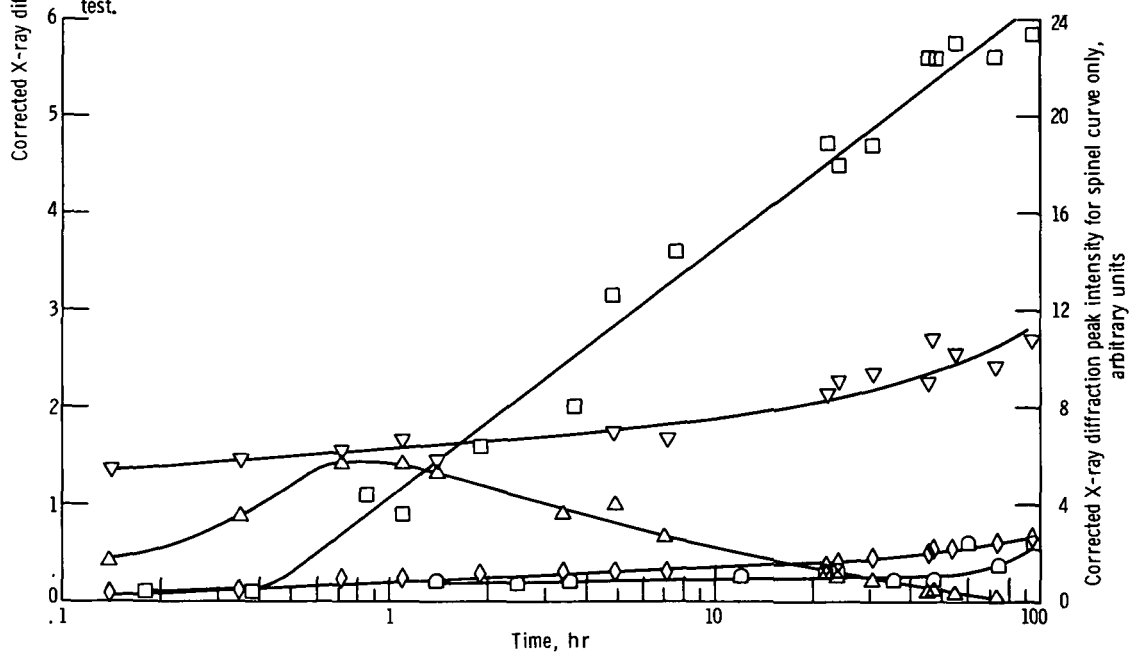


(d) Cyclic oxidation temperature, 1100° C. Spinel NiAl_2O_4 ($a_0 = 8.05 \times 10^{-10}$ m) predominant at end of test.

Figure 5. - Concluded.



(a) Isothermal oxidation temperature, 1000°C . Trace phases: Cr_2O_3 at 0.1 to 100 hours; NiTiO_3 at 70 to 80 hours; NiO at 80 to 100 hours. Spinel NiAl_2O_4 ($a_0 = 8.05 \times 10^{-10}\text{ m}$) and NiCr_2O_4 ($a_0 = 8.35 \times 10^{-10}\text{ m}$) presented at end of test.



(b) Isothermal oxidation temperature, 1100°C . Spinel NiAl_2O_4 ($a_0 = 8.05 \times 10^{-10}\text{ m}$) predominant at end of test.

Figure 6. - Oxidation products formed on 713C.

