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DYNAMIC OXIDATION BEHAVIOR AT 1000° AND 1100° C OF FOUR NICKEL-BASE CAST ALLOYS, NASA-TRW VIA, B-1900, 713C, AND 738X

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16. Abstract

The superalloys NASA-TRW VIA, B-1900, 713C, and 738X were tested cyclically and isothermally for resistance to oxidation in high velocity gas streams for 100 hours at specimen temperatures of 1000° and 1100° C. Alloys VIA and B-1900, which were the most oxidation resistant, displayed slight and very similar weight changes and metal losses. Alloy 713C also sustained only slight metal losses, but it exhibited some tendency to spall. Alloy 738X was found to be the most susceptible to cyclic oxidation; this resulted in heavy spalling, which in turn caused high weight losses and high metal losses. Oxidation test results are related to the amounts of chromium, aluminum, and the refractory metals in the alloys investigated.

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SUMMARY

Four nickel-base superalloys (NASA-TRW VIA, B-1900, 713C, and 738X) were selected to represent a range of chromium, aluminum, titanium, and refractory metal contents. These superalloys were evaluated for oxidation resistance in a high-gas-velocity burner rig operated in both cyclic and isothermal modes. Maximum exposure time was 100 hours, and specimens were tested at material temperatures of 1000° and 1100° C. Alloy evaluations and comparisons were based on weight change, metal loss, X-ray diffraction data, and specimen appearance and metallography. Alloys VIA and B-1900, both relatively low in chromium and high in aluminum content, were found to be most resistant to oxidation. These alloys displayed very similar behavior, slight weight changes, and slight metal losses whether exposed cyclically or isothermally at 1000° or 1100° C. On the basis of weight loss, alloy 713C, high in both chromium and aluminum content, was slightly less resistant to oxidation for both test modes. Metal losses for alloy 713C were slight and similar to those for alloys VIA and B-1900. Alloy 738X, higher in chromium content and lower in aluminum content than alloy 713C, displayed the poorest oxidation resistance. Weight losses and metal losses were very high for this alloy which was most severely affected by cyclic oxidation. For 738X, the 100-hour cyclic exposures at 1000° and 1100° C resulted in metal losses per side of 51 and 140 micrometers, respectively. No thermal fatigue cracking occurred in isothermal exposure, and only 738X developed a thermal fatigue crack at 1000° C during cyclic exposure. At 1100° C all four alloys developed thermal fatigue cracks during cyclic exposure.

INTRODUCTION

Efforts to improve nickel-base superalloys for gas turbine applications have been devoted primarily to the enhancement of the high temperature strength of these materials. Over the years the success of these efforts has been considerable. Improved stress-rupture/temperature capabilities for the nickel-base superalloys have resulted from increases in alloying additions of titanium, aluminum, and the refractory metals and accompanying reductions in chromium content (ref. 1). Although higher strengths have permitted increased use temperatures, the oxidation resistance of the nickel-base superalloys has not kept pace. We are faced with a need to impart the best possible inherent oxidation resistance to these superalloys and to apply protection systems to prevent excessive oxidation which can result from surface scaling, internal oxidation, oxide spalling, and oxide vaporization (ref. 2). As a result of these processes, the load-carrying capacity is reduced, the stress concentrations imposed reduce fatigue resistance, and oxide spalling and oxide vaporization result in increased oxidation rates.

To properly evaluate the oxidation resistance of a superalloy consideration must be given to the environmental test conditions (refs. 2 and 3). For example, results obtained for some superalloys under cyclic conditions at high gas velocities are far different than those obtained with the same materials tested isothermally (ref. 4). Even greater differences have been noted when comparing superalloy oxidation results from cyclic, high gas velocity environment tests against the results from static tests (ref. 4).

A program to study the oxidation behavior of some nickel-base superalloys which represent a range of alloy chemical composition was undertaken at the NASA Lewis Research Center. The four alloys studied were NASA-TRW VIA, B-1900, 713C, and 738X. These nickel-base superalloys offer some range in content of the elements chromium and aluminum which play a critical role in the oxidation of these alloys (refs. 2 and 5). In the overall program the four alloys were evaluated in cyclic and isothermal furnace tests and in high-gas-velocity burner rig tests for gas turbine engine environment simulation. The program was planned so that it would provide the following:

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

The results of this program are presented in separate NASA reports. These reports deal with

(1) Cyclic and isothermal static oxidation behavior (ref. 6)
(2) Identification of the oxides in the scales formed at temperature (ref. 7)
(3) Dynamic oxidation behavior (this report)

(4) A summary of the entire program and its implications for future efforts for further oxidation studies or for nickel-base superalloy chemistry modifications (ref. 8)

In this report dynamic oxidation evaluations were performed at 1000° and 1100° C for times up to 100 hours in a high-gas-velocity burner rig (ref. 4) in which the specimens were exposed to a Mach 1 stream of hot gas resulting from the combustion of Jet-A fuel. Tests were performed in both cyclic and isothermal modes for up to 100 hours. Although 100 hours is a relatively short exposure time when compared to aircraft gas turbine exposure lives, the 1000° and 1100° C test temperatures are higher than aircraft gas turbine operating temperatures for the uncoated alloys. It is felt that the relatively high test temperatures compensate for the relatively short test time, resulting in exposures sufficient to point up meaningful oxidation behavior differences due to alloy chemical compositions. At appropriate intervals during both modes of testing specimens were weighed, inspected for cracks and spalling, and photographed. Representative specimens were examined by X-ray diffraction and then sectioned for metallograpic examination and measurement of thickness change.

MATERIALS AND SPECIMEN PREPARATION

The chemical compositions of the nickel-base superalloys VIA, B-1900, 713C, and 738X are given in table I. An inspecition of the table shows the major compositional differences for the alloys to be in chromium, aluminum, titanium, and the refractory metals. In this comparison alloys VIA and B-1900 are relatively low in chromium and high in refractory metals, while alloys 713C and 738X are high in chromium and lower in refractory metals. Aluminum contents were very similar for VIA, B-1900, and 713C, but alloy 738X contained only slightly more than half as much aluminum.

Superalloy test specimens were vacuum cast to shape by a commercial source, and all specimens except those of alloy 713C were heat treated to turbine usage specification:

(1) Alloy VIA: heat for 32 hours at 900° C in argon, cool in argon.

(2) Alloy B-1900: heat for 4 hours at 1080° C in argon, cool in argon.

(3) Alloy 738X: heat for 2 hours at 1120° C in argon, cool in argon.

After the heat treatment, all the specimens, which were intentionally cast oversize, were ground to size with at least a 0.25-millimeter skin of cast surface removed. This was done to minimize any as-cast surface differences among the specimens. The final specimen shape is shown in figure 1. The tapered edges of the specimen are referred to as the leading edges in this report. After grinding, all the specimens were glass-bead blasted to a uniform matte surface. This was done to minimize ground surface differences.

The thickness (6.4 mm nominal dimension) of each specimen was measured at the center of the specimen hot zone which was in the metallographic sectioning plane (fig. 1). A bench micrometer with a precision of 1 micrometer was used for these measurements. All specimens were then degreased, ultrasonically cleaned in alcohol, dried with a hot air blower, weighed to ±0.2 milligram, and individually wrapped for storage until a test exposure.

APPARATUS AND TEST PROCEDURE

Figure 2 shows a photograph and a schematic representation of the high-gas-velocity oxidation apparatus used in this investigation and described in detail in reference 4. The Jet-A fueled burner rig was operated at combustion gas velocities of 800 and 850 meters per second. These velocities correspond to Mach 1 conditions for material temperatures of 1000° and 1100° C, respectively. Specimens of each alloy were rotated in the oxidizing gas stream with the tapered edges of the specimens closest to the nozzle. Two types of test modes were used, cyclic and isothermal:

(1) Cyclic - 1 hour at temperature followed by a Mach 1 forced-air cooling to room temperature in 3 minutes

(2) Isothermal - repeated 12-hour average heating periods at temperature followed by still-air cooling to room temperature at the end of each period

Four specimens, one of each alloy, were run cyclically and isothermally for total exposure times of 8, 24, 48, 72, and 100 hours. Temperatures were measured using a slip-ring thermocouple arrangement connected to a spare specimen in the rotating fixture and were controlled by means of a stationary control thermocouple downstream of the test specimens. Temperature measurement and checks were also made with a calibrated optical pyrometer. Specimen temperatures were maintained within $\pm 8^{\circ}$ C of the desired 1000° and 1100° C exposure temperatures.

After exposure the specimens were weighed, inspected for cracks and spalling, and photographed. Surface scales for an X-ray diffraction analysis were removed down to the bare metal substrate over an area of approximately 1 square centimeter from the 8- and 100-hour exposure specimen hot zone regions. A high-speed diamond deburring tool was used for the scale removal. All specimens were then sectioned as shown in figure 1 and metallographically polished and etched with a solution of water, nitric acid, acetic acid, and hydrofluoric acid (33:33:33:1 parts by volume ratio). Thickness measurements exclusive of oxide scales were made on the etched sections. The zone of microstructural alteration due to the depletion or enrichment of alloying elements, generally referred to as the gamma prime dissolution zone (ref. 9), was also measured. Five such measurements of both types were made with an optical micrometer having a precision of ±1 micrometer. Optical micrometer measurements of the section widths of untested specimens of each superalloy sectioned, metallographically polished and etched, agreed within ±1 micrometer with bench micrometer measurements made on these specimens before sectioning and without oxidation exposure.

