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OXIDATION OF ALLOYS IN NICKEL-ALUMINUM SYSTEM WITH THIRD-ELEMENT ADDITIONS OF CHROMIUM, SILICON, AND TITANIUM AT 1100° C

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16. Abstract

The oxidation behavior of 31 compositions in the γ(Ni), γ'(Ni_3Al), and β(NiAl) phase regions of the Ni-Al system containing 0, 1, 3, or 10 atom percent Cr, Si, or Ti was investigated. Specimens were isothermally and cyclically exposed in air at 1100° C (2012° F) for 100 hours. Alloy thickness changes and weight changes were measured. The oxidation products were examined by X-ray diffraction and by metallography. Combining all results from these observations, a qualitative comparison is made of the oxidation resistance of all compositions studied.

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SUMMARY

A study was made to determine the individual effect of chromium, silicon, and titanium on the isothermal oxidation rate and cyclic spall resistance of single-phase alloys in the nickel-aluminum (Ni-Al) system. Additions of 1, 3, and 10 atom percent of chromium, silicon, or titanium were substituted for the aluminum in Ni-10Al (γ), Ni-25Al (γ'), and Ni-50Al (β). These 27 alloys, the Ni-Al binaries, and unalloyed nickel for comparison were isothermally and cyclically oxidized in still air at 1100° C (2012° F) for up to 100 hours. Alloy thickness changes and weight changes were measured. The oxidation products were examined by X-ray diffraction and by metallography. By combining the information from all the measurements and observations of this study, a qualitative comparison was made of the oxidation resistance of the compositions investigated. None of the γ alloys had better oxidation resistance than nickel, particularly under cyclic condition. Some of the γ' alloys were more oxidation resistant than nickel, and others were not. The best of the γ' alloys were as oxidation resistant as the best of the β alloys. All the β alloys were more oxidation resistant than nickel, and, therefore, more oxidation resistant than any of the γ alloys.

INTRODUCTION

An experimental survey was made of the oxidation and spalling of alloys in the nickel-aluminum (Ni-Al) system with chromium (Cr), silicon (Si), and titanium (Ti) additions. The Ni-Al system is fundamental to Ni-base superalloys. The matrix of these alloys consists of Ni-solid solution (γ), the main strengthening phase is $Ni_3(Al, Ti)$ (γ'), and the oxidation resistant coating often applied is NiAl (β). The elements

Cr, Si, and Ti are alloying elements used in commercial superalloys, in addition to being strong oxide formers. An understanding of the oxidation behavior of these three phases (γ, γ', and β) and particularly how that behavior is affected by the strong oxide formers present in Ni-base superalloys (Cr, Si, and Ti) could contribute to several areas of superalloy technology. Such information could serve as useful guides in alloy development. It could be helpful in the improvement of protective coatings for such alloys. Finally, it might contribute to an understanding of the oxidation behavior of commercial superalloys.

A great deal has been reported on the Ni-Cr system (refs. 1 to 3), but there is a paucity of data on the Ni-Al system (refs. 2 and 4) and even less for ternary Ni-Al base alloys (refs. 1, 5, and 6). A systematic high-temperature (i.e., $>900^\circ$ C ($>1652^\circ$ F)) investigation on the Ni-Al system is given in reference 4. Under isothermal conditions, it was found that the scale morphologies and oxidation rates were dependent on Al content, time, temperature, and oxygen pressure. At 1100° C (2012° F) and 0.1 torr of oxygen, a binary alloy with about 17 weight percent (31 at. %) or more of Al formed a single external scale of αAl_2O_3. The oxidation kinetics obeyed a parabolic rate law and the rate constant was three orders of magnitude smaller than for pure Ni. Below about 5 weight percent (10 at. %) Al, an internal oxide of Al_2O_3 was formed with an external NiO scale and some $NiAl_2O_4$ near the NiO-subscale interface. The kinetics obeyed a parabolic rate law and the rate constant was about an order of magnitude larger than for pure Ni. In reference 7 it was shown that the presence of Cr in the Ni-Al system would lower the Al content necessary for the formation of a single external scale of Al_2O_3. Thus, at 1100° C (2012° F), 11.8 atomic percent Al in the Ni-20Cr-Al alloy was sufficient to form a single external Al_2O_3 scale, that is, about 1/3 the amount required in the binary Ni-Al alloy. An earlier investigation (ref. 6) in the Ni-Cr-Al system showed that Al contents of ≥ 4 weight percent Al effected an improved oxidation resistance. In the Ni-Al-Si system only isothermal tests on dilute alloys were reported (ref. 8). These involve γ phase alloys with 5 to 7 weight percent Si plus Al. Between 1000° and 1200° C (1832° and 2152° F), the more resistant alloys were those with the higher Si plus Al content. With zero Al content the oxidation resistance increased with up to 7-weight-percent Si. For the binary Ni-Ti alloys between 1000° and 1200° C (1832° and 2192° F), the investigation of reference 9 showed that the oxidation resistance decreased with increasing Ti (0.53 to 16.7 wt %). Thus, in the Ni-Al binary system the data are predominantly isothermal and for short times (≤ 20 hr). Some cyclic tests for over 200 hours were reported, but only net weight changes were measured (ref. 10). Again, in the Ni-Cr-Al system the data are for short-time isothermal studies.

The present investigation was initiated as an experimental survey intended as a step towards filling the voids in the literature. It consists of oxidation studies of γ, γ', and β phase compositions. Cyclic data were obtained where only isothermal information has previously been available, and oxidation times up to 100 hours, substantially longer than most of the existing test data, were obtained. Also a temperature of 1100° C (2012° F) was chosen for this study. This is in the temperature range where the more advanced Ni-base superalloys have usable strengths. At present these superalloys require protective coatings at this temperature. Thus, data collected at 1100° C (2012° F) may not only aid the development of alloy coatings but also contribute to the development of greater intrinsic oxidation resistance for these advanced, high-strength superalloys. Furthermore, this high temperature will serve as a severe test parameter for the better separation of the oxidation behavior of the compositions investigated. Specifically, the purpose of this investigation was to determine the effect of Cr, Si, and Ti on the isothermal and cyclic oxidation resistance of single-phase alloys in the Ni-Al system. Thus, 0, 1, 3, and 10 atom percent of Cr, Si, and Ti were substituted for the Al in the Ni-10Al, Ni-25Al, and Ni-50Al alloys. These 30 alloys, together with unalloyed Ni for comparison, were isothermally and cyclically oxidized in air at 1100° C (2012° F). Alloy thickness changes and weight changes were measured. The oxidation products were examined by X-ray diffraction and metallography.

EXPERIMENTAL PROCEDURES

Sample Preparation

Alloys were prepared by vacuum casting. The chemical analysis of the starting materials is given in table I(a). Nickel was heated to its melting point in an Al_2O_3 crucible under a vacuum of 1 to 10 micrometers. The other elements were then added to the Ni melt under 50 torr of argon. The melt was poured into a preheated, 870° C (1598° F) zircon mold having a 1.9 centimeter (3/4-in.) diameter by 10.2-centimeter (4-in.) long cylindrical sample section. The pour temperature was between 1425° C (2597° F) and 1675° C (3047° F), depending on the composition of the melt. The castings were annealed 24 hours at 1200° C (2152° F) in sealed quartz tubes that had been evacuated and back filled with argon. The purpose of the annealing treatment was to stabilize the alloy before the 1100° C (2012° F) oxidation exposure. The castings were then centerless ground to remove surface scale and to provide a surface finish to 32 rms or better. The cylinders were sliced into 2-millimeter thick disks, and a hole was drilled or electric discharge machined near the edge of each disk so it could be suspended in the furnace. The flat surfaces were polished to a 1/2 micrometer finish. Experience at this laboratory indicates that this surface finish results in reproducible oxidation rates. Before oxidation material was provided from each casting for chemical analysis (table I(b)), metallography, and X-ray diffraction (table II).

TABLE I. - CHEMICAL ANALYSES

(a) Starting materials

Material	Purity, %	Impurities, ppm							
		Si	Fe	Ga	Mn	Mo	Cu	Ca	C
Nickel rod	99.99	---	--	--	--	--	-	--	46
Aluminum shot	99.99	60	20	30	--	--	-	--	--
Chromium pellets	99.999	100	10	--	10	10	5	20	--
Titanium wire	99.97	250	60	--	--	--	-	--	--
Silicon ingot	(a)	---	--	--	--	--	-	--	--

[a] Semiconductor grad.

(b) Cast alloys

Nominal composition, at. %	Actual composition, at. %
Ni-10Al	Ni-9.81Al
Ni-9Al-1Cr	Ni-8.9Al-1.2Cr
Ni-7Al-3Cr	Ni-7.1Al-2.8Cr
Ni-10Cr	Ni-9.93Cr
Ni-9Al-1Si	Ni-9.50Al-1.10Si
Ni-7Al-3Si	Ni-8.16Al-3.43Si
Ni-10Si	Ni-11.0Si
Ni-9Al-1Ti	Ni-8.24Al-1.0Ti
Ni-7Al-3Ti	Ni-7.1Al-2.5Ti
Ni-10Ti	Ni-9.8Ti
Ni-25Al	Ni-24.9Al
Ni-24Al-1Cr	Ni-24.47Al-0.78Cr
Ni-22Al-3Cr	Ni-22.59Al-2.86Cr
Ni-15Al-10Cr	Ni-15.73Al-9.98Cr
Ni-24Al-1Si	Ni-23.57Al-1.02Si
Ni-22Al-3Si	Ni-22.91Al-2.92Si
Ni-15Al-10Si	Ni-15.69Al-9.74Si
Ni-24Al-1Ti	Ni-23.0Al-0.99Ti
Ni-22Al-3Ti	Ni-22.04Al-3.40Ti
Ni-15Al-10Ti	Ni-15.51Al-10.03Ti
Ni-50Al	Ni-50.5Al
Ni-49Al-1Cr	Ni-48.8Al-1.1Cr
Ni-47Al-3Cr	Ni-47.6Al-2.6Cr
Ni-40Al-10Cr	Ni-39.1Al-10.3Cr
Ni-49Al-1Si	Ni-48.8Al-1.1Si
Ni-47Al-3Si	Ni-46.8Al-2.9Si
Ni-40Al-10Si	Ni-39.5Al-9.88Si
Ni-49Al-1Ti	Ni-49.6Al-1.10Ti
Ni-47Al-3Ti	Ni-47.6Al-3.1Ti
Ni-40Al-10Ti	Ni-40.1Al-10.4Ti

(c) Cast nickel impurities

C	46 ppm
Ag	Trace
Al	Faint trace
Fe	Very weak
Mg	Faint trace

TABLE II. - X-RAY DIFFRACTION DATA[a]

(a) Chromium containing alloys, nickel-aluminum (Ni-Al) binary alloys, and nickel

[Composition given in at. %.]