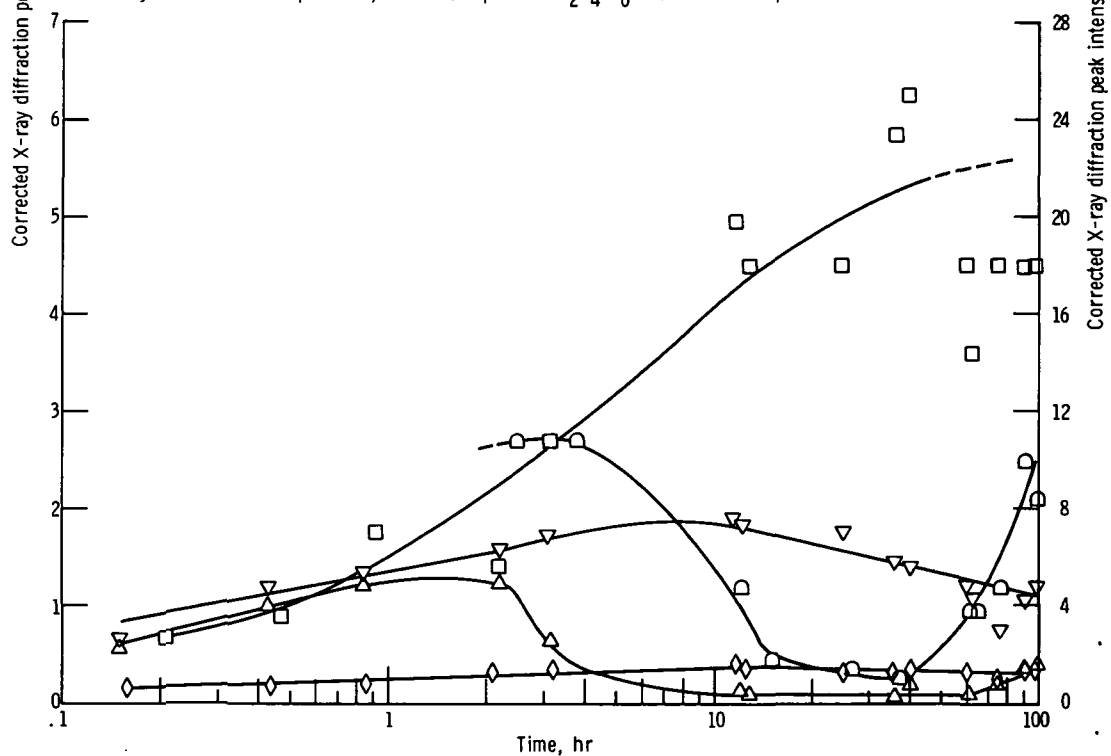
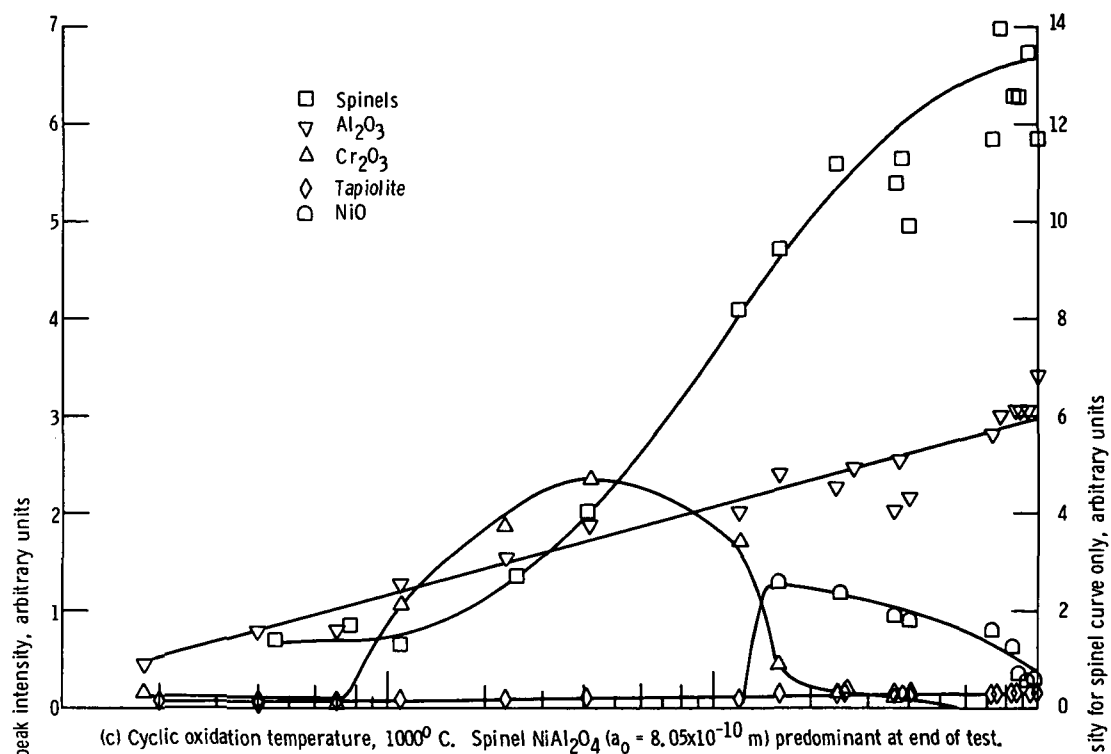


Figure 6. - Concluded.

