

UNIVERSITY OF ARKANSAS

Oxidation And Agglomeration Resistance Of Thin Gage Dispersion Strengthened Alloys

Final Report



for

The National Aeronautics & Space Administration
Grant NGR 04-001-029

FACILITY FORM 602	N71-11573 (ACCESSION NUMBER)	_____ (THRU)
	44 (PAGES)	01 G3 (CODE)
	NASA-CR-111807 (NASA CR OR TMX OR AD NUMBER)	17 (CATEGORY)

JUNE 1970

Dept. of Mechanical Engineering
D. M. Scruggs Principal Investigator

N 71 11573

CR 111807

OXIDATION AND AGGLOMERATION
RESISTANCE OF THIN GAGE
DISPERSION STRENGTHENED
ALLOYS

FINAL REPORT

D. M. Scruggs
Department of Mechanical Engineering
University of Arkansas

30 June 1970

For
The National Aeronautics & Space Administration
Grant NGR 04-001-029

.

FOREWORD

This work was carried out under the guidance of Mr. Bland Stein of NASA Langley. His support and suggestions are gratefully acknowledged.

Two research assistants contributed in great measure to this work, C. K. Moore and H. M. Foote. We are indebted to Mr. K. S. Kim for his excellent efforts with the Electron Microscope.

TABLE OF CONTENTS

	Page
FOREWORD	i
LIST OF TABLES	iii
LIST OF FIGURES	v
SUMMARY	1
INTRODUCTION	2
EXPERIMENTAL PROCEDURES	6
RESULTS	8
DISCUSSION	29
CONCLUSIONS AND RECOMMENDATIONS	31
APPENDIX	33
BIBLIOGRAPHY	35

LIST OF TABLES

Table No.	Title	Page
I	Oxidation rates of an 80 Ni - 20 Cr alloy.	3
II	Dispersion strengthened alloys examined in the present study.	6
III	Four alloys examined in the present study and the etchants used for metallographic examination.	7
IV	Oxidation weight change for nickel-2% thoria at various times and temperatures in air at ambient and 8 Torr pressure.	9
V	Oxidation weight change for 80 nickel-20 chromium-2% thoria at various times and temperatures in air at ambient and 8 Torr pressure.	11
VI	Oxidation weight change for 62 cobalt-18 chromium-20 nickel 2 volume percent thoria at various times and temperatures in air at ambient and 8 Torr pressure.	13
VII	Oxidation weight change for 50 cobalt-30 chromium-20 nickel 2 volume percent thoria at various times and temperatures in air at ambient and 8 Torr pressure.	14
VIII	Microhardness (DPH) of nickel-2 volume percent thoria alloy after 1000 hours at specified temperatures and pressures.	18
IX	Microhardness (DPH) of nickel-2 volume percent thoria alloy at various times and temperatures at ambient pressure.	18
X	Microhardness (DPH) of nickel-2 volume percent thoria alloy at various times and temperatures at a pressure of 8 Torr.	19

XI	Microhardness (DPH) of 80 nickel-20 chromium-2 volume percent thoria alloy after 3000 hours at specified temperatures and pressures.	19
XII	Microhardness (DPH) of 80 nickel-20 chromium-2 volume percent thoria alloy at various times during exposure to 2000 F at two different pressures.	20
XIII	Microhardness (DPH) of cobalt-20 nickel-18 chromium-2 volume percent thoria alloy after 1000 hours at specified temperatures and pressures.	20
XIV	Microhardness (DPH) of cobalt-20 nickel-18 chromium-2 volume percent thoria alloy at various times during exposure to 2000 F at two different pressures.	21
XV	Microhardness (DPH) of cobalt-20 nickel-30 chromium-2 volume percent thoria alloy after 1000 hours at specified temperatures and pressures.	21
XVI	Microhardness (DPH) of cobalt-20 nickel-30 chromium-2 volume percent thoria alloy at various times during exposure to 2000 F at two different pressures.	22

LIST OF FIGURES

Figure No.	Title	Page
1.	The total metal loss in inches $\times 10^{-3}$ (mils) for nickel - 2 volume percent thoria sheet as a function of time and temperature.	10
2.	The total metal loss in inches $\times 10^{-3}$ (mils) for 80 nickel - 20 chromium - 2 volume percent thoria sheet as a function of time and temperature.	12
3.	TD Ni alloy after 1000 hours at 1400 F (760 C) and ambient pressure. 800X	16
4.	Porous oxide scale (upper portion of photograph) on TD Ni after 1000 hours at 2000 F (1093 C) at ambient pressure. 800X	16
5.	Oxide clusters in TD NiCr after 70 hours at 2000 F (1093 C) and 8 Torr. 800X	16
6.	Second phase oxide particles (cubic in appearance) in the oxide scale of TD NiCr. This is a 1000 hour, 1800 F (982 C) ambient pressure sample. 800X	16
7.	Plane polarized light micrograph of second phase oxide particles in the oxide scale of TD NiCr exposed for 3000 hours at 2000 F (ambient pressure). 800X	17
8.	Typical structure of TD Co alloy after exposure for any given time or temperature. This sample is 316 hours at 1800 F in air. 800X	17
9.	Rare occurrence of continuous oxide in TD Co alloy. This sample is 1000 hours at 1800 F and 8 Torr. 800X	17
10.	Typical structure of TD Co+ alloy after exposure. This sample is 1000 hours at 1800 F and 8 Torr. 800X	17

11.	Electron micrograph of a replica of a TD Ni sample exposed 1000 hours at 1800 F (982 C) at ambient pressure. 30,000X	23
12.	Electron micrograph of a replica of as-received TD NiCr. 30,000X	23
13.	Electron micrograph of a replica of a TD NiCr sample after 3000 hours exposure at 2000 F (1093 C) and ambient pressure. 30,000X	24
14.	Electron micrograph of TD Co as-received (replica). 30,000X	24
15.	Electron micrograph of TD Co replicated sample after 1000 hours exposure at 2000 F (1093 C) and 8 Torr. 30,000X	25
16.	Electron micrograph of a replica of TD Co+ after 1000 hours exposure at 2000 F (1093 C) and 8 Torr. 30,000X	25
17.	Cumulative particle size distribution of thorium in TD Ni after 1000 hours at 1800 F (982 C) and ambient pressure.	26
18.	Cumulative particle size distribution of thorium in TD NiCr after 1000 hour exposure at 2000 F (1093 C) and ambient pressure.	26
19.	Cumulative particle size distribution of thorium in TD Co after 1000 hours at 2000 F (1093 C) and ambient pressure, together with the as-received distribution.	27
20.	Cumulative particle size distribution of thorium in TD Co+ after 1000 hours at 2000 F (1093 C) and 8 Torr.	28
1A.	Schematic of oxidation test apparatus consisting of mirror image furnace tubes with 5 heat zones in each and one side maintained at 8 Torr by pumping against a controlled leak at H.	34

SUMMARY

Four potential candidate materials for thin sheet aircraft applications were tested in air at 760 and 8 Torr in the temperature range 1200 to 2000 F (650 to 1093 C). All materials were dispersion strengthened with thoria, 2 volume percent, and were nickel base (TD Ni), 80 nickel - 20 chromium (TD NiCr), cobalt base - 20 nickel - 18 chromium (TD Co), and cobalt - 20 nickel - 30 chromium (TD Co+).