Type of oxidation	Part of scale X-rayed	γ alloys: Ni-(10-x)Al-xCr			γ' alloys: Ni-(25-x)Al-xCr			β alloys: Ni-(50-x)Al-xCr			Ni-Al binary phases:			Ni
		x = 1	x = 3	x = 10	x = 1	x = 3	x = 10	x = 1	x = 3	x = 10	Ni-10Al	Ni-25Al	Ni-50Al	
As cast	--------	Ni solid solution (a_o = 3.534)	Ni solid solution (a_o = 3.536)	Ni solid solution (a_o = 3.531)	Ni_3Al (a_o = 3.581)	Ni_3Al (a_o = 3.568)	Ni_3Al (a_o = 3.561)	NiAl (a_o = 2.892)	NiAl (a_o = 2.877)	[b]NiAl (a_o = 2.872)	Ni solid solution (a_o = 3.543)	Ni_3Al (a_o = 3.575)	NiAl (a_o = 2.889)	Ni (a_o = 3.520)
Isothermal	Retained	NiO $NiCr_2O_4$	NiO $NiCr_2O_4$	NiO $NiCr_2O_4$	Al_2O_3 $NiCr_2O_4$ $NiAl_2O_4$	NiO $NiCr_2O_4$ [c]Al_2O_3	Al_2O_3 $NiAl_2O_4$	Al_2O_3	Al_2O_3	Al_2O_3 $NiCr_2O_4$ NiO	NiO $NiAl_2O_4$	Al_2O_3 $NiAl_2O_4$	Al_2O_3	NiO
	Spall	NiO $NiCr_2O_4$	NiO $NiCr_2O_4$	NiO $NiCr_2O_4$	Al_2O_3 $NiAl_2O_4$ NiO	Al_2O_3 [c]NiO	Al_2O_3 $NiAl_2O_4$	No spall detected	Few flakes not X-rayed	Al_2O_3 NiO	No spall detected	Al_2O_3 $NiAl_2O_4$ NiO	No spall detected	No spall detected
Cyclic	Retained	NiO $NiCr_2O_4$	NiO $NiCr_2O_4$	NiO $NiCr_2O_4$	NiO Al_2O_3 $NiAl_2O_4$ $NiCr_2O_4$	NiO $NiAl_2O_4$ Al_2O_3	NiO Al_2O_3 Cr_2O_3 $NiCr_2O_4$	Al_2O_3	Al_2O_3	Al_2O_3 $NiAl_2O_4$	NiO $NiAl_2O_4$	NiO $NiAl_2O_4$ Al_2O_3	Al_2O_3	NiO
	Spall	NiO $NiCr_2O_4$	NiO $NiCr_2O_4$	NiO $NiCr_2O_4$	NiO $NiAl_2O_4$ Al_2O_3	NiO $NiAl_2O_4$ Al_2O_3	NiO $NiAl_2O_4$ Al_2O_3	Few flakes not X-rayed	Al_2O_3 $NiAl_2O_4$ [c]NiO	Al_2O_3 $NiAl_2O_4$ NiO [c]Cr_2O_3	NiO $NiAl_2O_4$	NiO $NiAl_2O_4$ Al_2O_3	Al_2O_3 [c]NiO	No spall detected

[a] The phase with the strongest lines in the X-ray diffraction pattern is listed first, followed, in order, by phases with weaker lines.

[b] Few extra lines which are very weak and were not identified.

[c] Suspected phase, indefinite pattern.

TABLE II. - Continued. X-RAY DIFFRACTION DATA[a]

(b) Silicon containing alloys

Type of oxidation	Part of scale X-rayed	γ alloys: Ni-(10-x)Al-xSi			γ' alloys: Ni-(25-x)Al-xSi			β alloys: Ni-(50-x)Al-xSi		
		x = 1	x = 3	x = 10	x = 1	x = 3	x = 10	x = 1	x = 3	x = 10
As cast	--------	Ni solid solution (a_o = 3.537)	Ni solid solution (a_o = 3.531)	Ni solid solution (a_o = 3.515)	Ni_3Al (a_o = 3.572)	Ni_3Al (a_o = 3.558)	Ni_3Al (a_o = 3.548)	[b]NiAl (a_o = 2.92-2.89)	NiAl (a_o = 2.888)	NiAl (a_o = 2.880)
Isothermal	Retained	NiO	NiO	NiO	NiO Al_2O_3 $NiAl_2O_4$	Al_2O_3 $NiAl_2O_4$	NiO Al_2O_3 $NiAl_2O_4$	Al_2O_3	Al_2O_3	Al_2O_3
	Spall	No spall detected	NiO $NiAl_2O_4$	NiO	Al_2O_3 NiO $NiAl_2O_4$	Al_2O_3 $NiAl_2O_4$	NiO $NiAl_2O_4$	No spall detected	No spall detected	Few flakes not X-rayed
Cyclic	Retained	NiO [c]$NiAl_2O_4$	NiO $NiAl_2O_4$	NiO	NiO Al_2O_3 $NiAl_2O_4$	NiO $NiAl_2O_4$ Al_2O_3	NiO $NiAl_2O_4$	Al_2O_3	Al_2O_3	Al_2O_3
	Spall	NiO $NiAl_2O_4$	NiO $NiAl_2O_4$	NiO	NiO $NiAl_2O_4$ Al_2O_3	NiO $NiAl_2O_4$ Al_2O_3	NiO $NiAl_2O_4$ SiO_2	No spall detected	No spall detected	Few flakes Al_2O_3 $NiAl_2O_4$

[a] The phase with the strongest lines in the X-ray diffraction pattern is listed first, followed, in order, by phases with weaker lines.

[b] Few extra lines which are very weak and were not identified.

[c] Suspected phase, indefinite pattern.

TABLE II. - Concluded. X-RAY DIFFRACTION DATA[a]

(c) Titanium containing alloys

Type of oxidation	Part of scale X-rayed	γ alloys: Ni-(10-x)Al-xTi			γ' alloys: Ni-(25-x)Al-xTi			β alloys: Ni-(50-x)Al-xTi		
		x = 1	x = 3	x = 10	x = 1	x = 3	x = 10	x = 1	x = 3	x = 10
As cast	--------	Ni solid solution (a_o = 3.548)	Ni solid solution (a_o = 3.536)	Ni solid solution (a_o = 3.565)	Ni_3Al (a_o = 3.570)	Ni_3Al (a_o = 3.579)	Ni_3Al (a_o = 3.579)	NiAl (a_o = 2.879)	NiAl (a_o = 2.888)	[b]NiAl (a_o = 2.93-2.87)
Isothermal	Retained	NiO	NiO $NiTiO_3$ $NiAl_2O_4$	NiO $NiTiO_3$ TiO_2	NiO Al_2O_3 $NiAl_2O_4$ TiO_2	NiO Al_2O_3 $NiAl_2O_4$ $NiTiO_3$	$NiTiO_3$ TiO_2 $NiAl_2O_4$	Al_2O_3	Al_2O_3	Al_2O_3 TiO_2 $NiAl_2O_4$
	Spall	No spall detected	NiO $NiTiO_3$ $NiAl_2O_4$	NiO $NiTiO_3$ TiO_2	NiO Al_2O_3 $NiAl_2O_4$	Al_2O_3 NiO $NiAl_2O_4$ [c]Cr_2O_3	NiO $NiTiO_3$ $NiAl_2O_3$	No spall detected	No spall detected	No spall detected
Cyclic	Retained	NiO $NiAl_2O_4$	NiO $NiAl_2O_4$ $NiTiO_3$	NiO $NiTiO_3$	NiO $NiAl_2O_4$ Al_2O_3	NiO $NiAl_2O_4$ $NiTiO_3$ Al_2O_3	NiO $NiAl_2O_4$ Al_2O_3	Al_2O_3	Al_2O_3	Al_2O_3 TiO_2 $NiAl_2O_4$
	Spall	NiO $NiTiO_3$ $NiAl_2O_4$	NiO $NiAl_2O_4$ $NiTiO_3$	NiO $NiTiO_3$	NiO Al_2O_3 $NiAl_2O_4$	NiO $NiAl_2O_4$ $NiTiO_3$	NiO $NiAl_2O_4$ $NiTiO_3$	Few flakes not X-rayed	No spall detected	No spall detected

[a] The phase with the strongest lines in the X-ray diffraction pattern is listed first, followed, in order, by phases with weaker lines.

[b] Few extra lines which are very weak and were not identified.

[c] Suspected phase, indefinite pattern.

Table I(b) shows that the actual composition in every case is close to the nominal composition. Each composition represents one casting from which came all the oxidation specimens and material for analysis. The nominal compositions are used throughout this paper. All compositions are given in atom percent. Figure 1 is a plot in triangular coordinates of the nominal compositions of the alloys used in this investigation. Although it was desired to have all single-phase samples, the X-ray diffraction data (table II) and metallography revealed that three of the β alloys were not single phase, namely, the Ni-40Al-10Cr, Ni-49Al-1Si, and Ni-40Al-10Ti alloys. The composition of the chromium alloy is in the region of a known phase diagram (ref. 11), and according to that diagram Ni-40Al-10Cr should be a β phase alloy. Apparently, this alloy suffered segregation, and equilibrium was not established.