RESULTS AND DISCUSSION

The four alloys were oxidized in a Mach 1 hot gas stream at specimen temperatures of 1000° and 1100° C in both cyclic and isothermal modes for times up to 100 hours. Alloy oxidation behavior was judged by weight change, specimen appearance, X-ray diffraction, metal thickness loss, and metallography. Results are presented and discussed in that order.

Weight Change

In the following discussion on weight change no mention is made regarding the important role of vaporization of oxides such as chromium oxide (Cr_2O_3) (ref. 2). The X-ray results discussed in a subsequent section are such that positive statements regarding the consistent presence of Cr_2O_3 are not possible. However, based on the alloy classification of Goward (ref. 5), whereby all four alloys are considered to be alumina formers, Cr_2O_3 (although not forming initially) is likely to form at some point in time during the oxidation of 713C and 738X. With regard to the elements nickel, chromium, and aluminum, the classification by Goward (ref. 5) indicates that 738X would be the first to form Cr_2O_3 followed later by the formation of Cr_2O_3 on 713C. Therefore, it is possible that Cr_2O_3 vaporization could account for some of the 738X and 713C weight losses to be discussed and which are attributed to oxide spalling.

The specific weight change data recorded for the specimens receiving 100-hour exposures (cyclic and isothermal) at 1000° and 1100° C are plotted in figures 3 to 6. Weight change data points for specimens exposed for less than 100 hours are not plotted but fall near the curves established by the 100-hour exposure specimens. Table II summarizes the cumulative specific weight changes after a 100-hour total exposure. For computing specific weight change, the weight change measurements were divided by an area of 30 square centimeters, the estimated area of the specimen over which most of the oxidation occurred.

Alloys VIA and B-1900 were very similar in their cyclic and isothermal oxidation behavior at 1000° C as indicated in figures 3 and 4 and table II. Both alloys showed very similar low weight gains over the entire 100-hour exposure; this indicates the formation of a protective scale with oxidation behavior essentially the same for both exposure modes. In contrast to alloys VIA and B-1900, alloys 713C and 738X both lost weight continuously over the 100-hour exposures with the weight losses for 738X being the greater. Although the final 100-hour weight losses for cyclic and isothermal exposures given in table II were very similar for alloys 713C and 738X, some short-time effect of test mode is evident when comparing the slopes of the curves for the cyclic and isothermal exposures in figures 3 and 4. In figures 3 and 4 the greater weight loss rates for the cyclic exposures over the isothermal exposures for at least the first 40 hours of exposure are evident. This comparison reflects the susceptibility of these alloys to spalling as a result of cycling (visual evidence presented in the next section). However, this effect diminishes beyond 40 hours of exposure as shown in figures 3 and 4, and by 100 hours the weight losses for cyclic and isothermal exposure were very similar. This behavior suggests that possibly in isothermal oxidation the oxide layer which developed in about the first 40 hours of exposure has reached a critical thickness for spalling to occur. This behavior may be due to differences in thermal expansion and mechanical properties of the phases in the oxide layer and the underlying alloy. Once spalling has occurred at about 40 hours, further spalling of alloys 713C and 738X would then be dependent on the condition of the spalled surface and the subsequent 12-hour average isothermal exposures.

At 1100° C alloys VIA and B-1900 were again very similar in their oxidation behavior in both test modes as shown in figures 5 and 6. However, at 1100° C slight but increasing weight losses with increasing exposure times were the case in contrast to the weight gains experienced at 1000° C. The somewhat greater weight losses at 1100° C given in table II for VIA and B-1900 for cyclic exposure over isothermal exposure may reflect some slight tendency for the occurrence of spalling under cyclic conditions. The lower weight loss for alloy B-1900 in comparison to VIA indicates that B-1900 may be slightly more resistant to oxidation at 1100° C than is VIA.

In a previous work (ref. 4) alloy B-1900 displayed weight losses over three times as great as those measured in the present study. Conditions were essentially the same for both studies. The differences in weight losses are believed to reflect differences in heat compositions, as-cast against ground surfaces, and the occurrence of multiple cracking of the B-1900 specimens (ref. 4). Exposed crack surfaces have been noted to be more susceptible to oxidation than major sample surfaces. In the present study B-1900 cracked in cyclic exposure at 1100° C but only one crack resulted.

As at 1000° C alloys 713C and 738X lost weight continuously during the 1100° C exposures as shown in figures 5 and 6. The 100-hour weight losses given in table II show 713C to be less resistant to oxidation than VIA and B-1900 and insensitive to test mode. The fact that the 713C isothermal weight loss at 100 hours was greater than the cyclic weight loss is thought to be fortuitous and to reflect the nonuniformity in the spalling observed for 713C - spalling being inherently a nonuniform process. The oxidation behavior of 738X at 1100° C was by far the poorest of the alloys tested. Weight loss rates were much greater than for the other alloys as can be seen in figures 5 and 6. Note here that the specific weight change scales for figures 5 and 6 have been compressed in comparison to figures 3 and 4 and that the scale for figure 5 is broken to accommodate the high specific weight loss of 738X. The 100-hour weight losses for 738X given in table II were very high and show the susceptibility of the alloy to spalling as a result of cycling. The cyclic weight loss sustained by 738X was three times the weight loss resulting from isothermal exposure.

Specimen Appearance

Figure 7 shows specimens of alloys 713C and 738X after 48 hours of cyclic and isothermal exposure at 1000° C. This figure typifies the difference in appearance (due to spalling) which persisted between specimens exposed cyclically and isothermally for times up to 48 hours. Beyond 48 hours of exposure the spalling behavior was such that no difference in specimen appearance was evident; however, spalling was heavier for 738X than for 713C. This observation, which was referred to in the previous section on weight gain, correlates with the observed short-time effect of test mode evidenced by differences in weight loss rates for the two exposure modes. The greater weight loss rates for at least the first 40 hours of cyclic exposure for 713C and 738X (738X having the greater weight loss rate) correspond with the observed degrees of spalling.

Figures 8 and 9 show the specimens as they appeared after 100 hours of cyclic exposure at 1000° and 1100° C, respectively. Specimen appearance after isothermal exposure at both temperatures was very similar and therefore is not shown. Figure 8 shows that after 100 hours of cyclic exposure at 1000° C alloys VIA and B-1900 were very similar in appearance with smooth surfaces indicating very little if any spalling. The surfaces for alloys 713C and 738X were rough with obvious indications of spalling - alloy 738X showing the greater spall tendency. In addition, for alloy 738X at 1000° C, a barely visible thermal fatigue crack in the leading edge of the specimen was noted at the 84-hour exposure point. This was the only incidence of thermal fatigue cracking noted for any specimen exposed at 1000° C. However, in a previous study (ref. 4) the B-1900 tested at 982° C in the cyclic burner rig developed thermal fatigue cracks in only 40 cycles. In this study B-1900 did not crack in 100 cycles. The difference in behavior may be due to differences in the shape of the leading edges of the burner rig specimens run in the two studies. In the reference 4 study the burner rig specimens were tested in the as-cast condition with leading edges having a sharp radius. In this study the grinding operations performed on all burner rig specimens to reach final test dimensions sometimes resulted in more rounded leading edges. The resulting blunting at the leading edges would tend to make the specimens more resistant to thermal shock.

At 1100° C slight spalling was observed for both alloys VIA and B-1900 as shown in figure 9. In the cyclic mode, both alloys suffered leading edge thermal fatigue cracks. These cracks which were apparent for VIA after 100 hours were apparent for B-1900 after only 24 hours. For the 713C and 738X alloys spalling was heavier than for VIA and B-1900 as indicated in figure 9 by the darker appearances of 713C and 738X when compared to VIA and B-1900. Alloy 738X was the darkest and spalled the most. Although the appearance of the isothermally exposed specimens was very similar to the appearance of the cyclically exposed specimens in the photographs, and therefore not shown, a visual inspection of the specimens indicated much greater spalling for the cyclically exposed 738X over the isothermally exposed 738X. Both 713C and 738X developed leading edge thermal fatigue cracks during cyclic exposure only at 1100° C. For 713C a crack was first noted after 56 hours, but for 738X a crack had developed by 24 hours.