The exposed specimens were examined by optical microscopy, microhardness testing, electron microscopy, and thoria particle size analysis.

Oxidation rate data were collected. Microscopy of the TD NiCr suggested that controversy over the composition of the oxide layer on nickel - chromium alloys may be traceable to the formation of a chromium sesqui-oxide (Cr_2O_3) layer saturated with nickel - chromium spinel (NiOCr_2O_3), that precipitates upon slow cooling from elevated temperatures. TD NiCr scaled at 1600 F (870 C) and below while the cobalt alloys exhibited excellent scaling resistance.

All alloys showed evidence of softening at time and temperature. Particle size analysis demonstrated that no agglomeration of thoria had occurred. Softening was attributed to relaxation of retained cold work except for the low pressure cobalt base samples. The greater softening of these samples was attributed to selective chromium loss by evaporation.

Because of severe oxidation and scaling TD Ni is not recommended for high altitude, high Mach number service. Pre-oxidized TD NiCr is acceptable at all temperatures to 2000 F (1093 C) for at least 3000 hours and both TD cobalt alloys to at least 1000 hours.

INTRODUCTION

There exists a need for thin gage oxidation resistant superalloys for the skin of high-flying high Mach number aircraft of the future as well as thin gage afterburner shells, furnace walls and the like.

The principal objective of this study was to determine the suitability of dispersion strengthened alloys for this kind of service. The temperature range of interest was 1200 to 2000 F and the air pressure variation 8 Torr to ambient.

Properties to be examined were resistance to oxidation and resistance to agglomeration of the dispersoid.

Secondary objectives were to examine the oxidation behavior and to explain the mechanism of agglomeration, where it occurred.

It was desired to examine all candidate alloys that exhibited reasonable oxidation resistance. All available alloys or those under development were nickel-chromium or nickel-cobalt-chromium analysis, with thorium as the principal dispersoid.

Oxidation behavior of these alloys was of interest in three respects. First, the effect of long-time exposure on thin sheet was uncertain; and second, the effect at 8 Torr needed to be examined. Third, the literature concerning the oxidation behavior of nickel-chromium alloys was not at all in agreement on the oxidation mechanism involved.

Before examining nickel-chromium the oxidation behavior of pure nickel is of interest. This topic is covered in detail by Hauffe¹. The oxidation of nickel forms an adherent layer of NiO, which is a p type semi-

conductor. The rate controlling mechanism is by Ni diffusion through the oxide layer. The ΔH for the process between 750 and 1650 F (400 and 900 C) is 34 kcal/mole and ΔS is -17.3 cal/mole - °C.

Hauffe refers to work by Wagner and Zimens and Pfeiffer and Hauffe, that shows a small amount of chromium increases the oxidation rate as would be expected since the Cr^{+3} increases the electronic conductivity of the NiO .

Hauffe published data from two sources showing that more than 6 percent chromium in nickel reduces the accelerating effect of smaller amounts of chromium, at least at 1800 F (982 C). Beyond that point nickel chromium alloys are more oxidation resistant than nickel.

Table I is a compilation of data on 80 Ni - 20 Cr alloy by Gulbransen and Andrew².

Table I

T, °F	T, °C	k'' , gm^2/cm^4 - sec.	ΔH	ΔS	ΔF
1200	650	2.32×10^{-15}	38,150	-15.7	52,650
1380	750	1.46×10^{-14}	38,150	-16.2	54,750
1560	850	9.49×10^{-14}	38,150	-15.8	55,900
1610	875	1.81×10^{-13}	38,150	-15.1	55,450

Oxidation rates of an 80 Ni - 20 Cr alloy.

Note: k'' is the parabolic rate constant in the equation: $E^2 = k''t$

(where t is time, and E is scale thickness).

These rates compare to about 6×10^{-13} at 1607 F (875 C) for ultra pure nickel¹. Other rate data can be found in Gulbransen and Andrew³, Wood and Hodgkiess⁴, Ignatov and Shamgunova⁵, and Jones and Westerman⁶, the latter reference concerned with the oxidation rate of a nickel alloy containing

2% dispersed thoria. Wilcox and Clauer⁷ and Cole, et al.⁸, have made further observations of nickel-chromium dispersion strengthened with thoria. These authors agree on at least three points:

1. Alloys of 80 nickel - 20 chromium are superior to pure nickel, insofar as oxidation rate is concerned.
2. Minor impurities or small alloy additions have a marked effect on rate.
3. At reasonable times (10 hrs.) and temperatures (above 1380 F (750 C)), the protective oxide layer is not NiO.

Beyond these points, however, the actual mechanism of oxidation is much in question.

Hauffe¹ discusses the oxidation mechanism of nickel chromium alloys in detail, p. 170 - 193, and concludes that because of CrO_3 volatilization, NiCr_2O_4 spinel is favored at 2012 F (1100 C) and above and that the formation of Cr_2O_3 is improbable. Ignatov and Shamgunova⁵ report $\alpha - \text{Cr}_2\text{O}_3$ formation below 1292 F (700 C) and double layer films above 1472 F (800 C) with the outer layer consisting of NiCr_2O_4 . X-ray examination of these layers indicated a quite consistent spinel with a lattice parameter of 8.31 Å. Unfortunately, the chemical analysis of the specimen alloy is not completely given in regard to Mn, Fe, etc. content. These elements are very important in regard to spinel formation. Gulbransen and Andrew³ report only small traces of NiCr_2O_4 spinel up to and including 2012 F (1100 C) in Ni - Cr heater alloys but express dissatisfaction with the X-ray diffraction of oxide scales. Burks and Rickert⁹ examined nickel alloys containing 30, 60, and 80 percent chromium. In all cases only Cr_2O_3 was found. They further calculate that chromium content in the alloy

must fall to about 10^{-7} before NiCr_2O_4 becomes the stable phase at 2012 F (1100 C). Wood and Hodgkiess⁴ conclude that only Cr_2O_3 scale occurs on nickel - chromium alloys with greater than 14.6% chromium. They worked with high purity alloy stock, and base their conclusions entirely on micro-probe analysis. They mention a re-occurring layer in a stratified scale of 49 nickel, 22 chromium. This amounts to a 2:1 atom ratio of Ni to Cr, which could well be a 3:1 mixture of NiO and NiCr_2O_4 . Unfortunately, they did not attempt any X-ray diffraction experiments.