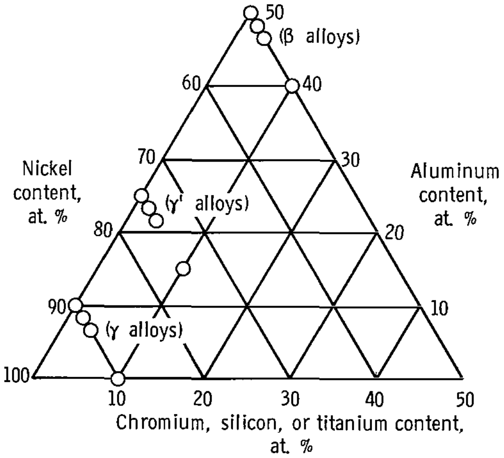


Figure 1. - Nominal compositions of alloys in this investigation.

Unalloyed Ni was also cast, machined, and subsequently oxidized in similar fashion to provide a baseline for comparison. An analysis of the casting from which the Ni specimens were made is given in table I.

Testing Procedure

Measurements. - Thickness measurements before oxidation testing were taken at eight positions along the diameter of each specimen with a bench micrometer. After oxidation, the specimens were cross sectioned along the diameter of the previous measurement, polished, and etched. The thickness of the unaffected alloy (excluding internal oxides and/or depletion zones when present) was measured using a filar eye piece at approximately the same eight positions. The average of the differences in thickness before and after oxidation is taken as the alloy recession. The accuracy of the thickness measurement, under the best of circumstances, was 0.005 millimeter. Where the reacted alloy - unaffected alloy interface was highly irregular, the accuracy decreased by as much as an order of magnitude.

Isothermal oxidation test. - Isothermal oxidation was carried out at 1100° C (2012° F) in still air for 100 hours. As shown schematically in figure 2 a continuously recording electrobalance was used for measuring the weight change. The accuracy of the apparatus was ±0.1 milligram. The specimens were suspended by a thin quartz rod into the furnace's hot zone and by platinum wire above the hot zone to the balance.

Cyclic oxidation test. - Cyclic oxidation was carried out at 1100° C (2012° F) in still air for a total time at temperature of 100 hours. Each cycle consisted of 1 hour at temperature followed by 45 minutes in ambient air. It took $1\frac{1}{2}$ minutes for the specimens to reach temperature when inserted in the furnace. When withdrawn from the furnace, the specimens cooled to 550° C (1022° F) in 1 minute and reached room temperature in

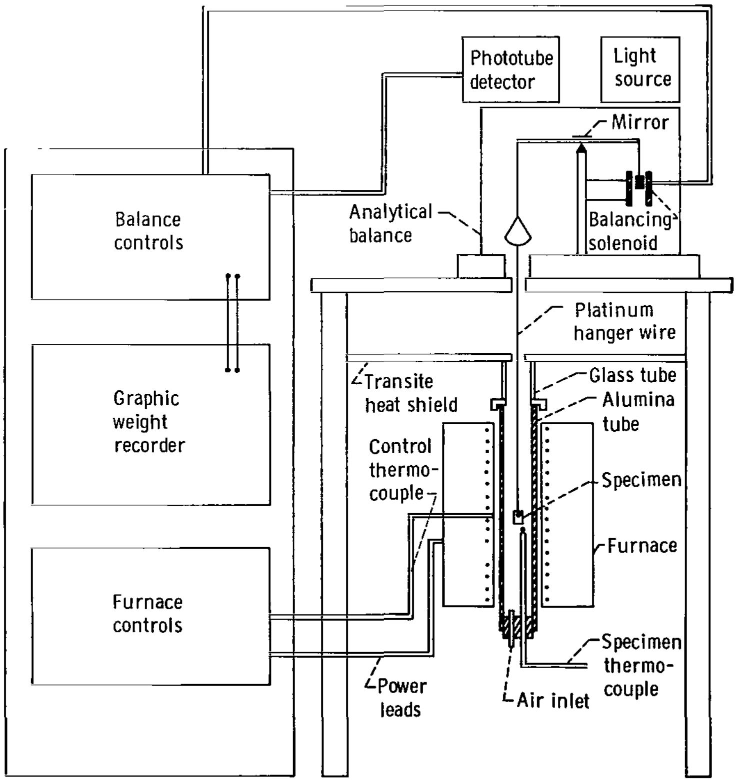
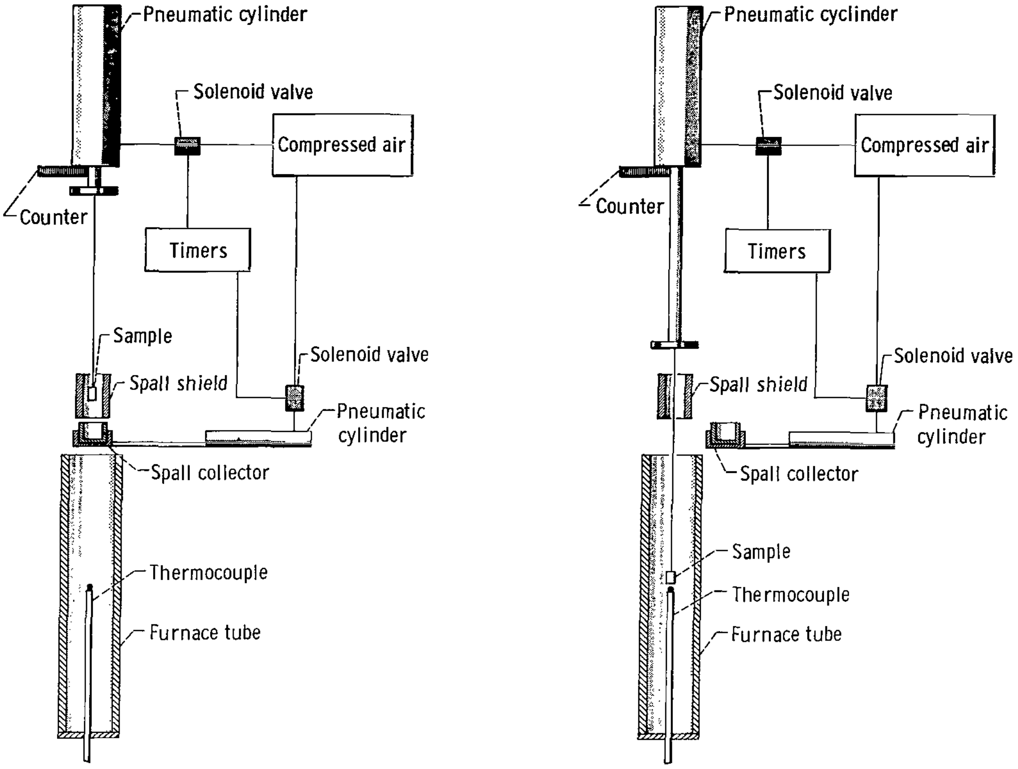


Figure 2. - Continuous weight-gain apparatus.



(a) Cooling position.

(b) Heating position.

Figure 3. - Automatic cycling and spall collecting apparatus.

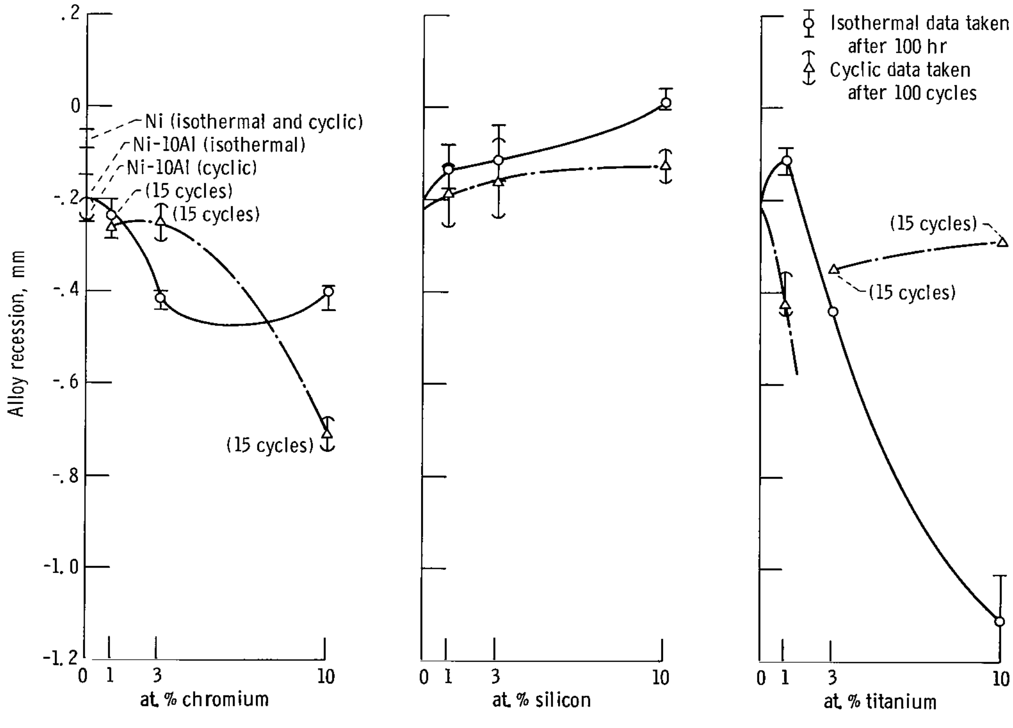
7 minutes. As shown schematically in figure 3, the samples were automatically cycled in and out of the furnace by a pneumatic cylinder controlled by timers operating solenoid valves. The apparatus was equipped with a spall collector that was automatically positioned under the sample during the cooling portion of each cycle. Thus, spalls could be collected and analyzed. The specimens were periodically weighed between cycles. After oxidation, the specimens were analyzed by X-ray diffraction. The retained scales were X-rayed in situ on the diffractometer; the spalls in the Debye-Scherrer camera. The cross section of each specimen was examined metallographically. The etchant in each case consisted of 92 parts hydrochloric acid, five parts sulphuric acid, and three parts nitric acid.

RESULTS

In the next sections the major results of this study are presented. Alloy recession data, the most direct measure of the amount of alloy consumed by oxidation, is presented first. Weight change data as a function of time are presented as the only kinetic measurements. Information regarding scale identity and microstructures is also given.