X-Ray Diffraction

The results of the X-ray diffraction analyses of the oxide scales removed from the hot zone specimen surfaces after 8- and 100-hour cyclic and isothermal exposures at 1000° and 1100° C were all very similar. The 32 analyses are tabulated in table III for the four alloys and all the test conditions. In the majority of the analyses only nickel solid solution (NiSS) and/or a phase whose diffraction pattern corresponded to the ASTM card for the mineral tapiolite were detected in the oxide scales removed. The ASTM card for this mineral gives the formula $(Fe,Mn)(Ta,Nb)_2O_6$. 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 the ASTM card for tapiolite. What is called tipiolite in this report is probably $(Ni,Co,Cr)(Ta,Nb,W,Mo)_2O_6$ as was concluded in the high temperature diffractometer study on the oxidation products of VIA, B-1900, 713C and 738X (ref. 7). Weak indications of aluminum oxide (Al_2O_3) were noted for B-1900 after 100 hours of isothermal exposure at 1100° C, and Al_2O_3 was also noted for 713C at 8 and 100 hours of cyclic exposure at 1000° C. Weak indications of Cr_2O_3 were noted only for 738X at 8 and 100 hours of cyclic exposure at 1000° C. General inspection of the X-ray results in table III do not disclose any consistent trends for the presence or relative intensity of a particular oxide dependent on exposure time, exposure temperature, or test mode. The frequent presence of tapiolite, however, indicates that this oxide forms readily and is found in the ground-off scale even on specimens where spalling took place. This result suggests that tapiolite is closely associated with the metal substrate - the nickel solution phase always being present as a major phase.

All four of the alloys tested can be considered to be in the class of alloys termed "precipitation strengthened" Ni-Cr-Al-Ti alloys (ref. 2). The evaluation of such alloys is discussed in reference 1. These alloys fall in the category of "alumina formers" as classified by Goward in reference 5 where the combined effect of aluminum and chromium was taken into consideration. The general lack of Al_2O_3 in the ground-off scales is believed due to the occurrence of spalling (even in the case of isothermal exposure where periodic shutdowns are necessary) and the method of scale removal wherein the metal substrate becomes a major portion of the scale sample. Thus, we feel that in actuality thin Al_2O_3 scales form on all four alloys but are almost entirely lost due to spalling or diluted to nondetectability by the preponderance of nickel solid solution in the collected scale. Also, it should be pointed out here that the inherent strength of the Al_2O_3 X-ray pattern is much less than the X-ray patterns for nickel solid solution or tapiolite. Of course, as aluminum depletion occurs at the alloy surface, less protective oxides such as Cr_2O_3 and NiO form. This is the case for 738X which has the lowest aluminum content.

Metallography and Metal Loss

The microstructures of alloys VIA and B-1900 and of 713C and 738X in the as-received condition and after cyclic exposures of 100 hours at 1000° and 1100° C are shown in figures 10 and 11, respectively. Only the microstructures for the cyclically exposed specimens are shown since with only one exception these microstructures are representative of the microstructures of isothermally exposed samples. This exception is discussed later in this section. Table IV lists the metal losses per side and the gamma prime dissolution depths (hereinafter referred to as depletion depths) for the four alloys for 100-hour cyclic and isothermal exposures at 1000° and 1100° C. As stated in the APPARATUS AND TEST PROCEDURE section, five measurements for metal loss and five measurements for depletion depth were made for each specimen. When comparing the after-test thickness of a specimen (average of five optical micrometer measurements) with the initial thickness of the specimen (measured by bench micrometer) the range for the five measurements must be taken into account when assessing the loss of specimen thickness (metal loss). As a result of test exposures, specimen surfaces are irregular to the extent that the range for the five optical micrometer measurements made on a specimen quite often exceeded the magnitude of the decrease in specimen thickness found by subtracting the average of the five measurements from the initial bench micrometer measurement. Although metal loss will be specifically discussed for each alloy in this section, it is well to state now that with the previous measurement particulars in mind the metal losses for alloys VIA, B-1900, and 713C are considered to be real but very slight. However, metal losses for alloy 738X are more appreciable.

Figure 10 shows the microstructure of the VIA and B-1900 alloys as-received and after cyclic exposure at 1000° and 1100° C. Few microstructural changes were evident for VIA and B-1900 after the 1000° C cyclic exposure. The surface of both alloys remained fairly smooth with a very thin discontinuous oxide layer. Table IV shows the metal losses and depletion depths for alloys VIA and B-1900 to be independent of exposure mode and very similar to one another. These metal losses of 2 to 8 micrometers are considered to be very slight particularly since the range for the five measurements on which the average values are based are of a similar magnitude.

For the 1100° C cyclic exposure the microstructures in figure 10 for VIA and B-1900 are again similar. The surfaces of both alloys are rougher than at 1000° C with the oxide present being somewhat thicker but discontinuous. Alloy VIA exhibited a somewhat rougher surface and a somewhat greater depletion depth than B-1900. Depletion depths at 1100° C for the two alloys were two to three times what was measured at 1000° C, but again they were independent of test mode. Below the depletion zone both alloys showed gamma prime coarsening to a similar degree. Metal loss was again very slight, in the 2 to 8 micrometer range.

For alloys 713C and 738X indications of oxidation and microstructural changes were more pronounced than for VIA and B-1900. The microstructures for 1000° C cyclic exposures for 713C and 738X shown in figure 11 indicate rougher surfaces, more continuous oxide scales, and the occurrence of internal oxidation. The region of internal oxidation consists of the upper portion of the depletion zone where the typical salt and pepper suboxide formation takes place. Depletion depths for 1000° C exposures given in table IV for 713C and 738X were considerably greater than the depletions for VIA and B-1900. The metal losses for cyclic and isothermal exposures for 713C were slight, and their similarity indicates insensitivity to test mode. However, for alloy 738X metal losses were appreciable: 51 micrometers for cyclic exposure and 29 micrometers for isothermal exposure. The greater metal loss for the cyclic exposure correlates with the observed heavier spalling for cyclic exposure in comparison to isothermal exposure.

The microstructures in figure 11 for 713C and 738X after a 1100° C cyclic exposure show less oxide scale than after a 1000° C cyclic exposure. This is thought to be due to the heavier spalling noted at 1100° C. This spalling was made particularly evident for alloy 738X where indications of internal oxidation noted at 1000° C were absent at 1100° C. This likely resulted from greater oxidation at 1100° C at the relatively unprotected alloy surface - an explanation supported by the higher 738X metal loss at 1100° C in comparison to 1000° C, 140 micrometers against 51 micrometers. As expected from the spalling observations, the metal loss for 738X exposed cyclically was much greater than the metal loss resulting from the isothermal exposure, 140 micrometers against 55 micrometers. Metal losses for 713C at 1100° C were slight.

An exception to the otherwise consistent microstructural similarities between cyclically and isothermally exposed specimens referred to at the beginning of this section was the case for alloy 738X at 1100° C. In this instance, the 100-hour depletion depth for isothermally exposed 738X was over twice the depletion depth of cyclically exposed 738X, 123 micrometers against 55 micrometers. This can be explained by considering the heavier spalling observed for cyclically exposed specimens in comparison to isothermally exposed specimens. As already stated, this spalling was reflected by a metal loss for a cyclic exposure of 140 micrometers and a metal loss for an isothermal exposure of 55 micrometers. Here the metal loss comparison for the two test modes is just the reverse of the depletion depth comparison; that is, the metal losses for the cyclic exposure are more than twice the metal losses for the isothermal exposure. The depletion depth for 738X is less in the case of cyclic testing since spalling removes any protective oxide and the depleted zone is consumed to a greater extent than in the isothermal test where spalling is not as severe and the depleted zone has some protection.

CONCLUDING REMARKS

In this report high gas velocity oxidation testing was accelerated by subjecting the test alloys to higher than normal use temperatures while limiting exposure times to 100 hours. Differences in oxidation behavior which relate to alloy chemistry were observed. Most resistant to oxidation were the low chromium, high aluminum alloys B-1900 and VIA. Of intermediate resistance was the higher chromium content alloy 713C which contained about the same amount of aluminum. Least oxidation resistant was alloy 738X, which was high in chromium and contained only about half as much aluminum as the other three alloys.

Alloys B-1900 and VIA are ranked together because of their very similar low weight changes, low metal losses, minimal spalling, and less drastic microstructural changes. Their similarity in behavior is not surprising since their chemical compositions are similar, particularly in regards to chromium and aluminum which play a critical role in the oxidation of these alloys. Alloy 713C, intermediate in oxidation resistance, falls closer to the behavior of B-1900 and VIA than it does to 738X. Weight changes for 713C reflect some tendency to spall, but metal losses were slight and very similar to those for B-1900 and VIA. Although generally dissimilar to alloys VIA and B-1900 in composition, the fairly good oxidation behavior of 713C is attributed to its 6 weight percent aluminum content, which is similar to that of B-1900 and VIA. The higher chromium content of 713C may result in some Cr_2O_3 formation and subsequent vaporization which would contribute to the higher weight losses observed.

Alloy 738X was by far the poorest in oxidation; it sustained great weight losses and metal thickness losses which correlated with the heavy spalling observed (Cr_2O_3 vaporization may also have played a part). The poor oxidation behavior of 738X is attributed primarily to its relatively low aluminum content.

As stated in the INTRODUCTION, this report is a portion of a program to study the oxidation behavior of four nickel-base superalloys which represent a range in chromium, aluminum, and refractory metal contents. Information regarding other facets of the oxidation behavior of these four nickel-base superalloys can be found in references 6 and 7 and the program summary report (ref. 8).