Previous work concerning the stability of dispersion strengthened alloys has generally been directed toward short times at high temperatures.

Worn and Marton¹⁰ studied thoria dispersed in nickel and concluded that iron, chromium, and sulfur contamination favored coarsening of the dispersoid. Weeton and Quatnetz¹¹ demonstrated that sulfur contamination caused definite agglomeration in thoria dispersed nickel. They concluded that hydrogen cleaning has a favorable effect on dispersoid stability.

Chang¹² examined an 80 nickel - 20 chromium - thoria alloy containing about 5% diffused aluminum held at 2300 F (1260 C) for 200 hours. No agglomeration was detected. Raymond and Neumann¹³ studied the high temperature stability of two 80 nickel - 20 chromium - 2 volume percent thoria alloys from two different sources. Softening occurred in one alloy at temperatures above 1800 F (982 C). This alloy had a larger average particle size as fabricated, and suffered an apparent growth in average particle size from 820 Å to 885 Å. The second alloy was a product produced by a DuPont process and was apparently stable for 1 hour exposures at all temperatures in the study, up to 2400 F (1315 C).

EXPERIMENTAL PROCEDURES

Four different materials were examined during this study, Table II.

Number	Alloy Composition	Code
1	Nickel + 2 volume percent thoria	(TD Ni)
2	80 nickel - 20 chromium - 2% thoria	(TD NiCr)
3	Cobalt - 20 nickel - 18 chromium - 2% thoria	(TD Co)
4	Cobalt - 20 nickel - 30 chromium - 2% thoria	(TD Co+)

Table II

Dispersion strengthened alloys
examined in the present study.

All the alloys are products of the Fansteel Metallurgical Co. with alloys 1 and 2 furnished by that company and alloys 3 and 4 furnished from an Air Force-Pratt Whitney program. These alloys will be referred to by the short form code listed in Table II. TD Ni was used as 13-15 mil sheet, TD NiCr as 10 mil sheet, and because of shortage of alloy the cobalt base alloys were used as small pieces primarily 30 to 40 mils thick.

The TD Ni and TD NiCr were cut into coupons about 1 square inch. All samples were cleaned, weighed, and measured. The alloy samples were then exposed at 1200, 1400, 1600, 1800, and 2000 F at 8 Torr and ambient pressure in a twin gradient furnace, which is described in detail in the Appendix.

The furnace was cooled slowly at intervals and samples removed. The samples were visually examined, weighed, and a section cut for microscopy. Pieces cut for examination were mounted in a special jig that provided a 4:1 taper section in order to estimate oxidation penetration and provide

more area for viewing.

The etchants used for the 4 alloys are listed in Table III.

Code	Composition	Etch
TD Ni	100 nickel - 2% thoria	3 HNO ₃ : 2 Acetic Acid
TD NiCr	80 nickel - 20 chromium - 2% thoria	3 HCl: 1.5 HNO ₃ : 10 H ₂ O + CuCl ₂
TD Co	Cobalt - 20 nickel - 18 chromium - 2% thoria	Marbles reagent
TD Co+	Cobalt - 20 nickel - 30 chromium - 2% thoria	Marbles reagent

Table III

Four alloys examined in the present study and the etchants used for metallographic examination.

Microhardness readings were taken using a Bergsman tester, vickers diamond, and a 100 gm. load.

Particle size determination and distribution was carried out using replica electron microscope techniques, a Ziess TGZ-3 counter, and micrographs at 30,000 X.

RESULTS

Three kinds of data were evaluated concerning oxidation behavior; these were weight change, metal loss, and scaling behavior.

The TD Ni exhibited progressive weight gain with increasing temperature and time at ambient pressure but showed weight loss at 8 Torr for a few specimens. These data are presented in Table IV. The loss in specimen thickness is given in figure 1. Note that the values for air agree with the earlier oxidation study of Manning et al.¹⁴ TD Ni scales at all temperatures in the study with large areas of scaling at 1200 - 1600 F (650 - 870 C).

TD NiCr proved more resistant to oxidation and scaling than TD Ni. Weight changes were small, with both gains and losses recorded, Table V. Since this alloy was received early in the program, weight changes are reported to 3000 hours. The loss in specimen thickness is shown in figure 2. This alloy is quite superior in resistance to scaling at high temperatures; however, samples scale at 1200 - 1400 F (650 - 760 C) upon cooling and the 1600 F (870 C) samples show evidence of flaking during exposure.

In oxidation behavior the TD Co and TD Co+ alloys are indistinguishable. These alloys exhibited less metal loss than the TD NiCr and have excellent scale resistance at all temperatures. Despite good scale adherence both alloys consistently lost weight, Tables VI and VII. Because of the scarcity of material, these alloys were tested only at 1600, 1800 and 2000 F (870, 982 and 1093 C).

The structural stability of the alloys was investigated through optical

Oxidation weight change for
nickel-2% thoria at various
times and temperatures in air at
ambient and 8 Torr pressure.