Alloy Recession

The amount of recession of all compositions after 100 hours of isothermal and cyclic oxidation is given in figures 4 to 6. The magnitudes of these thickness changes are generally within experimental error. The accuracy of some of the measurements was less than that of others because of nonuniform interfaces. It is interesting to note that some data points indicate an alloy expansion. Although these positive changes are within experimental error, there is the possibility of an actual net expansion due to changes within the alloy. For example, the alloy near the scale-alloy interface may be depleted of Al during oxidation. This change in composition could shift the lattice parameters toward higher values, increasing the volume of the specimen. One of the difficulties of alloy recession determinations is locating the actual boundary of the unaf-

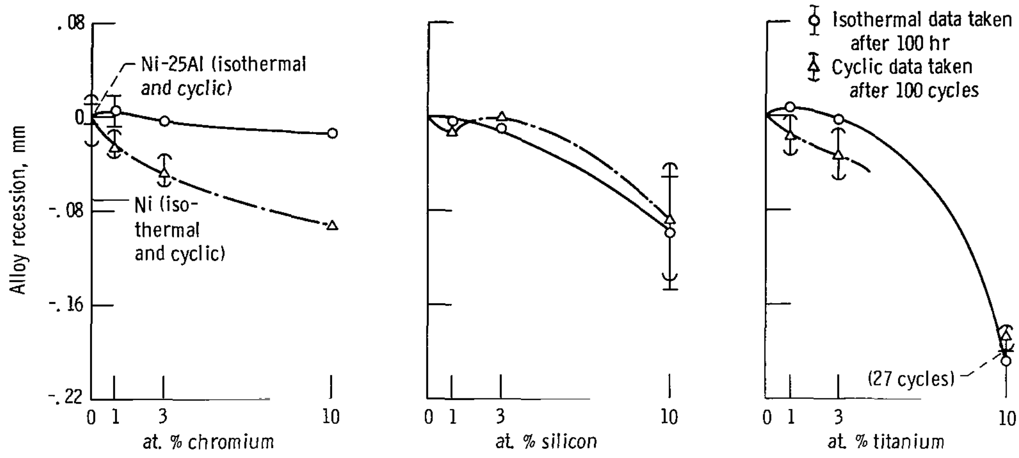


(a) Nickel, Ni-10Al, and γ alloys with chromium.

(b) γ alloys with silicon.

(c) γ alloys with titanium.

Figure 4. - Recession of nickel and γ-phase alloys. Temperature, 1100° C; air. (Range-of-value bars are shown only when range exceeds 0.025 mm.)

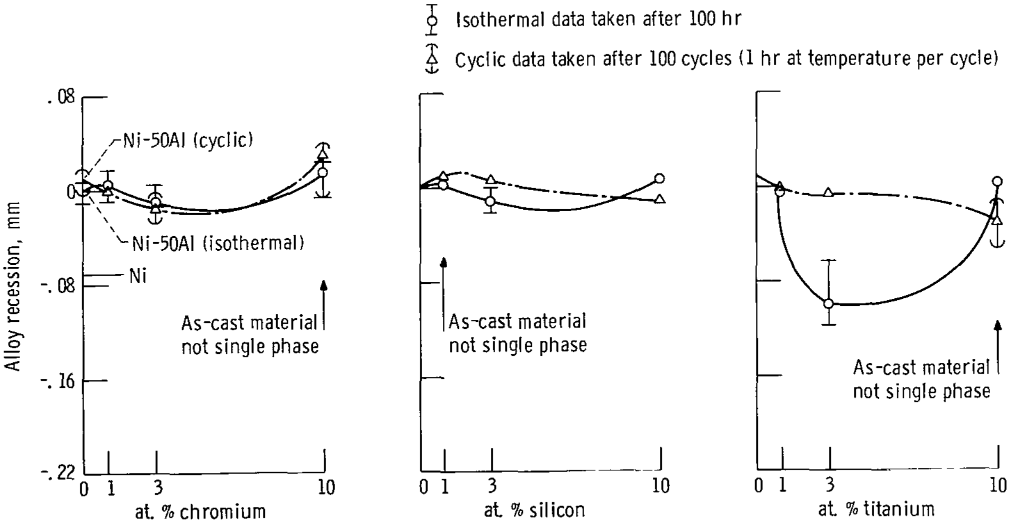


(a) Nickel, Ni-25Al, and γ' alloys with chromium.

(b) γ' alloys with silicon.

(c) γ' alloys with titanium.

Figure 5. - Recession of γ'-phase alloys tested at 1100° C in air. (Range-of-value bars are shown only when range exceeds 0.025 mm.)



(a) Nickel, Ni-50Al, and β alloys with chromium.

(b) β alloys with silicon.

(c) β alloys with titanium.

Figure 6. - Recession of β phase alloys tested at 1100° C in air. (Range-of-value bars are shown only when range exceeds 0.025 mm.)

fected alloy. Of the γ alloys (fig. 4) under isothermal conditions, the 1-, 3-, and 10-atomic-percent Si and the 1-atomic-percent Ti recessed to a lesser extent than Ni-10Al. Unalloyed Ni recessed the least of any of the γ phase materials except Ni-10Si. However, under cyclic oxidation, the Ni-10Si recessed more than Ni. The recession of Ni was identical under isothermal and cyclic conditions. The γ alloys that recessed less than Ni-10Al after cyclic oxidation are 1, 3, and 10 atomic percent Si. After either isothermal or cyclic oxidation no γ' alloys recessed less than Ni-25Al (fig. 5) and no β alloy recessed less than Ni-50Al (fig. 6).

Kinetic Data (Isothermal)

Graphs of the square of the specific weight change as a function of time were constructed for each composition. Where the curves were linear, parabolic rate constants were calculated and listed in table III. The oxidation mechanisms for most of these alloys are complex, so the rate constants represent an overall process that proceeds more or less parabolically. Figures 7 to 9 are logarithmic plots of the specific weight changes as functions of time for the alloys studied. The slopes were determined in those cases where a linear relation existed and are listed in table III.

Among the γ alloys (fig. 7), the 1-, 3-, and 10-atomic-percent Si and the 1-atomic-percent Ti gained less weight than Ni-10Al. The weight gain of 10-atomic-percent Si was even less than that of Ni, but its slope is greater than that for Ni (or for Ni-10Al). With the γ' alloys (fig. 8), the 1- and 3-atomic-percent Cr, the 1- and 3-atomic-percent Si, and the 3-atomic-percent Ti gained less weight than Ni-25Al. The 10-atomic-percent Si gained weight at roughly the same rate as Ni, and the 10-atomic-percent Ti gained weight at a greater rate. Among the β alloys (fig. 9), the 1-atomic-percent Si was the only alloy to gain less weight than Ni-50Al. The 3-atomic-percent Si and the 1-atomic-percent Ti gained roughly as much weight in 100 hours at Ni-50Al, but the slopes of their curves are greater.

Cyclic Oxidation

Figures 10 to 12 show the net specific weight changes during cyclic oxidation. These weight differences are the net effect of weight gain by oxidation and weight loss by spalling. For the γ alloys (fig. 10) only the 1-atomic-percent Si had a net specific weight change less than Ni-10Al after 100 hours at temperature. The Ni-10Al had no detectible spalling for the first three cycles, but thereafter spalled a great deal. Unalloyed Ni did not spall, its cyclic oxidation curve being identical to its isothermal

TABLE III. - OXIDATION RATES

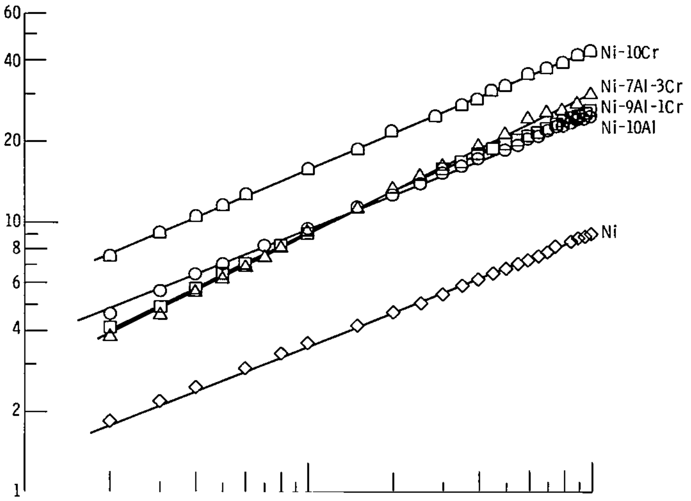
[100 hr, 1100° C, air]

Composition	Parabolic rate constant, $(mg/cm^2)^2$/hr	Slope of log-log graph (see figs. 7 - 15)
Ni	0.76	0.41
Ni-10Al	NP[a]	.42
Ni-9Al-1Cr	NP	Varies
Ni-7Al-3Cr	8.7	.53
Ni-10Cr	NP	.44
Ni-9Al-1Si	NP	Varies
Ni-7Al-3Si	NP	Varies
Ni-10Si	NP	.7
Ni-9Al-1Ti	NP	Varies
Ni-7Al-3Ti	9.8	.53
Ni-10Ti	NP	Varies
Ni-25Al	0.0077	0.46
Ni-24Al-1Cr	.0019	.48
Ni-22Al-3Cr	NP	.35
Ni-15Al-10Cr	.027	.50
Ni-24Al-1Si	NP	Varies
Ni-22Al-3Si	NP	Varies
Ni-15Al-10Si	1.21	.55
Ni-24Al-1Ti	NP	Varies
Ni-22Al-3Ti	NP	Varies
Ni-15Al-10Ti	3.9	.46
Ni-50Al	0.0021	0.52
Ni-49Al-1Cr	.0046	.50
Ni-47Al-3Cr	.016	.50
Ni-40Al-10Cr[b]	.31	.50
Ni-49Al-1Si[b]	NP	Varies
Ni-47Al-3Si	(c)	1.0
Ni-40Al-10Si	NP	Varies
Ni-49Al-1Ti	.0017	.58
Ni-47Al-3Ti	NP	Varies
Ni-40Al-10Ti[b]	.049	.48

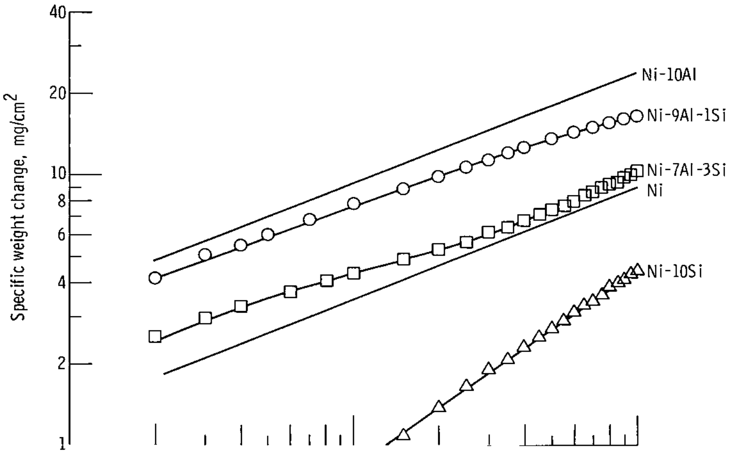
[a] Overall reaction rate is not parabolic.