SUMMARY OF RESULTS

This investigation deals with the oxidation of four nickel-base superalloys for times up to 100 hours in a high gas velocity burner rig. The alloys NASA-TRW VIA, B-1900, 713C, and 738X were selected to represent a range of chemical composition with the major differences being in the contents of chromium, aluminum, titanium, and the refractory metals. Two types of test modes were used:

(1) Cyclic - 1 hour at temperature followed by a Mach 1 forced-air cooling to room temperature in 3 minutes

(2) Isothermal - repeated 10- to 12-hour average heating periods at temperature followed by still-air cooling to room temperature at the end of each period

Oxidation behavior of the superalloys was judged by weight change, specimen appearance, X-ray diffraction, metallography, and metal thickness loss. The following results were obtained:

1. At 1000° C thermal cycling had no effect on either the slight weight change or slight metal loss for the alloys relatively low in chromium and high in refractory metals (VIA and B-1900) and for the alloy higher in chromium and lower in refractory metals (713C). The aluminum content of these three alloys was similar. The alloy highest in chromium, lower in refractory metals than VIA and B-1900, and lowest in aluminum (738X) was more severely affected by thermal cycling (resulting in spalling) than by isothermal exposure. This was demonstrated mainly by an approximate doubling of metal loss to 51 micrometers per side in cyclic exposure in comparison to the metal loss sustained in isothermal exposure.

2. At 1100° C, although weight change magnitudes were greater than at 1000° C, alloys VIA, B-1900, and 713C again displayed an insensitivity to thermal cycling in regards to weight change and metal loss. However, again as at 1000° C the oxidation behavior of alloy 738X was sensitive to cycling (resulting in spalling) as shown by a threefold increase in weight loss and a more than doubled metal loss of 140 micrometers per side.

3. Thermal fatigue cracking in the 1000° C tests occurred only with 738X and only after 84 hours of cyclic exposure. However, in the 1100° C cyclic tests all four alloys

developed thermal fatigue cracks with 738X and B-1900 showing cracks at 24 cycles while 713C developed a crack after 56 cycles. Alloy VIA was most resistant to thermal fatigue cracking showing a crack only after a 100-hour exposure.

Lewis Research Center,
National Aeronautics and Space Administration,
Cleveland, Ohio, March 21, 1974,
501-01.

REFERENCES

1. Fawley, Robert W.: Superalloy Progress. Ch. I of The Superalloys - Vital High Temperature Gas Turbine Materials for Aerospace and Industrial Power, Chester T. Sims and William C. Hagel, eds., Wiley & Sons, 1972, pp. 3-29.
2. Wasielewski, Gerald E.; and Rapp, Robert A.: High Temperature Oxidation. Ch. 10 of The Superalloys - Vital High Temperature Gas Turbine Materials for Aerospace and Industrial Power, Chester T. Sims and William C. Hagel, eds., Wiley & Sons, 1972, pp. 287-316.
3. Probst, Hubert B.: Effect of Environment on Erosion-Corrosion Processes. Aerospace Structural Materials. NASA SP-227, 1970, pp. 279-293.
4. Johnston, James R.; and Ashbrook, Richard L.: Oxidation and Thermal Fatigue Cracking of Nickel- and Cobalt-Base Alloys in a High Velocity Gas Stream. NASA TN D-5376, 1969.
5. Goward, G. W.: Current Research on the Surface Protection of Superalloys for Gas Turbine Engines. J. Metals, vol. 22, no. 10, Oct. 1970, pp. 31-39.
6. Barrett, Charles A.; Santoro, Gilbert J.; and Lowell, Carl E.: Isothermal and Cyclic Oxidation at 1000° and 1100° C of Four Nickel-Base Alloys: NASA-TRW VIA, B-1900, 713C, and 738X. NASA TN D-7484, 1973.
7. Garlick, Ralph G.; and Lowell, Carl E.: Alloy Composition Effects on Oxidation Products of VIA, B-1900, 713C, and 738X - A High Temperature Diffractometer Study. NASA TM X-2796, 1973.
8. Lowell, Carl E.; and Probst, Hubert B.: Effects of Composition and Testing Conditions on Oxidation Behavior of Four Cast Commercial Nickel-Base Superalloys. NASA TN D-7705, 1974.
9. Wasielewski, Gerald E.: Nickel-Base Superalloy Oxidation. General Electric Co. (AFML-TR-67-30, AD-809831), Jan. 1967.

TABLE I. - CHEMICAL COMPOSITION[a] OF TEST MATERIALS

Element	Composition, wt %			
	Alloy			
	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
Aluminum + titanium	6.22	7.29	6.87	6.96
Boron	.021	.014	.009	.012
Zirconium	.10	.06	.10	.08
Carbon	.11	.12	.13	.16
Tantalum	9.03	4.14	------	1.68
Columbium	.45	<.05	------	.85
Columbium + tantalum	9.48	4.19	2.10	2.53
Molybdenum	2.11	6.05	4.18	1.70
Tungsten	5.96	<.05	------	2.78
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	Balance	Balance	Balance	Balance

[a] Vendor's master heat chemical analyses.

TABLE II. - SPECIFIC WEIGHT CHANGES AFTER 100 HOURS OF DYNAMIC CYCLIC AND ISOTHERMAL EXPOSURE AT 1000° AND 1100° C

[Cyclic - 1 hr at 1000° or 1100° C, 3-min forced - air cooling to room temperature; isothermal - average 12-hr heating periods at 1000° or 1100° C, still-air cooling to room temperature.]

Alloy	Exposure temperature, °C			
	1000		1100	
	Exposure			
	Cyclic	Isothermal	Cyclic	Isothermal
	Specific weight change, mg/cm^2			
VIA	0.67	0.34	-3.41	-2.74
B-1900	.66	.26	-1.97	-1.54
713C	-3.16	-4.61	-8.43	-9.48
738X	-13.4	-11.9	-115.6	-38.1

TABLE III. - PHASES DETERMINED BY X-RAY DIFFRACTION IN SCALES REMOVED FROM ALLOYS CYCLICALLY OR ISOTHERMALLY EXPOSED AT 1000° OR 1100° C IN DYNAMIC OXIDATION APPARATUS FOR 8 AND 100 HOURS

[Cyclic - 1 hr at 1000° or 1100° C, 3-min forced-air cooling to room temperature; isothermal - average 12-hr heating periods at 1000° or 1100° C, still-air cooling to room temperature.]

Alloy	Exposure temperature, °C							
	1000				1100			
	Exposure							
	Cyclic		Isothermal		Cyclic		Isothermal	
	Exposure time, hr							
	8	100	8	100	8	100	8	100
	Phases							
VIA	NiSS[a]-S[b]	NiSS-S	NiSS-S TAP[c]-W	NiSS-S TAP-VW	NiSS-S TAP-W	NiSS-S TAP-W	NiSS-S TAP-W	NiSS-S TAP-W NiO-VW
B-1900	NiSS-S	NiSS-S	NiSS-S TAP-VW	NiSS-S TAP-VW	NiSS-S TAP-VW	NiSS-S	NiSS-S TAP-W	NiSS-S Al_2O_3-VW
713C	NiSS-S Al_2O_3-VW	NiSS-S Al_2O_3-VW NiO-VW	NiSS-S	NiSS-S TAP-VW NiO-W	NiSS-S TiO_2-VW	NiSS-S	NiSS-S	NiSS-S NiO-VW
738X	NiSS-S Cr_2O_3-W	NiSS-S Cr_2O_3-W	NiSS-S TAP-W	NiSS-S TAP-VW	NiSS-S TAP-W NiO-VW	NiSS-S TAP-W NiO-M	NiSS-S TAP-W	NiSS-S TAP-W

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[a] Nickel solid solution.

[b] Strengths referred to diffractometer pattern strengths and not necessarily to oxide concentration: strong, S; medium, M; weak, W; very weak, VW.

[c] Tapiolite, $(Ni, Co, Cr)(Ta, Nb, W, Mo)_2O_6$.

TABLE IV. - METAL LOSS PER SIDE AND GAMMA PRIME DEPLETION DEPTH FOR ALLOYS CYCLICALLY OR ISOTHERMALLY EXPOSED AT 1000° OR 1100° C IN DYNAMIC OXIDATION APPARATUS FOR 100 HOURS

[Cyclic - 1 hr at 1000° or 1100° C, 3-min forced-air cooling to room temperature; isothermal - average 12-hr heating periods at 1000° or 1100° C, still-air cooling to room temperature.]