	Wt. Change, gms/cm ² x 10 ⁻³			
Temperature °F	at time, hrs.			
	100	316	1000	
1200	+ 0.52	+ 1.51	+ 0.43	Ambient Air
1400	+ 1.72	+ 2.39	+ 2.48	
1600	+ 5.15	+ 4.65	+ 7.68	
1800	+ 8.42	+ 13.20	+ 17.80	
2000	+ 18.25	+ 25.40	+ 56.60	
1200	+ 0.27	- 0.12	+ 0.49	8 Torr
1400	+ 1.12	+ 1.04	+ 1.55	
1600	+ 2.26	+ 2.96	+ 5.05	
1800	+ 7.03	- 17.33	- 4.61	
2000	+ 13.60	+ 12.10	+ 2.12	

Table IV

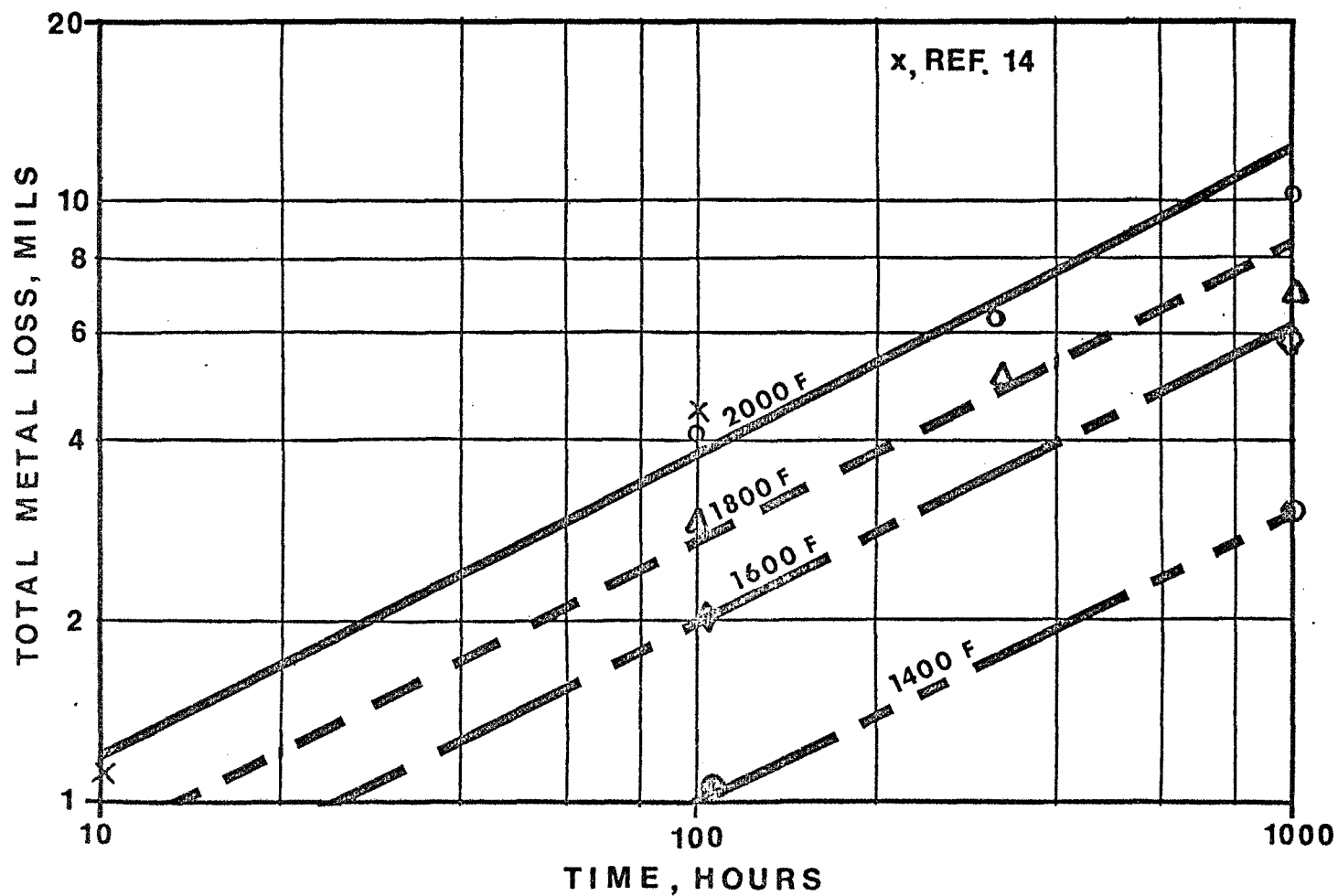


Figure 1. The total metal loss in inches $\times 10^{-3}$ (mils) for nickel - 2 volume percent thoria sheet as a function of time and temperature in air.

Two data points are included from Manning et al.¹⁴ by converting their weight gain data into metal thickness loss. The results given for 1800 F in air are the same as 2000 F, 8 Torr within experimental error.

Oxidation weight change for
80 nickel-20 chromium-2% thoria at various
times and temperatures in air at
ambient and 8 Torr pressure.

		Wt. Change, gms/cm ² x 10 ⁻³				
Temperature °F	at time, hrs.					
	70	316	1000	3000		
1200	-	- 3.31	- 5.27	+ 0.18	Ambient Air	
1400	-	- 3.39	+ 2.29	+ 1.85		
1600	-	0	+ 0.12	+ 0.16		
1800	+ 5.45	+ 6.85	- 3.04	- 0.49		
2000	+ 1.25	+ 4.12	- 1.00	- 3.88		
1200	-	- 1.60	- 0.86	+ 0.02	8 Torr	
1400	-	+ 1.69	+ 9.18	- 0.49		
1600	-	- 0.15	- 1.02	+ 0.24		
1800	- 1.00	- 1.58	- 7.20	+ 0.32		
2000	- 17.80	+ 1.63	+ 1.40	- 9.93		