[b] As cast material not single phase.

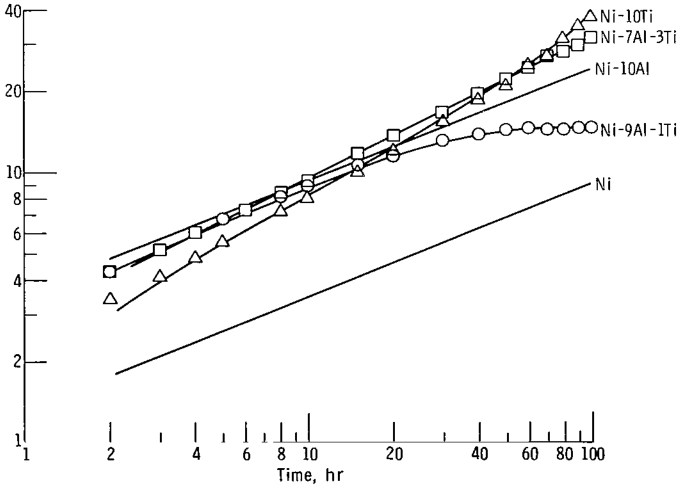
[c] Linear rate.



(a) Nickel-aluminum-chromium alloys.

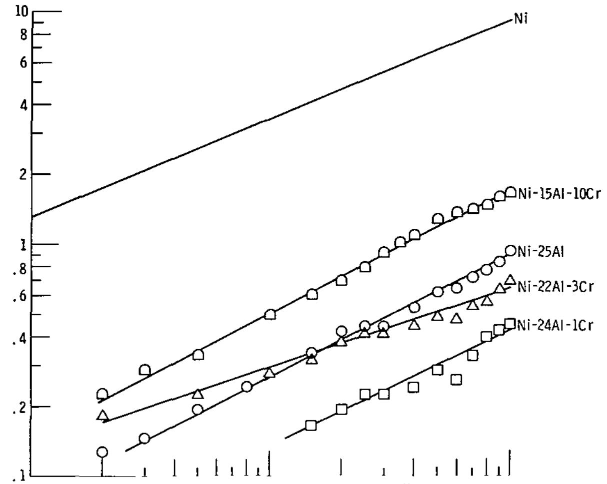


(b) Nickel-aluminum-silicon alloys.

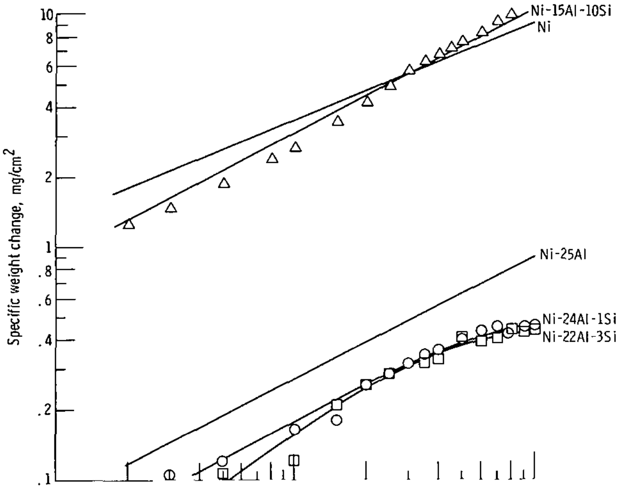


(c) Nickel-aluminum-titanium alloys.

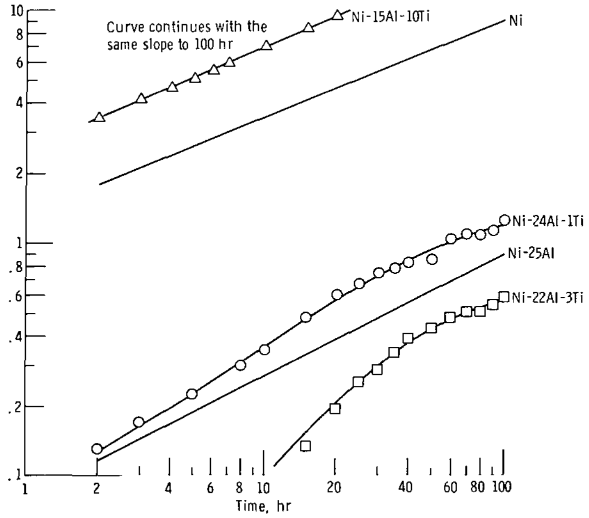
Figure 7. - Kinetic data for nickel, Ni-10Al, and γ alloys tested at 1100° C in air.



(a) Nickel-aluminum-chromium alloys.

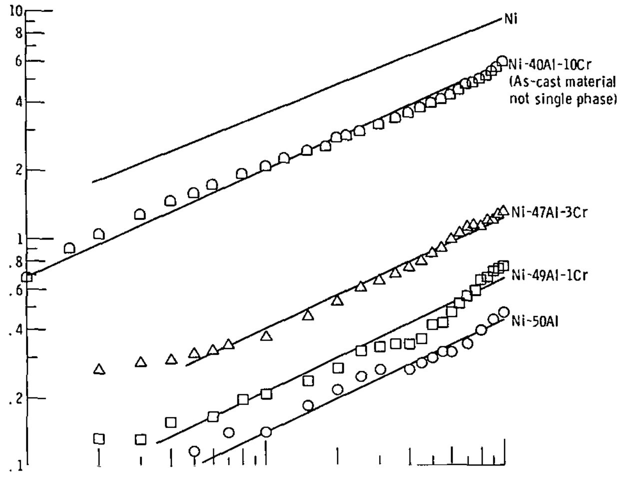


(b) Nickel-aluminum-silicon alloys.

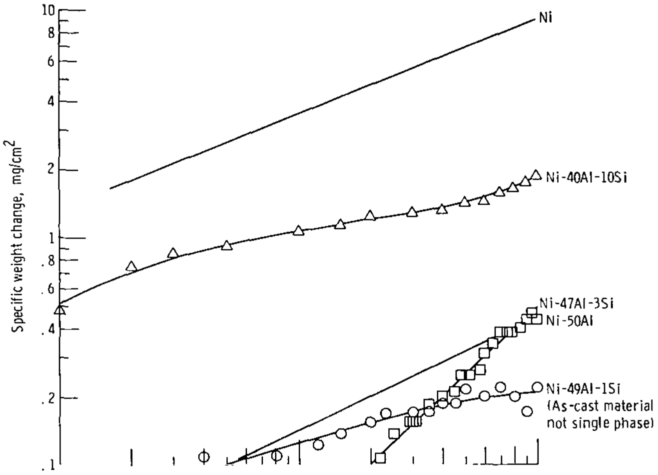


(c) Nickel-aluminum-titanium alloys.

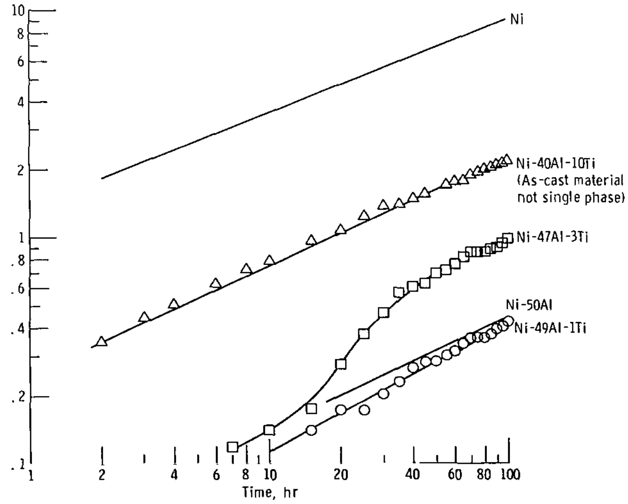
Figure 8. - Kinetic data for nickel, Ni-25Al, and γ' alloys tested at 1100° C in air.



(a) Nickel-aluminum-chromium alloys.

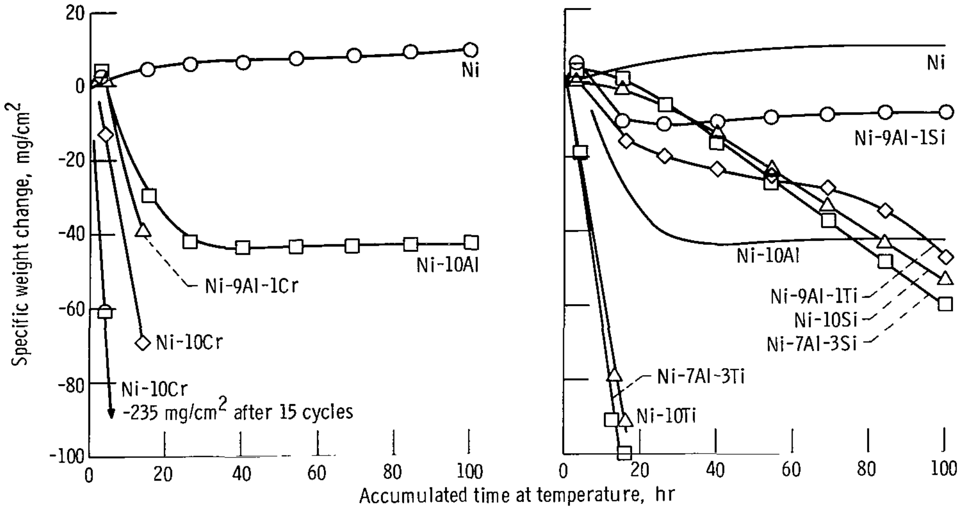


(b) Nickel-aluminum-silicon alloys.