Alloy	Exposure temperature, °C							
	1000		1100		1000		1100	
	Exposure							
	Cyclic	Isothermal	Cyclic	Isotherma	Cyclic	Isothermal	Cyclic	Isothermal
	Metal loss per side, µm				Gamma prime depletion depth, µm			
VIA	2	3	2	8	10	8	24	30
B-1900	8	6	2	5	6	7	19	15
713C	9	15	3	4	51	48	49	39
738X	51	29	140	55	21	22	55	123

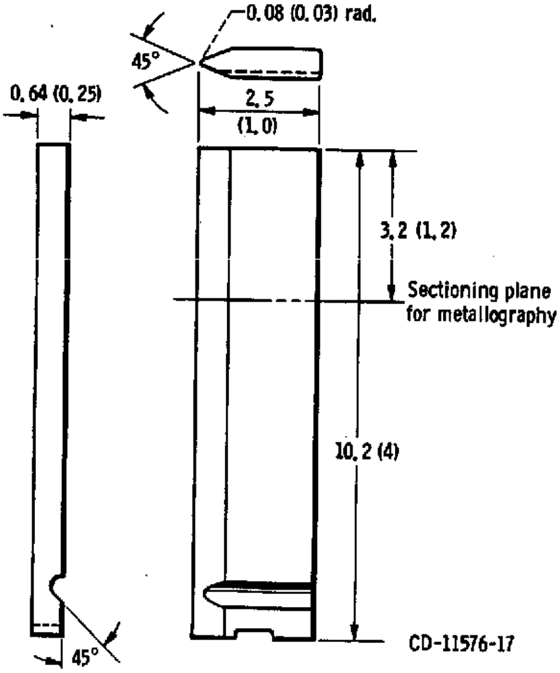
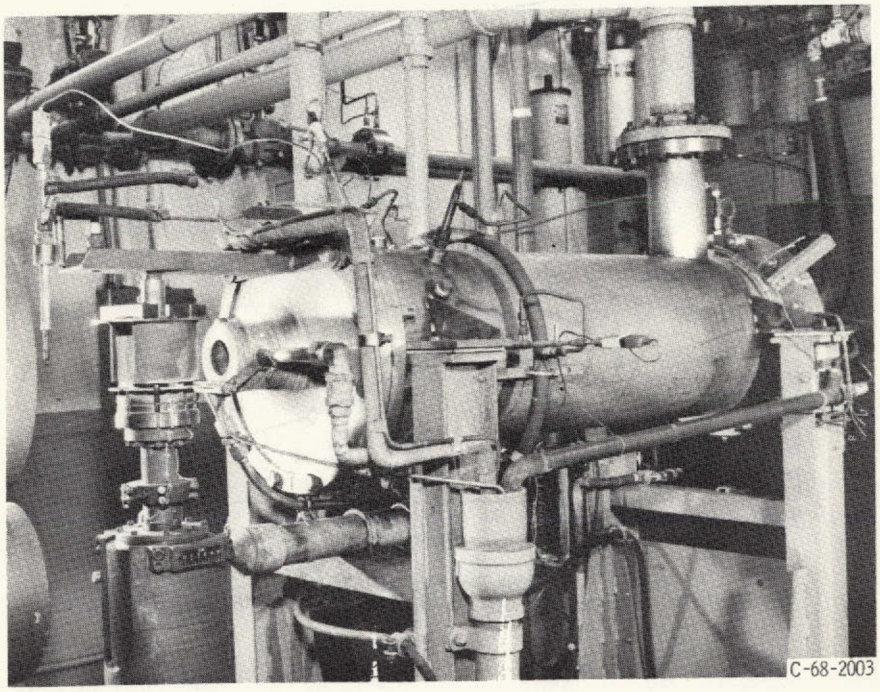
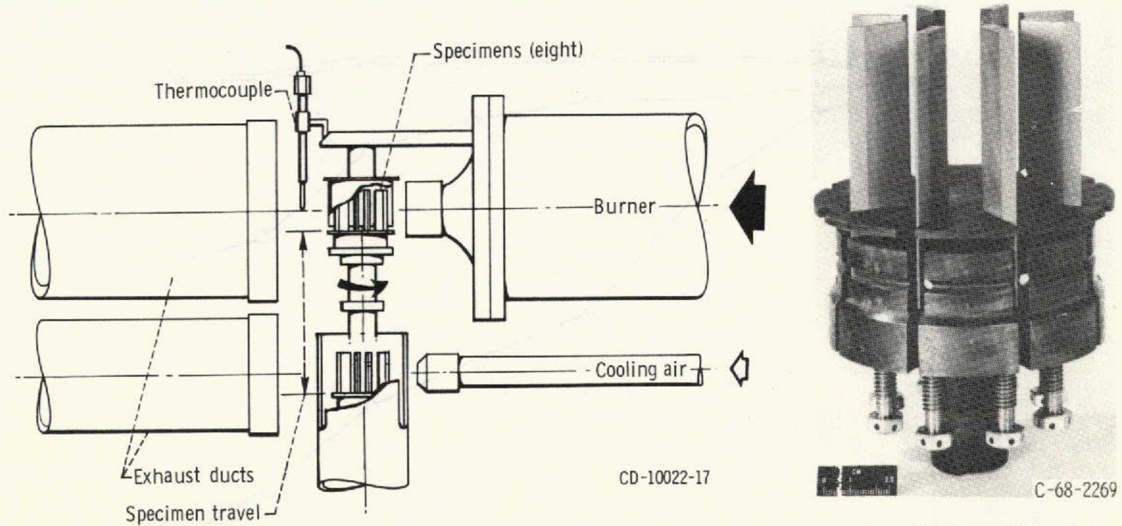


Figure 1. - Specimen used in dynamic oxidation tests. Dimensions are in centimeters (in.).



(a) Overall view.



(b) Schematic diagram.

(c) Specimen holder assembly.

Figure 2. - Dynamic oxidation apparatus.

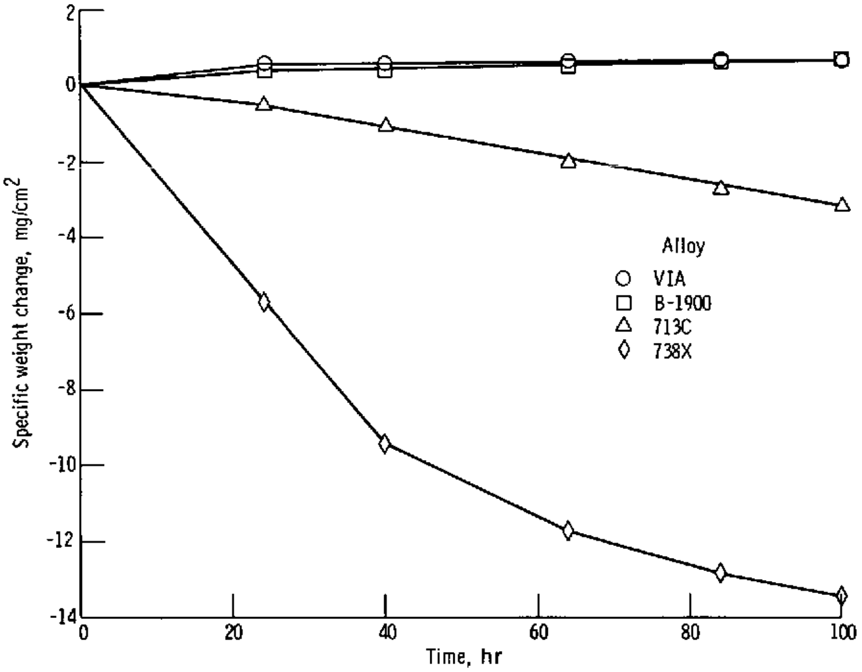


Figure 3. - Specific weight change of alloys resulting from cyclic exposure at 1000° C in dynamic oxidation apparatus. Cyclic: 1 hour at 1000° C, 3-minute forced-air cooling to room temperature.

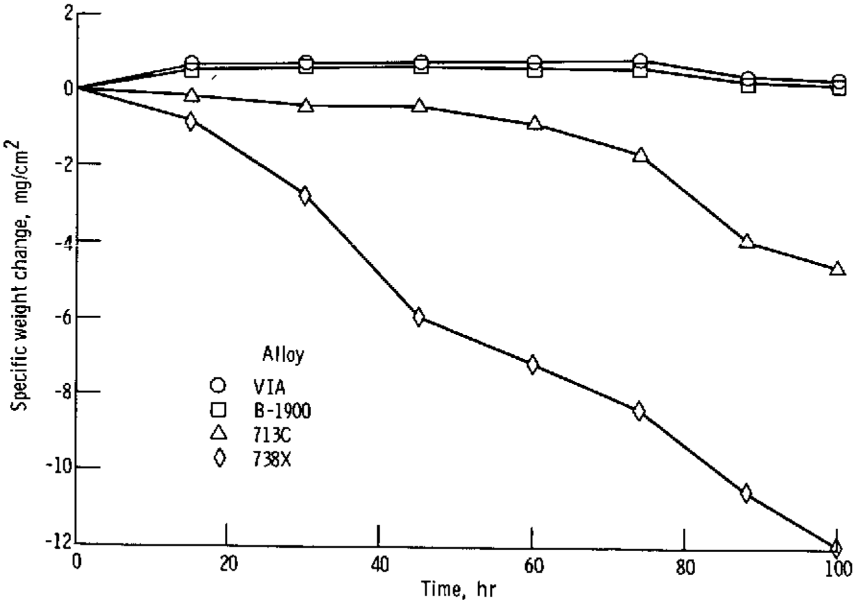


Figure 4. - Specific weight change of alloys resulting from isothermal exposure at 1000° C in dynamic oxidation apparatus. Isothermal: average 12-hour heating periods, still-air cooling to room temperature.