Table V

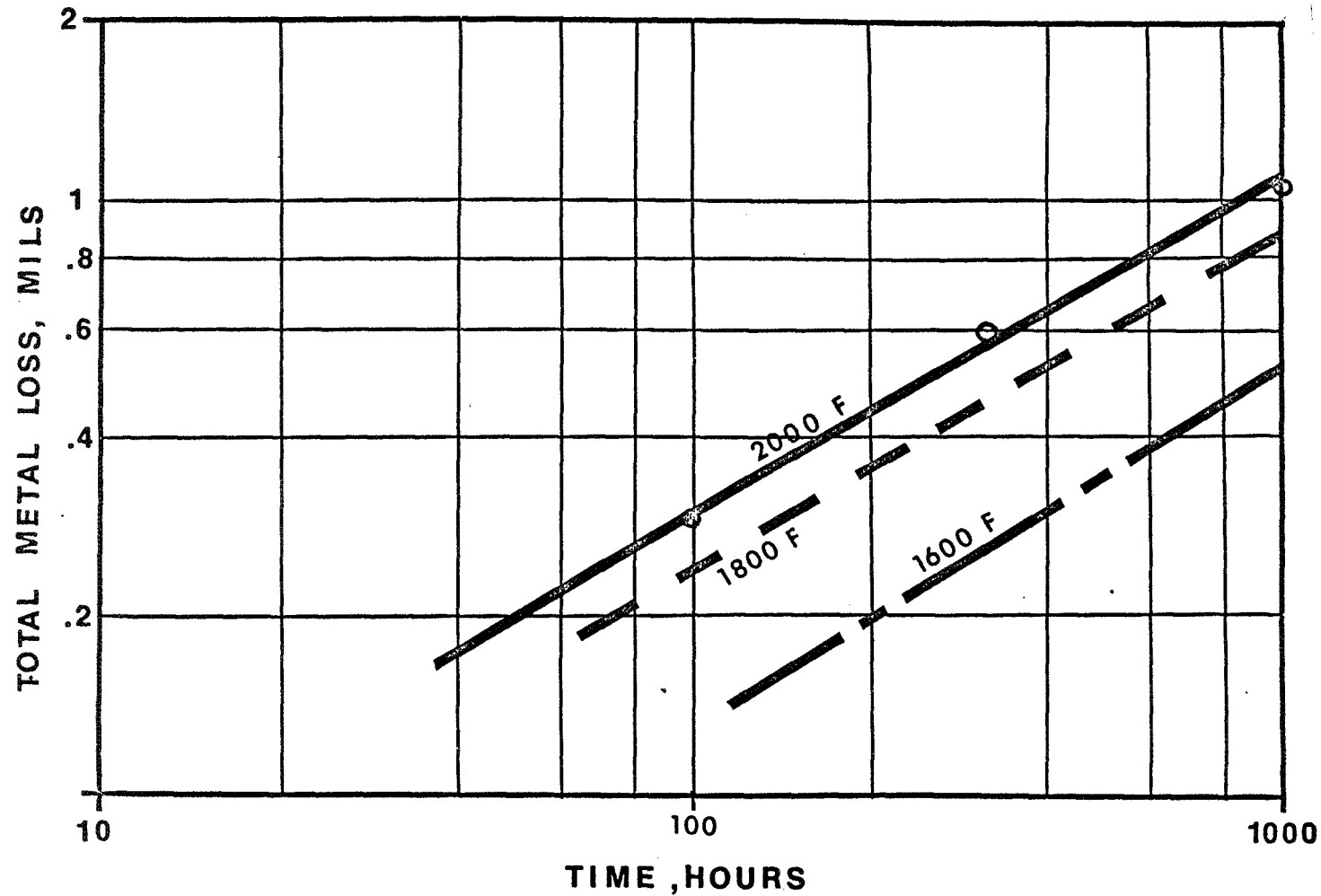


Figure 2. The total metal loss in inches $\times 10^{-3}$ (mils) for 80 nickel - 20 chromium - 2 volume percent thoria sheet as a function of time and temperature in air.

The results for ambient pressure are the same as those for 8 Torr within experimental error. Note that these results differ by an order of magnitude from those in figure 1 for unalloyed nickel - thoria.

Oxidation weight change for
62 cobalt-18 chromium-20 nickel
2 volume percent thoria at various
times and temperatures in air at
ambient and 8 Torr pressure.

		Wt. Change, gms/cm ² x 10 ⁻³			
Temperature °F	at time, hrs.				
	100	316	1000		
1600	- 4.25	- 1.55	+ 1.48	Ambient Air	
1800	- 0.40	- 1.74	- 1.58		
2000	+ 2.22	- 2.52	- 0.79		
1600	- 1.98	- 1.50	- 0.52	8 Torr	
1800	- 4.70	- 2.61	- 1.35		
2000	- 3.21	- 3.96	- 3.20		

Table VI

Oxidation weight change for
50 cobalt-30 chromium-20 nickel
2 volume percent thoria at various
times and temperatures in air at
ambient and 8 Torr pressure.

	Wt. Change, gms/cm ² x 10 ⁻¹³			
Temperature °F	at time, hrs.			
	100	316	1000	
1600	- 2.20	- 3.02	- 0.74	Ambient Air
1800	- 2.80	- 3.56	- 1.17	
2000	- 1.27	- 2.73	- 2.00	
1600	- 1.66	- 1.87	- 1.91	8 Torr
1800	- 3.66	- 4.11	- 1.62	
2000	- 1.87	- 4.58	- 1.96	

Table VII

microscopy, microhardness testing, electron microscopy, and subsequent particle size analysis.

The TD Ni and TD NiCr alloys were characterized by the formation of hollow sphere groupings of the large inclusion-like oxides visible in the optical microscope. A representative area of the TD Ni alloy after 1000 hours at 1400 F (760 C) at ambient pressure is shown in figure 3 at 800X. The porous oxide formed by TD Ni at 2000 F (1093 C) for the same time and pressure is shown in figure 4. The spherical (circular) oxide grouping is shown in figure 5 which is a micrograph of TD NiCr after 70 hours at 2000 F (1093 C) and 8 Torr. The arrows point to the oxide array.

Small second-phase oxide particles in the oxide scale of TD NiCr are shown circled in figure 6 in ordinary light and in figure 7 in plane polarized light (crossed filters). The typical structure of TD Co alloy at 800X is shown in figure 8. One of the rare occurrences of continuous oxide in the cobalt base alloys is shown in figure 9. The typical structure of the TD Co+ alloy is shown in figure 10 at 800X.

Microhardness of TD Ni samples after 1000 hours exposure is given in Table VIII. Microhardness variation of ambient pressure samples with time is given in Table IX and for 8 Torr samples in Table X.

The microhardness data for TD NiCr is given in Table XI for 3000 hour exposure, and in Table XII as a function of time. Microhardness readings for TD Co and TD Co+ show a significant drop with time for 8 Torr exposure. These data are given in Tables XIII and XIV for TD Co and Tables XV and XVI for TD Co+.

Two-stage electron microscope replicas of specimens from each alloy group were examined.