(c) Nickel-aluminum-titanium alloys.

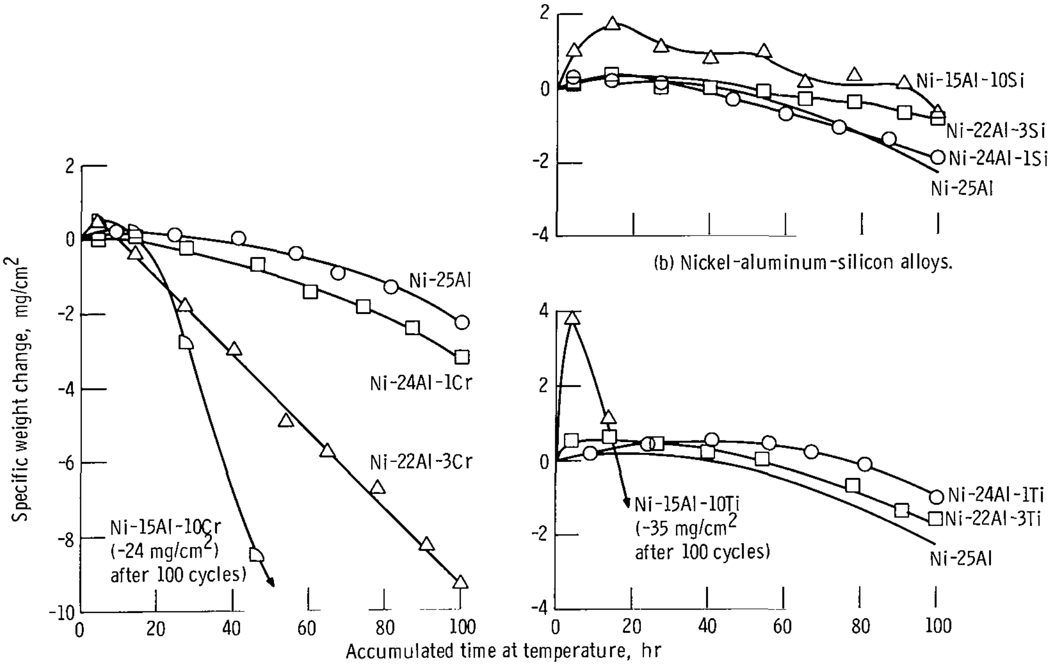
Figure 9. - Kinetic data for nickel, Ni-50Al, and β alloys tested at 1100° C in air.



(a) Nickel-aluminum-chromium alloys.

(b) Nickel-aluminum-silicon and nickel-aluminum-titanium alloys.

Figure 10. - Cyclic oxidation data for nickel, Ni-10Al, and γ alloys. Cycle: 1 hour at temperature (1100° C) per cycle; in air.

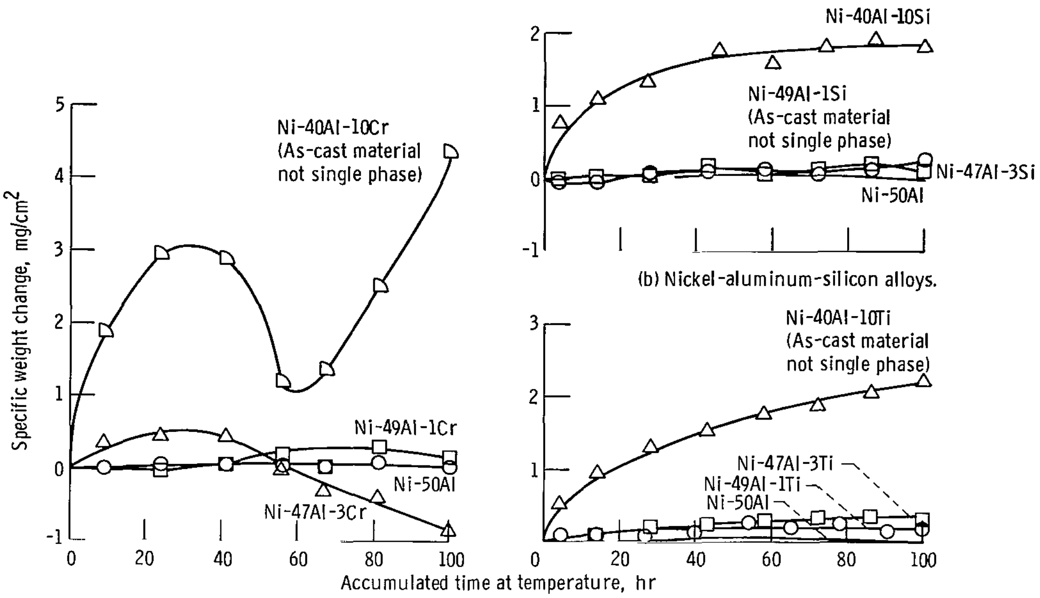


(b) Nickel-aluminum-silicon alloys.

(a) Nickel-aluminum-chromium alloys.

(c) Nickel-aluminum-titanium alloys.

Figure 11. - Cyclic oxidation data for nickel, Ni-25Al, and γ' alloys. Cycle: 1hour at temperature (1100° C) per cycle; in air.



(b) Nickel-aluminum-silicon alloys.

(a) Nickel-aluminum-chromium alloys.

(c) Nickel-aluminum-titanium alloys.

Figure 12. - Cyclic oxidation data for nickel, Ni-50Al, and β alloys. Cycle: 1 hour at temperature (1100° C) per cycle; in air.

curve. Among the γ' alloys (fig. 11) the 1-, 3-, and 10-atomic-percent Si and the 1- and 3-atomic-percent Ti had slightly less net specific weight change than Ni-25Al. For Ni-25Al no spalling was detected for the first 24 cycles, and the sample spalled only slightly thereafter. With the β alloys (fig. 12) the 1- and 10-atomic-percent Si and the 10-atomic-percent Ti had cyclic oxidation curves identical to their respective isothermal curves. Spalls from the 10-atomic-percent Si specimen were barely detected and were undetected for the 1-atomic-percent Si and the 10-atomic-percent Ti. The 3-atomic-percent Si and the 3-atomic-percent Ti samples had no detectible spalling, but their respective cyclic and isothermal curves were not identical. It must therefore be assumed that the samples spalled during the cyclic oxidation tests and that the spalls were blown out of the spall collector. The loss of spalls in this manner is possible since the specimens were not completely enclosed by the spall collector (fig. 3). For Ni-50Al no spalls were detected during the first 24 cycles and only slight spalling occurred thereafter.

Post-Oxidation Examination

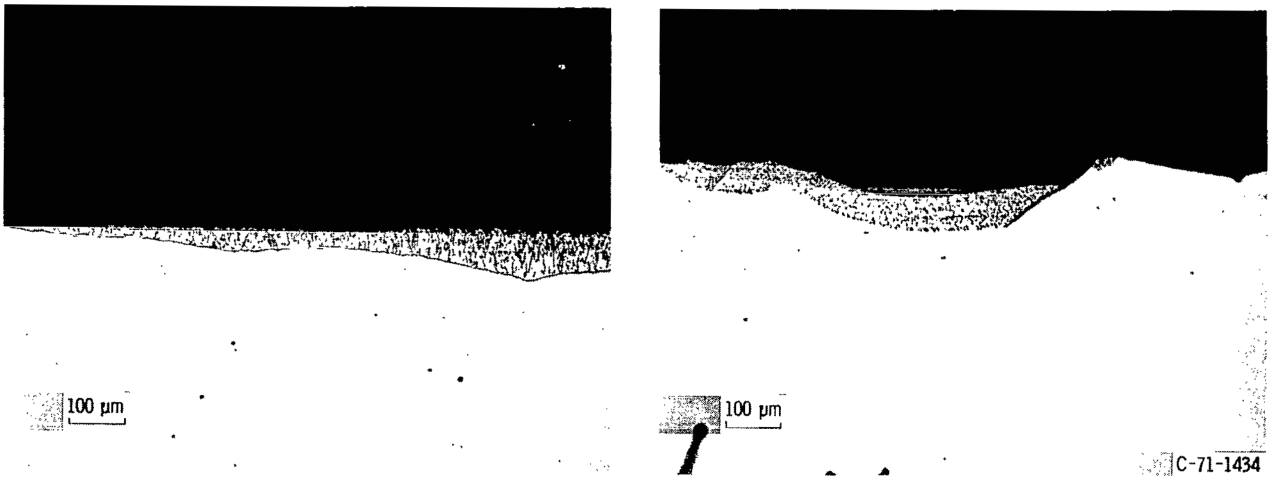
Table II lists the oxide phases detected by X-ray diffraction. The predominant phase in all the γ alloys was NiO, although strong spinel lines were observed in many cases. In some γ' alloys, NiO was the predominant phase, and in others, Al_2O_3 was predominant. All the γ' alloys had spinel phases. In β alloys Al_2O_3 was the predominant oxide and most often was the only oxide. Table IV lists compositions which formed internal oxides or depletion zones when oxidized. The term depletion zone is used here to mean the loss during oxidation of elements from the alloy near the scale-alloy interface. It includes the situation where, in a single-phase alloy, the next lower phase is stabilized near the interface and the situation where, in a multiphase alloy, one of the phases is no longer stable near the interface. No depletion zones were observed in any of the γ alloys. No internal oxide was observed in any of the β alloys. The γ alloys with internal oxides had morphologies similar to Ni-10Al (fig. 13). Those without an internal oxide appear as in figure 14. In the particular case illustrated in figure 14, the oxide scale was not very adherent. All γ' alloys had complex scales of various thicknesses.