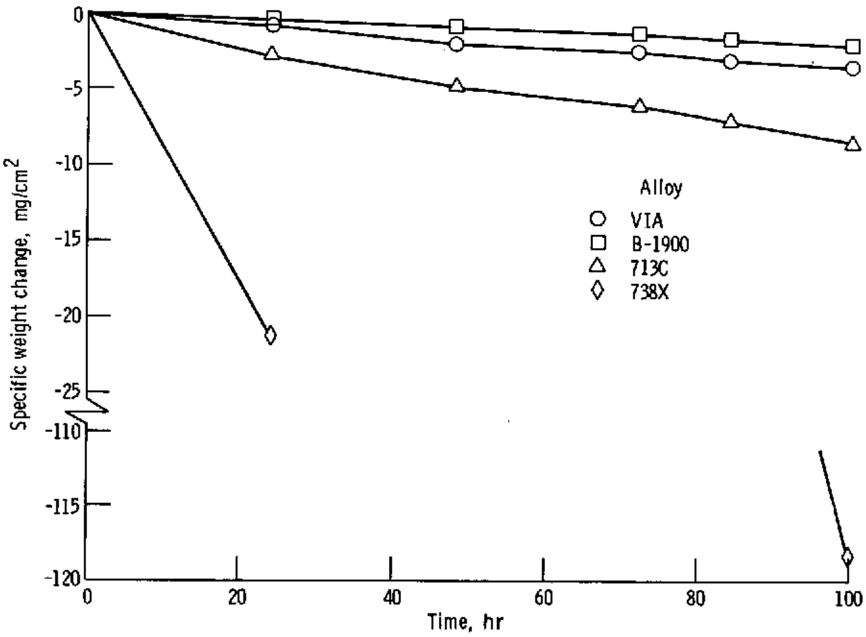


Figure 5. - Specific weight change of alloys resulting from cyclic exposure at 1100° C in dynamic oxidation apparatus. Cyclic: 1 hour at 1100° C, 3-minute forced-air cooling to room temperature.

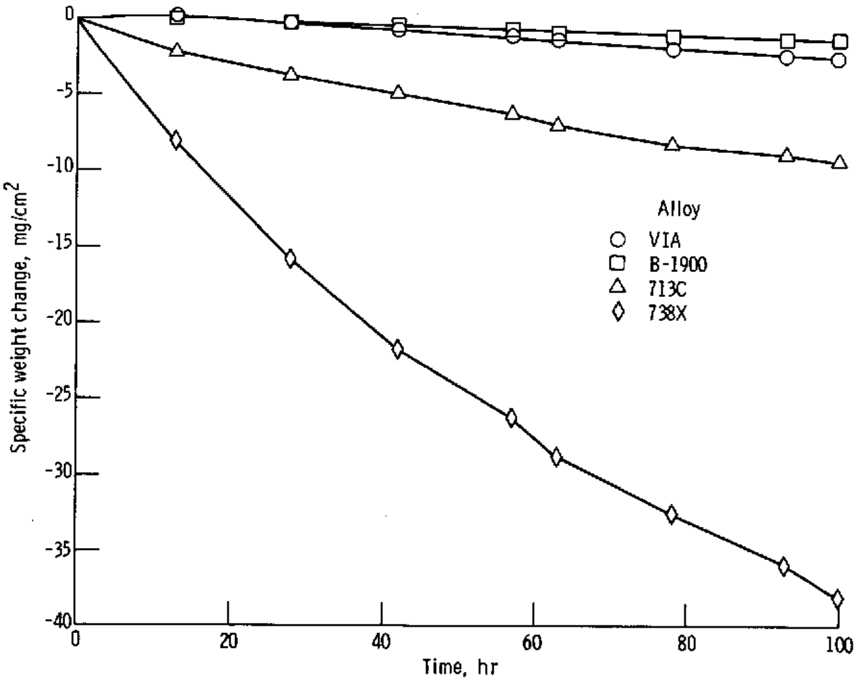


Figure 6. - Specific weight change of alloys resulting from isothermal exposure at 1100° C in dynamic oxidation apparatus. Isothermal: average 12-hour heating periods, still-air cooling to room temperature.

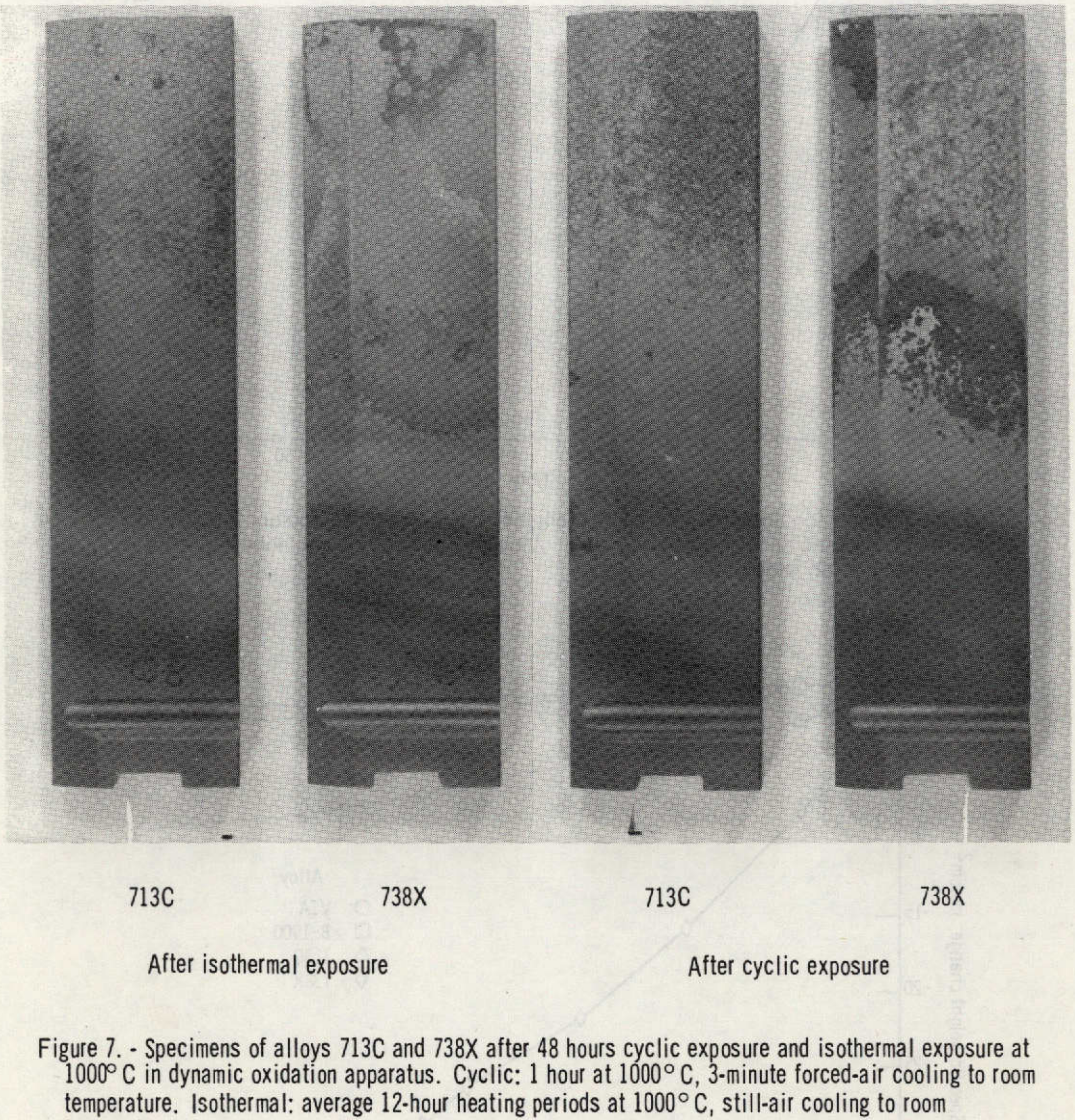
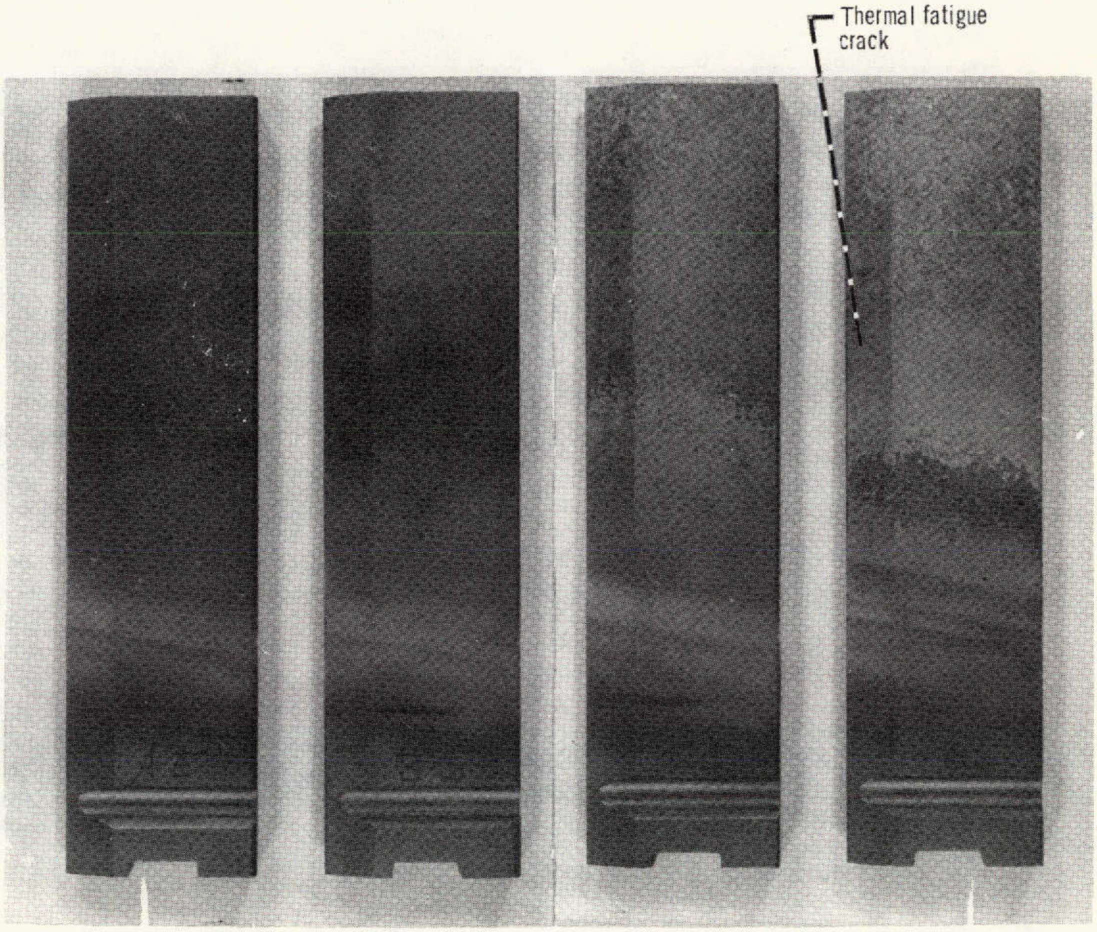