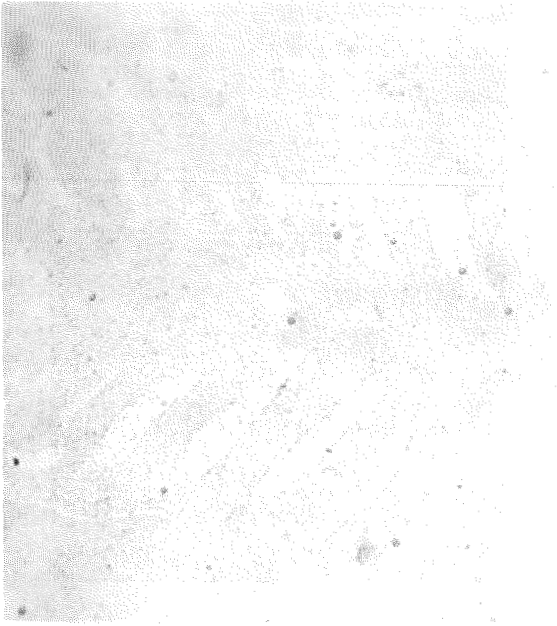


Figure 3. TD Ni alloy after 1000 hours at 1400 F (760 C) and ambient pressure. 800X

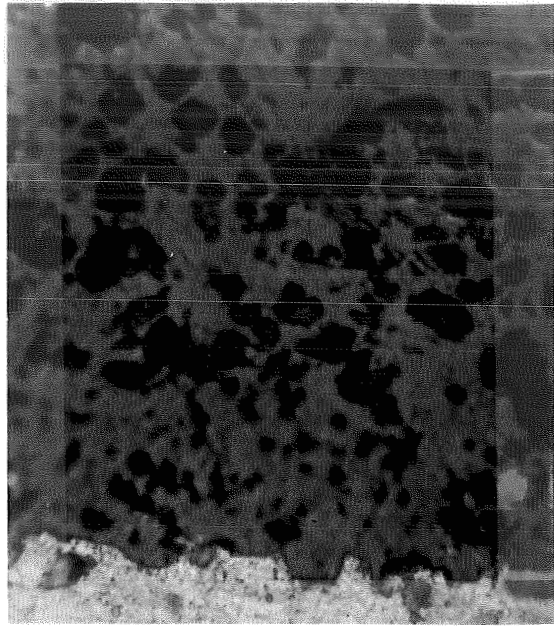


Figure 4. Porous oxide scale (upper portion of photograph) on TD Ni after 1000 hours at 2000 F (1093 C) at ambient pressure. 800X



Figure 5. Oxide clusters in TD NiCr after 70 hours at 2000 F (1093 C) and 8 Torr. 800X

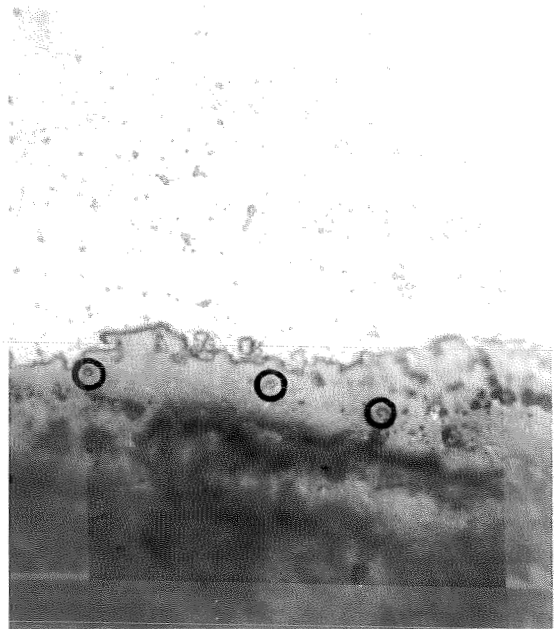


Figure 6. Second phase oxide particles (cubic in appearance) in the oxide scale of TD NiCr. This is a 1000 hour, 1800 F (982 C) ambient pressure sample. 800X

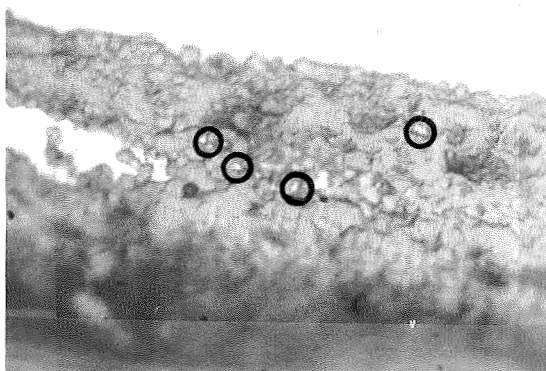


Figure 7. Plane polarized light micrograph of second phase oxide particles in the oxide scale of TD NiCr exposed for 3000 hours at 2000 F (ambient pressure). 800X

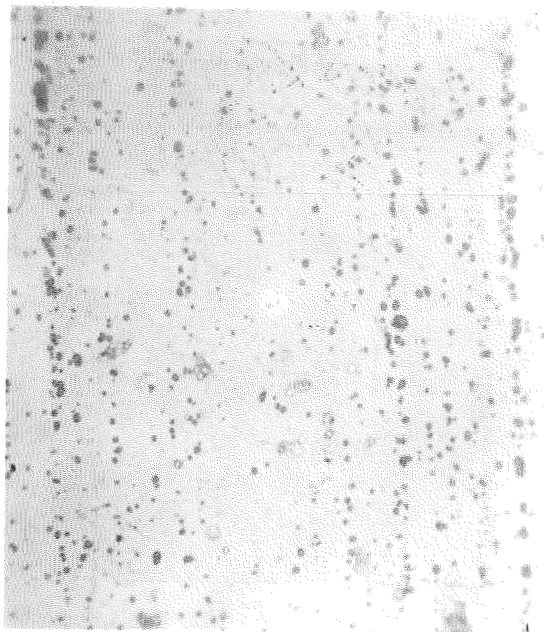


Figure 8. Typical structure of TD Co alloy after exposure for any given time or temperature. This sample is 316 hours at 1800 F in air. 800X

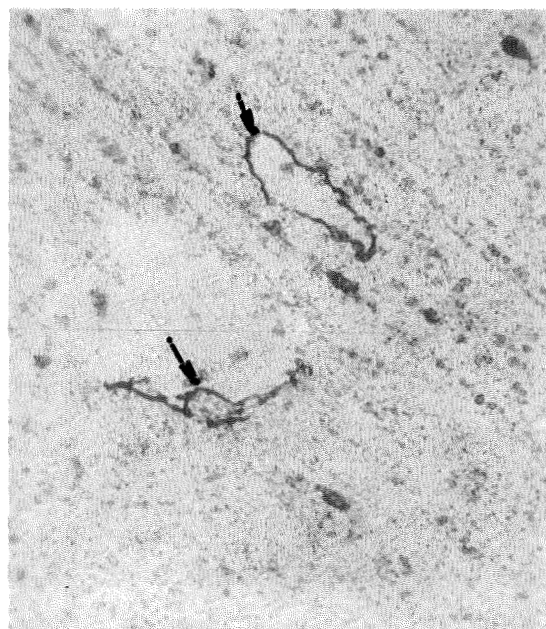


Figure 9. Rare occurrence of continuous oxide in TD Co alloy. This sample is 1000 hours at 1800 F and 8 Torr. 800X