TABLE IV. - OXIDIZED ALLOYS WITH AN INTERNAL OXIDE
OR A DEPLETION ZONE

[1100° C, air]

Phase	Internal oxide		Depletion zone	
	Isothermal (100 hr)	Cyclic (100, 1-hr cycles)	Isothermal (100 hr)	Cyclic (100, 1-hr cycles)
γ	Ni-10Al	Ni-10Al	(b)	(b)
	Ni-9Al-1Cr	Ni-9Al-1Cr[a]		
	Ni-7Al-3Cr	Ni-7Al-3Cr[a]		
	Ni-10Cr	-----------		
	Ni-7Al-3Si	Ni-7Al-3Si		
	Ni-7Al-3Ti	Ni-7Al-3Ti[a]		
	Ni-10Ti	-----------		
γ'	-----------	-----------	Ni-25Al	Ni-25Al
	-----------	-----------	-----------	Ni-24Al-1Cr
	-----------	-----------	-----------	Ni-22Al-3Cr
	-----------	-----------	Ni-15Al-10Cr	Ni-15Al-10Cr
	-----------	Ni-15Al-10Si	Ni-15Al-10Si	Ni-15Al-10Si
	-----------	-----------	-----------	Ni-24Al-1Ti
	Ni-22Al-3Ti	Ni-22Al-3Ti	Ni-22Al-3Ti	Ni-22Al-3Ti
	-----------	-----------	Ni-15Al-10Ti	Ni-15Al-10Ti[c]
β	(d)	(d)	Ni-40Al-10Ti[e]	Ni-40Al-10Ti[e]

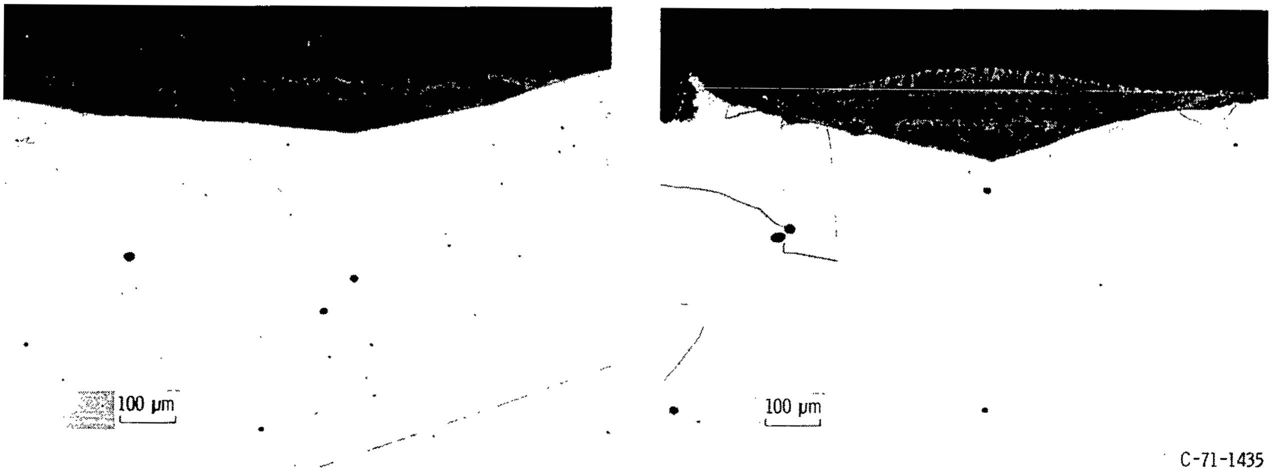
[a] 15 cycles.
[b] No γ alloys had a depletion zone.
[c] 27 cycles.
[d] No β alloys had an internal oxide.
[e] As-cast material not single phase.



(a) Isothermally oxidized and etched.

(b) Cyclically oxidized and etched.

Figure 13. - Ni-10Al oxidized in air at 1100° C for 100 hours at temperature. Note presence of internal oxide.



(a) Isothermally oxidized and etched.

(b) Cyclically oxidized and etched.

Figure 14. - Ni-9Al-1Si oxidized in air at 1100° C for 100 hours at temperature. Note absence of internal oxide.

Figure 15 shows a typical γ' alloy with a complex scale and a depletion zone. The sharp boundary of this zone suggests that a new phase, in this case γ, was formed. All the γ' alloys that had depletion zones were of this type, showing surface stabilization of γ. The thickness of the zone varied with the original composition of the alloy. Of the β alloys, the 1-atomic-percent Cr, and the 1- and 3-atomic-percent Si, and the 1- and 3-atomic-percent Ti had thin, single-layer scales as shown in figure 16 for Ni-50Al. Figure 16 is typical of these alloys. The 3- and 10-atomic-percent Cr, the 10-atomic-percent Si, and the 10-atomic-percent Ti had complex scales, as seen, for

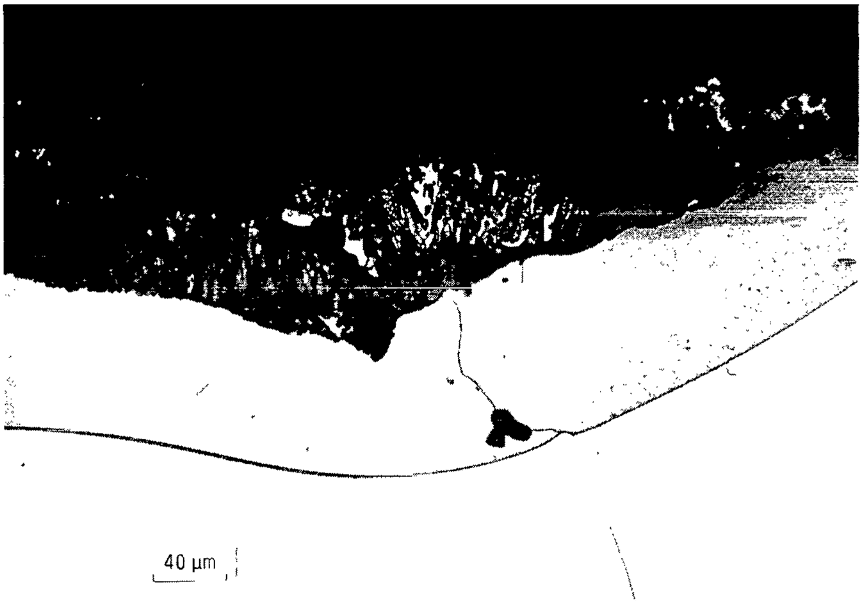


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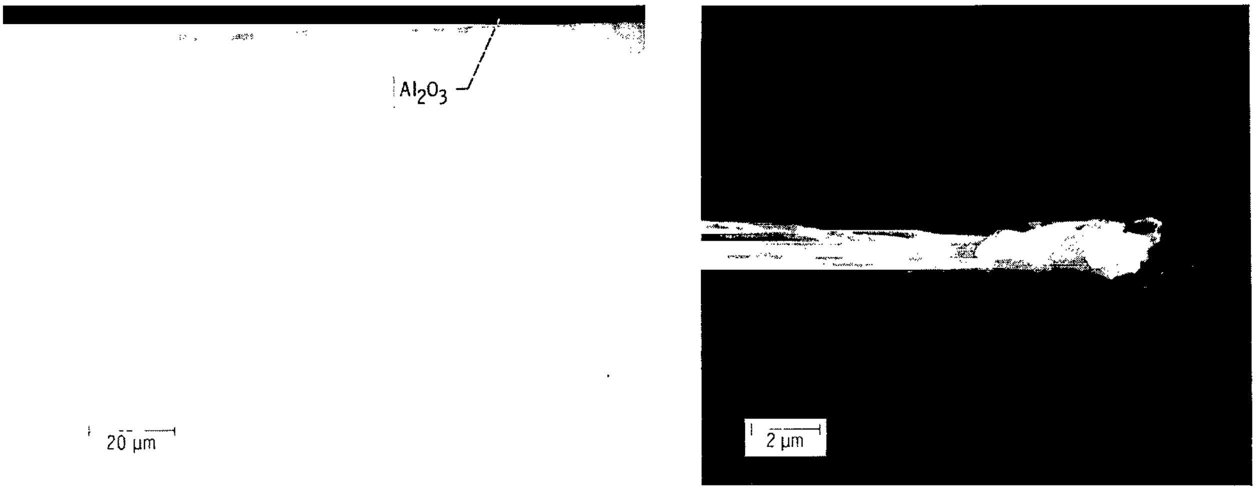
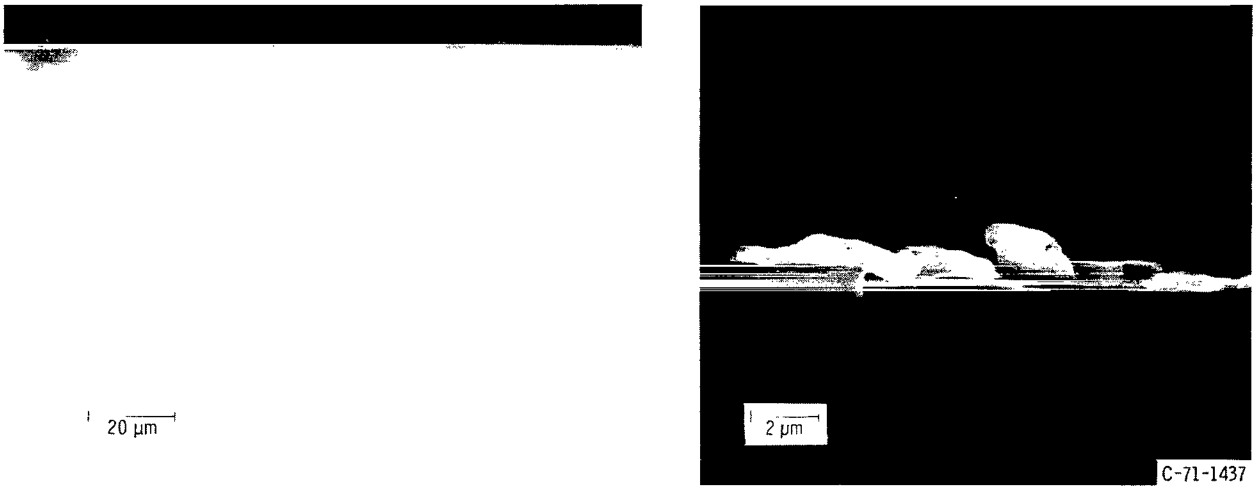
Figure 15. - Ni-15Al-10Si isothermally oxidized in air at 1100° C for 100 hours and etched. Note depletion zone with sharp boundaries beneath a complex scale.