Figure 7. - Specimens of alloys 713C and 738X after 48 hours cyclic exposure and isothermal exposure at 1000° C in dynamic oxidation apparatus. Cyclic: 1 hour at 1000° C, 3-minute forced-air cooling to room temperature. Isothermal: average 12-hour heating periods at 1000° C, still-air cooling to room temperature.



VIA B-1900 713C 738X

Figure 8. - Specimens after cyclic exposure for 100 hours at 1000° C in dynamic oxidation apparatus. Cyclic: 1 hour at 1000° C, 3-minute forced-air cooling to room temperature.

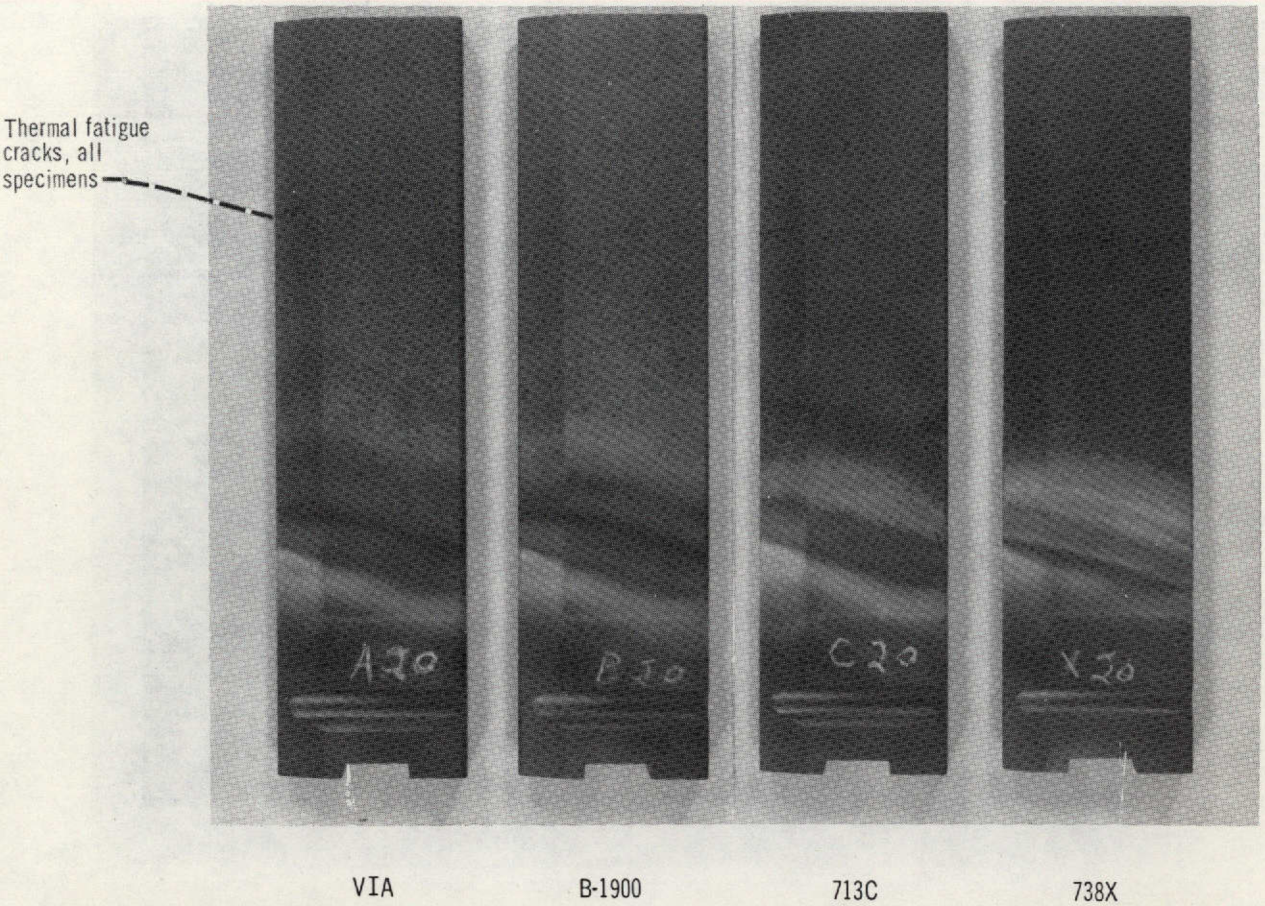
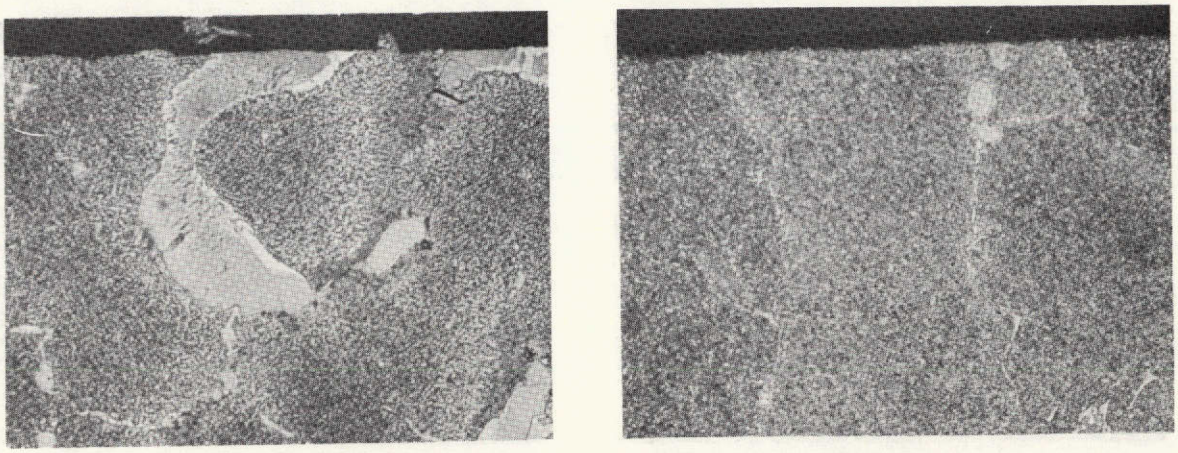
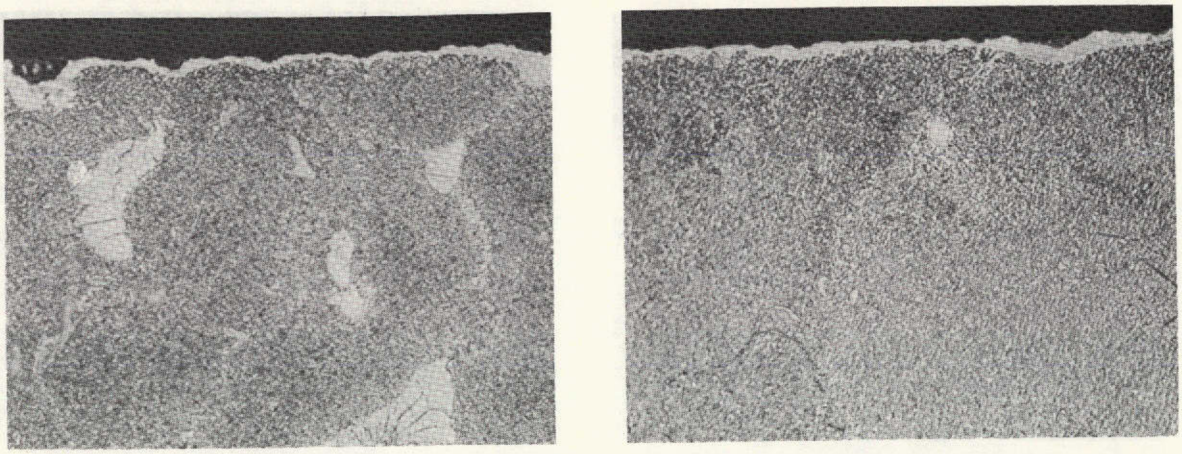


Figure 9. - Specimens after cyclic exposure for 100 hours at 1100° C in dynamic oxidation apparatus. Cyclic: 1 hour at 1100° C, 3-minute forced-air cooling to room temperature.