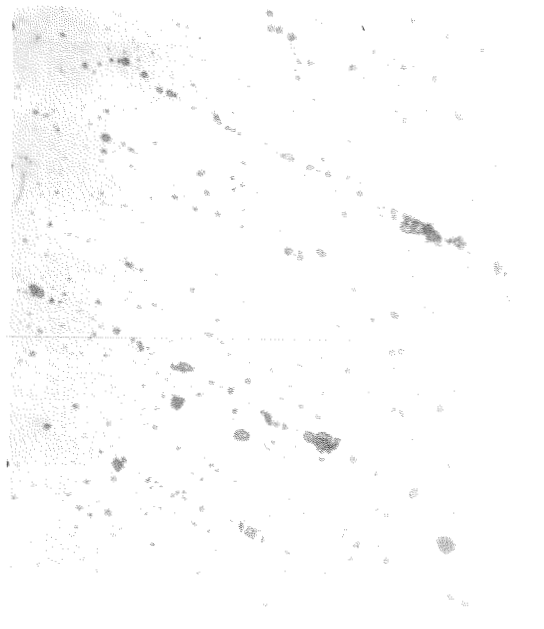


Figure 10. Typical structure of TD Co+ alloy after exposure. This sample is 1000 hours at 1800 F and 8 Torr. 800X

	As Received	Exposure Temperature °F				
		1200	1400	1600	1800	2000
Ambient Air Pressure	202	199	200	201	180	Oxidized
8 Torr	202	201	192	192	185	Oxidized

Microhardness (DPH) of nickel-
2 volume percent thoria alloy after
1000 hours at specified temperatures
and pressures.

Table VIII

Temperature °F	Time, hrs.		
	100	316	1000
1800	190	189	180
2000	193	189	Oxidized
As received hardness, 202			

Microhardness (DPH) of nickel-
2 volume percent thoria alloy at
various times and temperatures
at ambient pressure.

Table IX

Temperature °F	Time, hrs.		
	100	316	1000
1600	202	202	192
1800	201	198	185
2000	201	193	Oxidized
As received hardness, 202			

Microhardness (DPH) of nickel-
2 volume percent thoria alloy at
various times and temperatures
at a pressure of 8 Torr.

Table X

	As Received	Exposure Temperature °F				
		1200	1400	1600	1800	2000
Ambient Air Pressure	320	297	297	304	298	297
8 Torr	320	299	304	297	304	298

Microhardness (DPH) of 80 nickel-
20 chromium-2 volume percent thoria alloy
after 3000 hours at specified temperatures
and pressures.

Table XI

	As Received	Time, hrs.			
		100	316	1000	3000
Ambient Air Pressure	320	302	303	303	297
8 Torr	320	302	306	302	298

Microhardness (DPH) of 80 nickel-
20 chromium-2 volume percent thoria alloy
at various times during exposure to
2000 F at two different pressures.

Table XII

	As Received	Exposure Temperature °F		
		1600	1800	2000
Ambient Air Pressure	383	376	370	376
8 Torr	383	370	354	357

Microhardness (DPH) of
cobalt-20 nickel-18 chromium-
2 volume percent thoria alloy after
1000 hours at specified
temperatures and pressures.

Table XIII

	As Received	Time, hrs.		
		100	316	1000
Ambient Air Pressure	383	380	377	376
8 Torr	383	373	366	357

Microhardness (DPH) of
cobalt-20 nickel-18 chromium-
2 volume percent thoria
alloy at various times
during exposure to 2000 F
at two different pressures.

Table XIV

	As Received	Exposure Temperature °F		
		1600	1800	2000
Ambient Air Pressure	390	366	363	366
8 Torr	390	351	351	354

Microhardness (DPH) of
cobalt-20 nickel-30 chromium-
2 volume percent thoria alloy after
1000 hours at specified
temperatures and pressures.

Table XV

	As Received	Time, hrs.		
		100	316	1000
Ambient Air Pressure	390	387	370	366
8 Torr	390	376	366	354

Microhardness (DPH) of cobalt-
20 nickel-30 chromium-2 volume percent thoria alloy
at various times during exposure to 2000 F
at two different pressures.

Table XVI

Electron micrographs of each alloy were taken throughout the program. Figure 11 is a micrograph of TD Ni after 1000 hours exposure at 1800 F (982 C) at ambient pressure. Figure 12 is a micrograph of TD NiCr as received and Figure 13 is the same material after 3000 hours exposure at 2000 F (1093 C) at ambient pressure.

Figure 14 is an electron micrograph of TD Co as received and figure 15 is a specimen of TD Co after 1000 hours exposure at 2000 F (1093 C) at 8 Torr. Figure 16 shows the replicated structure of TD Co+ alloy after 1000 hours at 2000 F (1093 C) at 8 Torr.

The particle size distribution for TD Ni after 1000 hours at 1800 F (982 C) and ambient pressure is shown in figure 17. The particle size distribution for TD NiCr is plotted for a 1000 hour, 2000 F (1093 C), ambient pressure sample in figure 18. Data from Chang¹² for TD NiCr sheet



Figure 11. Electron micrograph of a replica of a TD Ni sample exposed 1000 hours at 1800 F (982 C) at ambient pressure. 30,000X

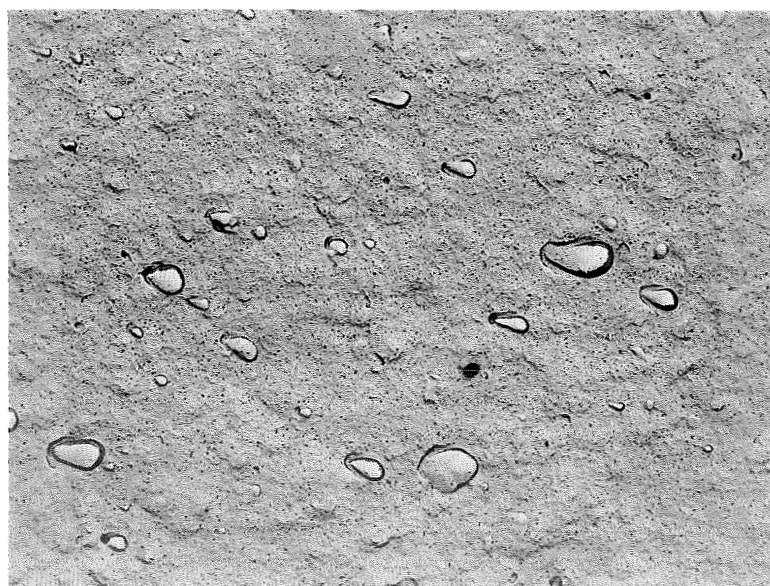


Figure 12. Electron micrograph of a replica of as-received TD NiCr. 30,000X



Figure 13. Electron micrograph of a replica of a TD NiCr sample after 3000 hours exposure at 2000 F (1093 C) and ambient pressure. 30,000X