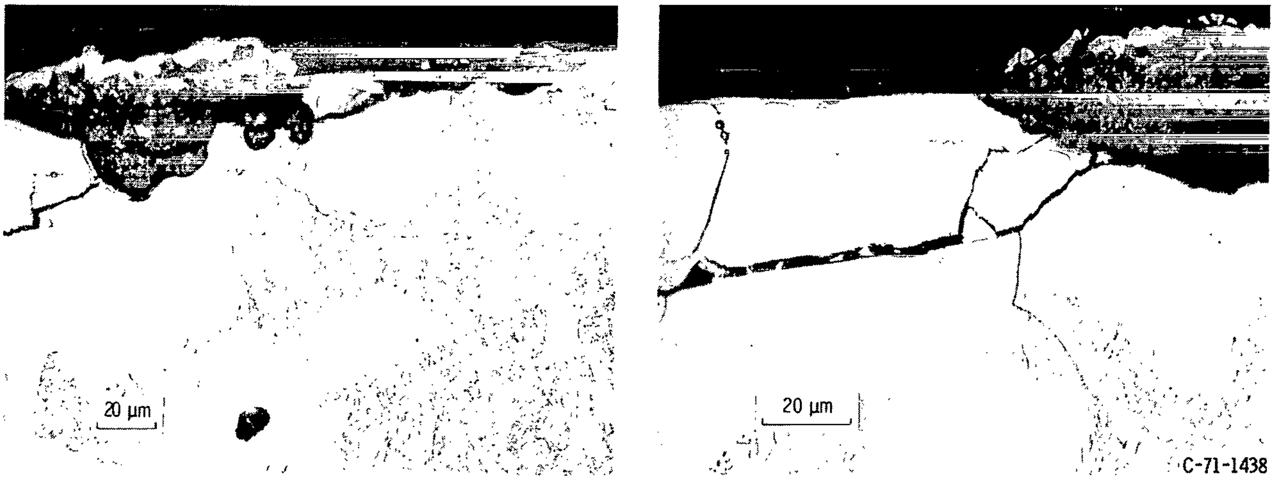


(a) Isothermally oxidized and etched.



(b) Cyclically oxidized and etched.

Figure 16. - Ni-50Al oxidized in air at 1100° C for 100 hours at temperature. Note a single layer scale of Al_2O_3.



(a) Isothermally oxidized and etched.

(b) Cyclically oxidized and etched.

Figure 17. - Ni-40Al-10Ti oxidized in air at 1100° C for 100 hours at temperature. Note complex scale. (The as-cast material was not single phase.)

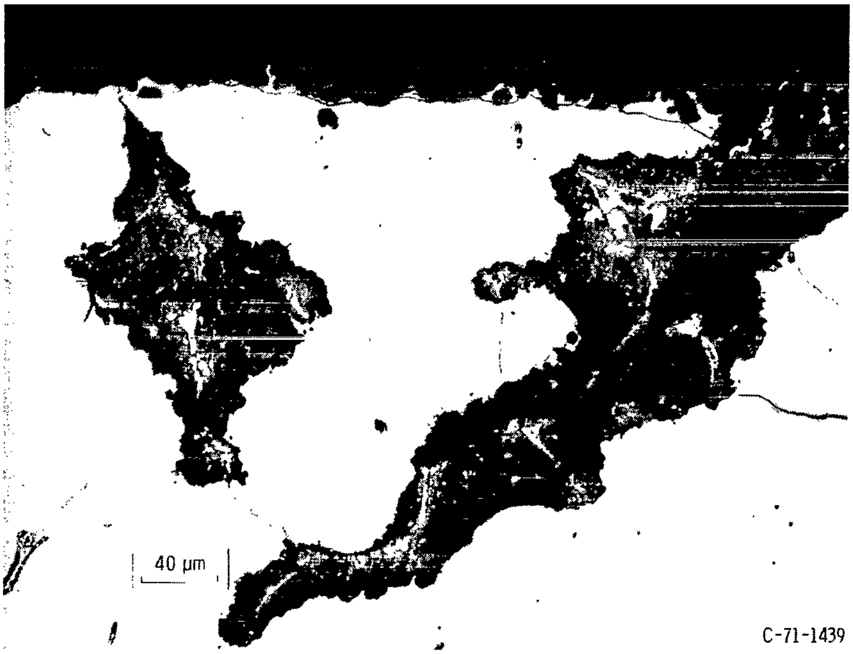


Figure 18. - Ni-40Al-10Cr cyclically oxidized in air at 1100° C for 100 hours at temperature and etched. Massive grain boundary attack shown occurred at only a few points along the alloy scale interface. (The as-cast material was not single phase.)

example, in figure 17 for the 10-atomic-percent Ti alloy. The 10-atomic-percent Cr displayed massive grain boundary attack at a few points along the alloy-scale interface as well as a complex scale (fig. 18). Electron microprobe scans showed Cr to be the predominant element in these oxidized grain boundaries.

DISCUSSION

Erroneous conclusions regarding the comparative oxidation resistance of a group of materials are possible if judgment is based solely on one criterion. For example, the net specific weight change for Ni-15Al-10Si is less than that for Ni-25Al (fig. 11(c)). Based on this observation it could be concluded that Ni-15Al-10Si is more oxidation resistant than Ni-25Al. However, if all the data given here are considered, then clearly Ni-25Al is more oxidation resistant. In this case the parabolic rate constant for Ni-15Al-10Si (which forms an internal oxide and a depletion zone) is two orders of magnitude greater than for Ni-25Al (table III). Thus, Ni-15Al-10Si may spall less but the amount of alloy consumed is greater. That this is the case is also evident from the recession data (fig. 5). Even isothermal weight changes by themselves may be misleading because of, for example, the vaporization of reaction products. Chromium, vanadium, molybdenum, and tungsten bearing alloys are known to form volatile oxides (ref. 12). From an engineering point of view the most meaningful oxidation parameter (or corrosion parameter in general) is the amount of alloy recession. Recession rates can help the designer to calculate the loss in load bearing capacity, assuming that an alloy of specified thickness will behave mechanically the same as a corroded alloy of the same thickness of unaffected alloy. There are difficulties, however, in the determination of alloy recession by thickness measurements. It is a destructive test and requires numerous specimens if it is used for following the rate of oxidation. Nonuniform interfaces, which are frequently encountered in oxidation, greatly diminish the accuracy of the measurement. Finally, the actual boundary of the unaffected alloy may be mistaken because dissolved or depleted elements may not be revealed by an optical observation.

In this study four criteria were used to determine those compositions with oxidation resistance better than their respective Ni-Al binary alloy. The criteria are (1) alloy recession (isothermal), (2) alloy recession (cyclic), (3) kinetic data (log-log curves), and (4) net specific weight change during cyclic oxidation. Those compositions found to be better than their respective binary alloy in at least one criterion and as good as in the remaining criteria were judged more oxidation resistant than their respective binary alloy.

Among the γ alloys Ni-9Al-1Si was the only one more oxidation resistant than Ni-10Al. None of the γ alloys were better than Ni. Among the γ' alloys Ni-24Al-1Si and Ni-22Al-3Si were more oxidation resistant than Ni-25Al. The γ' alloys with 0, 1, and 3 atomic percent of Cr, Si or Ti were more oxidation resistant than Ni. Of the β alloys, the only composition more oxidation resistant than Ni-50Al was Ni-49Al-1Si. However, the as-cast material was not single phase. All the β alloys were more oxidation resistant than Ni.

The better oxidation resistant alloys cited above had the following in common: all contained Si, none had an internal oxide nor a depletion zone, and none had an overall parabolic oxidation rate. The isothermal log-log curves for these alloys had varying slopes which decreased with time.

Based on these four criteria, the poorest oxidation resistant γ alloys were judged to be those with 10-atomic-percent Cr or Ti and the poorest γ' alloys were those with 10-atomic-percent Cr, Si, or Ti. The poorest β alloys were also those with 10-atomic-percent Cr, Si, or Ti.

SUMMARY OF RESULTS

Isothermal and cyclic oxidation of γ, γ', and β phase alloys of the nickel-aluminum (Ni-Al) system were performed at 1100° C (2012° F) for up to 100 hours at temperature. The cast alloys contained 0, 1, 3, and 10 atomic percents of chromium (Cr), silicon (Si), or titanium (Ti) substituted for the Al in Ni-10Al (γ), Ni-25Al (γ'), and Ni-50Al (β). Alloy thickness changes and weight changes were measured, and the oxidation products examined by X-ray diffraction and by metallography. Combining the information from all measurements and observations, a qualitative judgment of the oxidation resistance of each composition was made. Each composition was compared with the behavior of unalloyed nickel and the appropriate binary γ, γ', or β alloy. These comparison may be summarized as follows:

1. All γ alloys had poorer oxidation resistance than Ni. Only the 1-atomic-percent Si alloy was more oxidation resistant than Ni-10Al. The compositions with 10-atomic-percent Cr or Ti had the least oxidation resistance of the γ alloys.

2. The γ' alloys with 0-, 1-, and 3-atomic-percent Cr, Si, or Ti were more oxidation resistant than Ni. Those with 1- and 3-atomic-percent Si were more resistant than Ni-25Al and as resistant as the best of the β alloys. The compositions with 10-atomic-percent Cr, Si, or Ti had the least oxidation resistance of the γ' alloys.

3. All the β alloys were more oxidation resistant than Ni, but those with 10-atomic-percent Cr, Si, or Ti were less oxidation resistant than the other β alloys. The 1-atomic-percent Si was more oxidation resistant than Ni-50Al, but the as-cast material was not single phase.

4. The better oxidation resistant alloys cited had the following in common: all contained Si, none had an internal oxide nor a depletion zone, and none had an overall parabolic oxidation rate. The isothermal log-log curves for these alloys had varying slopes which decreased with time.

Lewis Research Center,
National Aeronautics and Space Administration,
Cleveland, Ohio, April 6, 1971,
129-03.

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