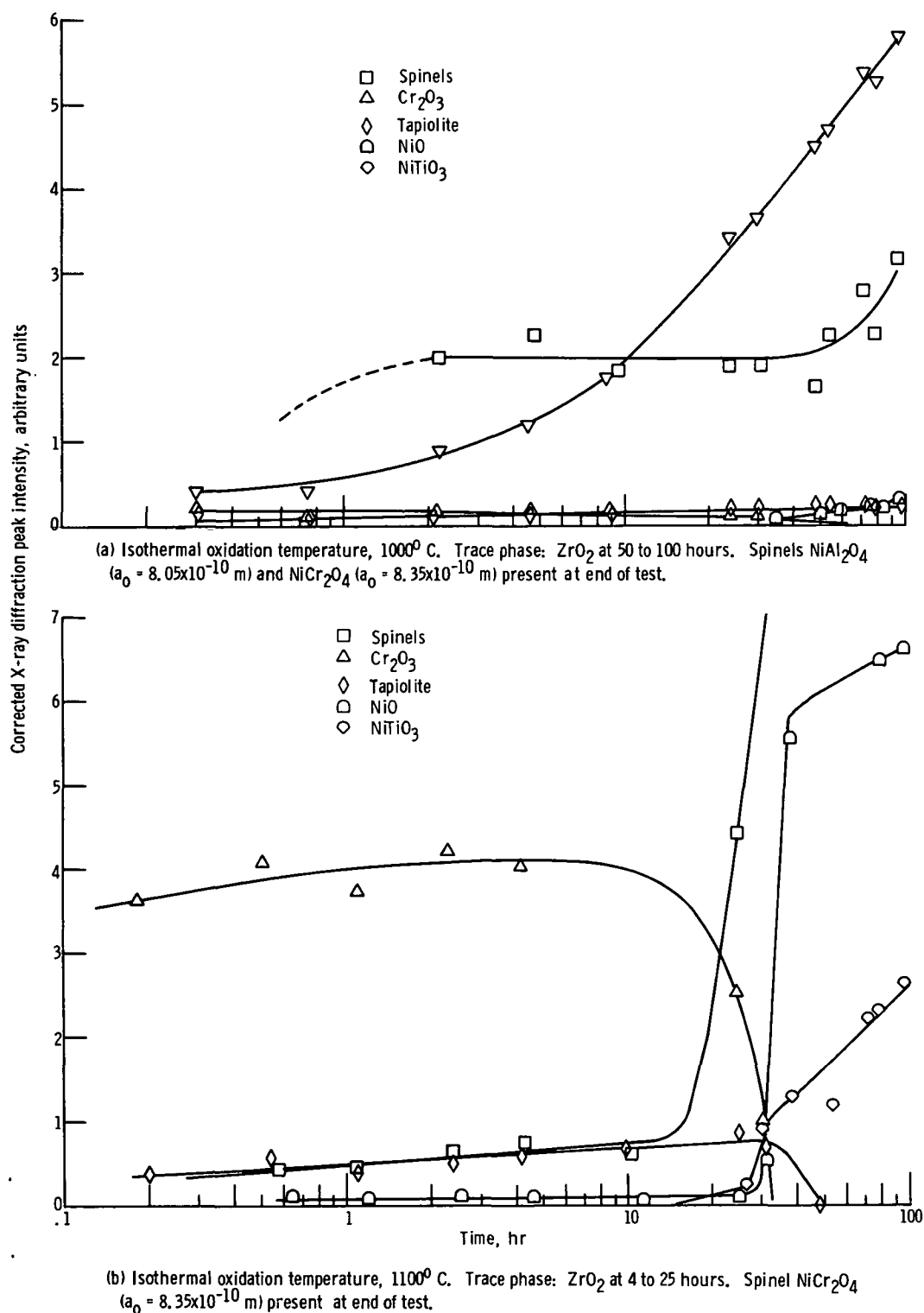


Figure 7. - Oxidation products formed on 738X.