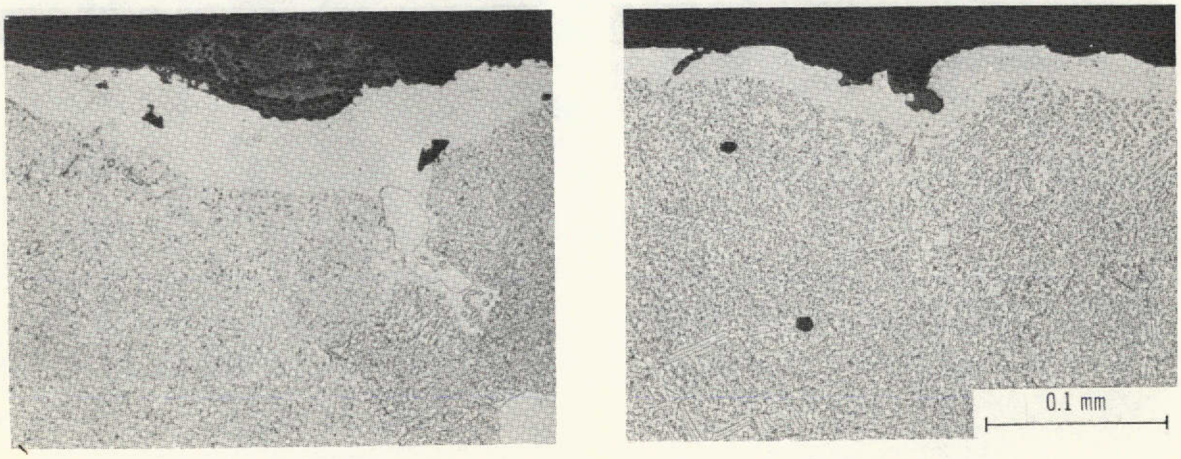
(a) Alloy VIA as-received.

(d) Alloy B-1900 as-received.



(b) Alloy VIA - 1000° C.

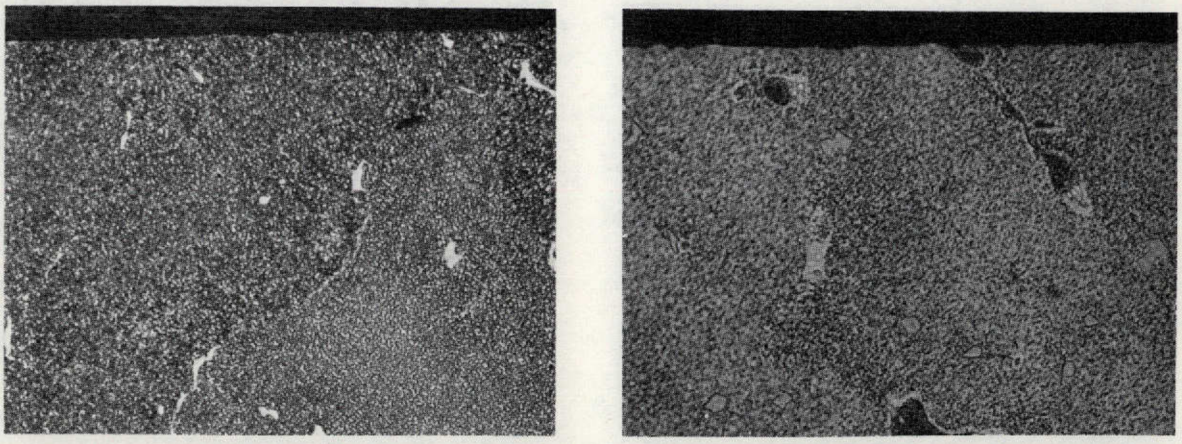
(e) Alloy B-1900 - 1000° C.



(c) Alloy VIA - 1100° C.

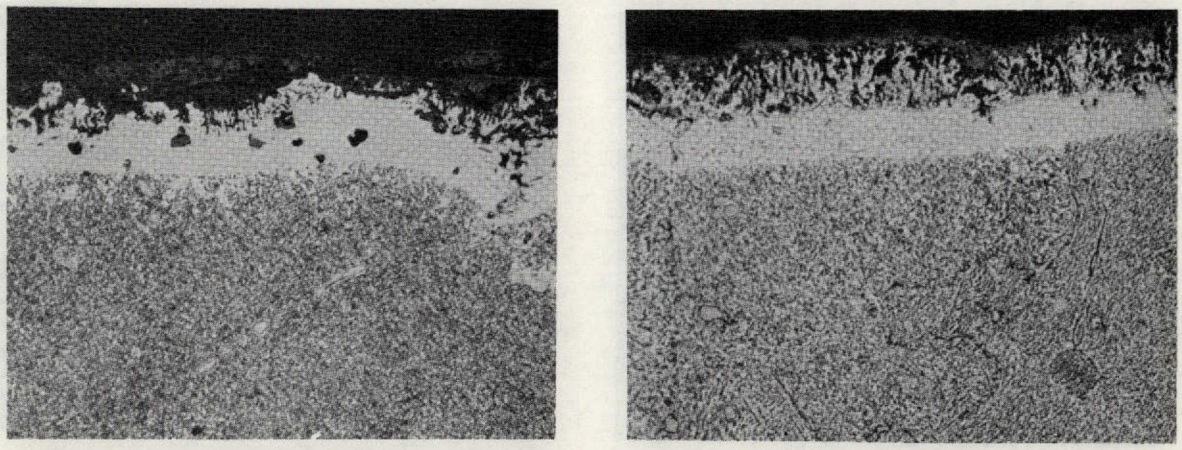
(f) Alloy B-1900 - 1100° C.

Figure 10. - Microstructures of alloys VIA and B-1900 as-received and after cyclic exposure for 100 hours at 1000° or 1100° C in dynamic oxidation apparatus. Cyclic: 1 hour at 1000° or 1100° C, 3-minute forced-air cooling to room temperature.



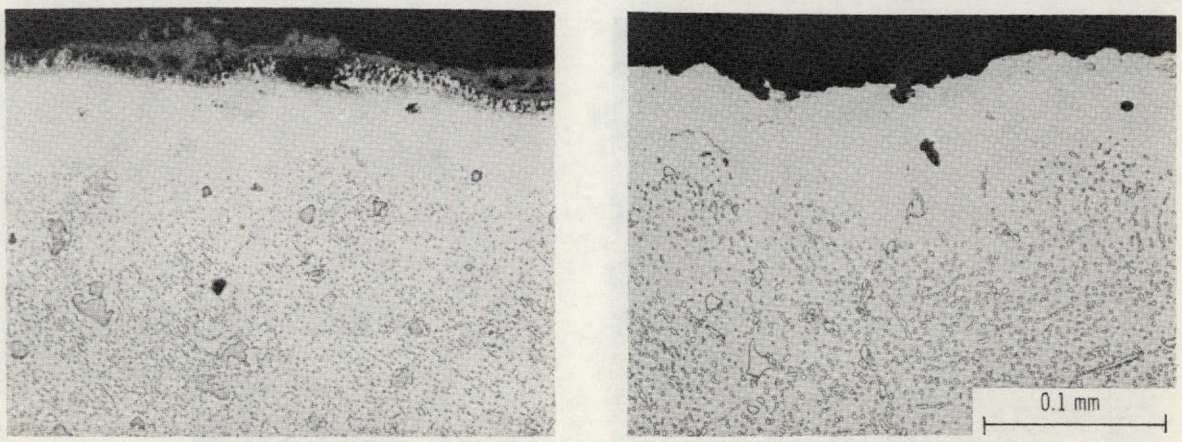
(a) Alloy 713C as-received.

(d) Alloy 738X as-received.



(b) Alloy 713C - 1000° C.

(e) Alloy 738X - 1000° C.



(c) Alloy 713C - 1100° C.

(f) Alloy 738X - 1100° C.

Figure 11. - Microstructures of alloys 713C and 738X as-received and after cyclic exposure for 100 hours at 1000° or 1100° C in dynamic oxidation apparatus. Cyclic: 1 hour at 1000° or 1100° C, 3-minute forced-air cooling to room temperature.

NASA-Langley, 1974 E-7865