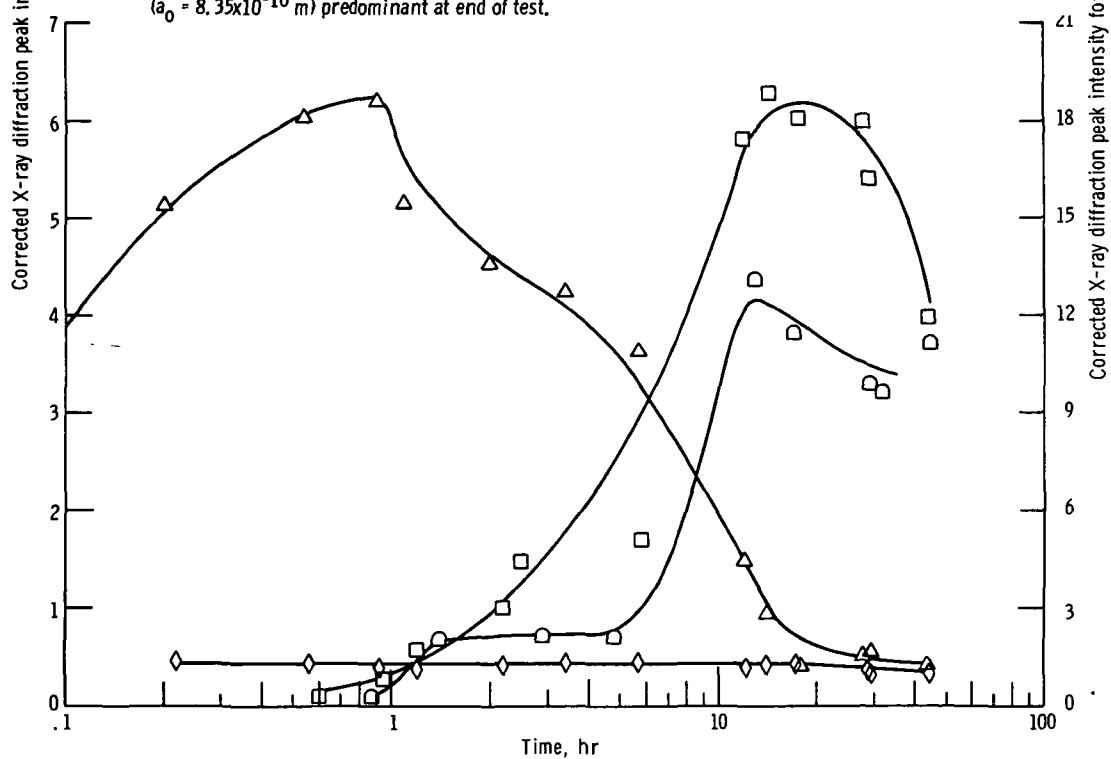
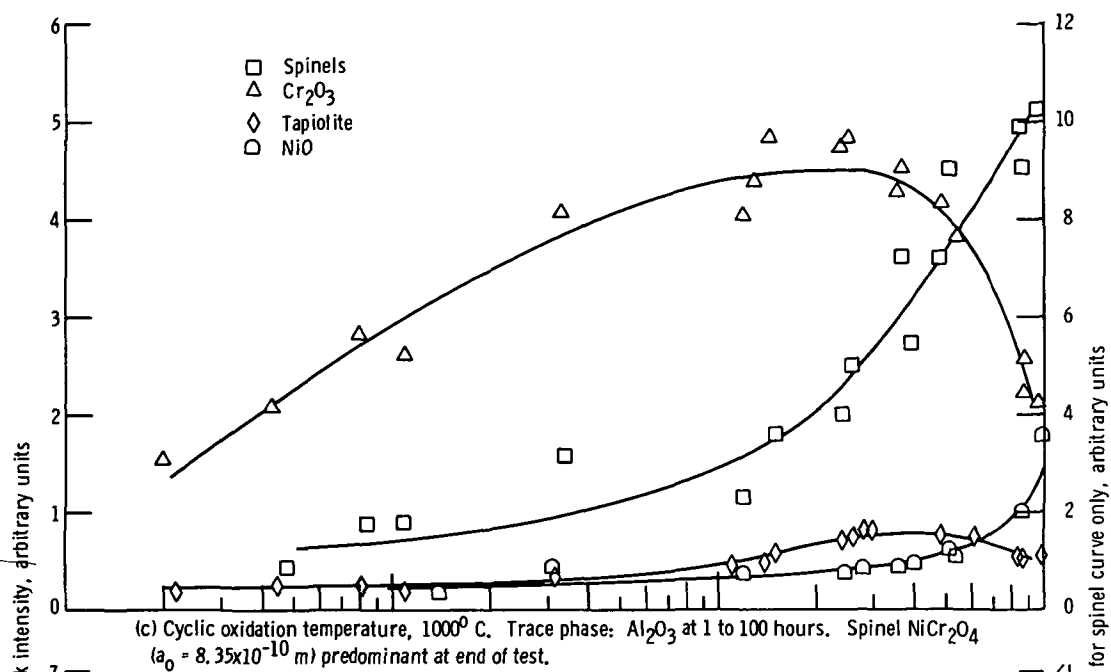


Figure 7. - Concluded.



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