Figure 14. Electron micrograph of TD Co as-received (replica). 30,000X

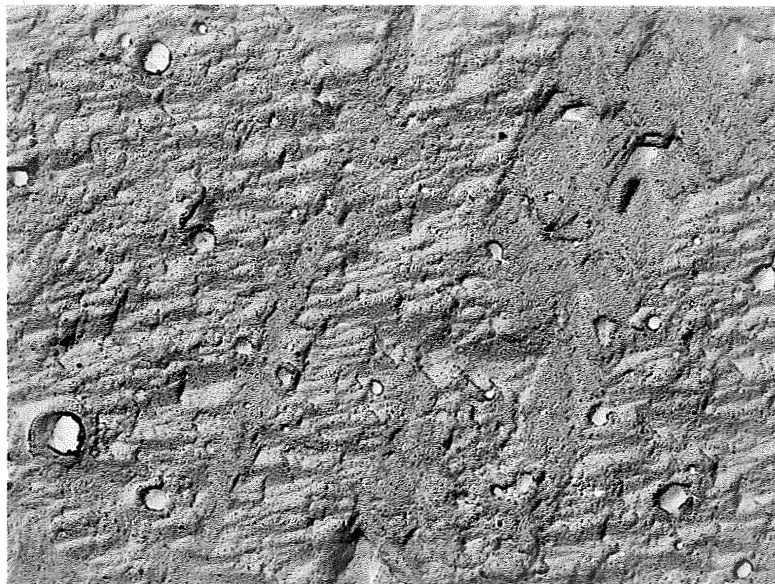


Figure 15. Electron micrograph of TD Co replicated sample after 1000 hours exposure at 2000 F (1093 C) and 8 Torr. 30,000X



Figure 16. Electron micrograph of a replica of TD Co+ after 1000 hours exposure at 2000 F (1093 C) and 8 Torr. 30,000X

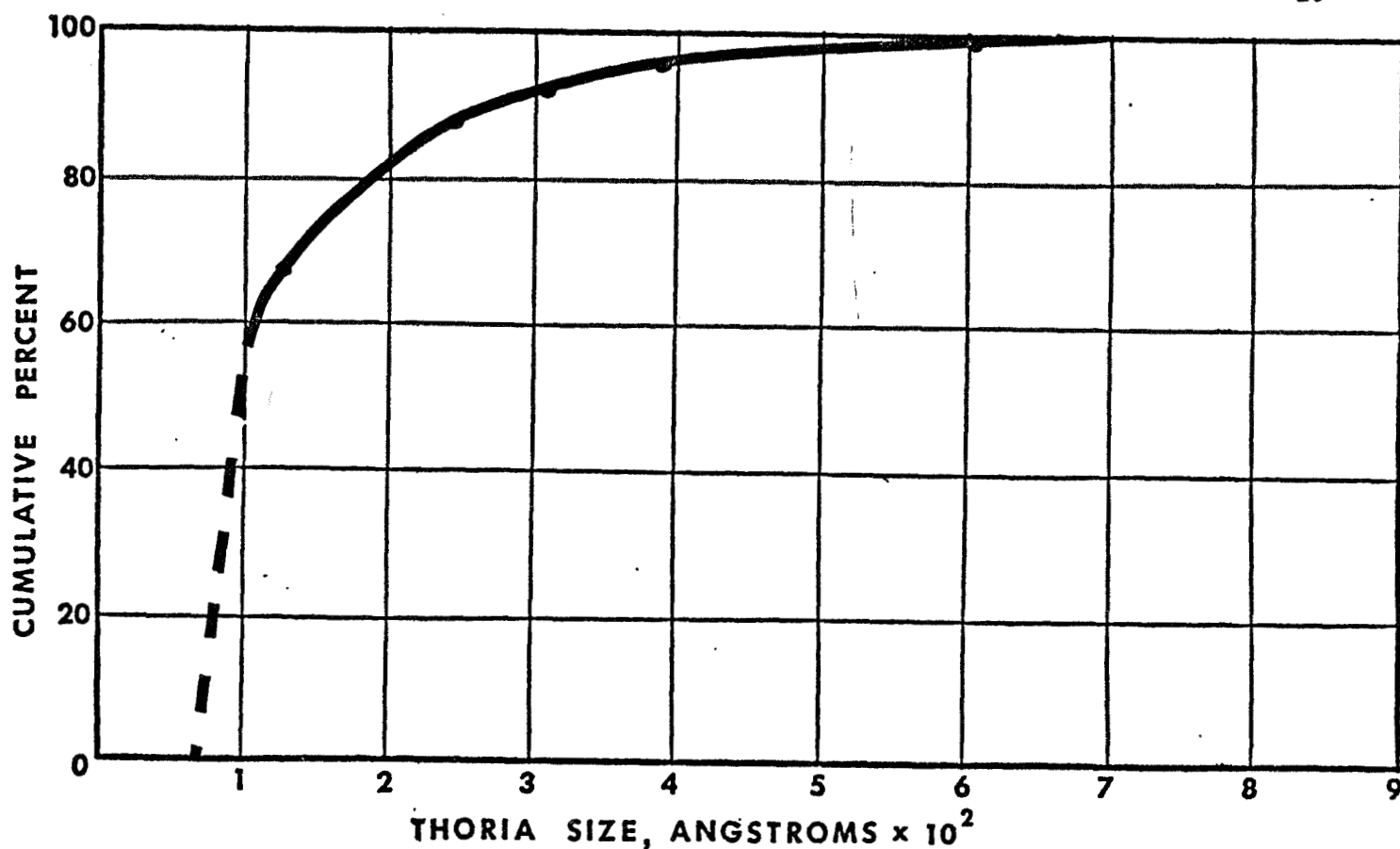


Figure 17. Cumulative particle size distribution of thoria in TD Ni after 1000 hours at 1800 F (982 C) and ambient pressure.

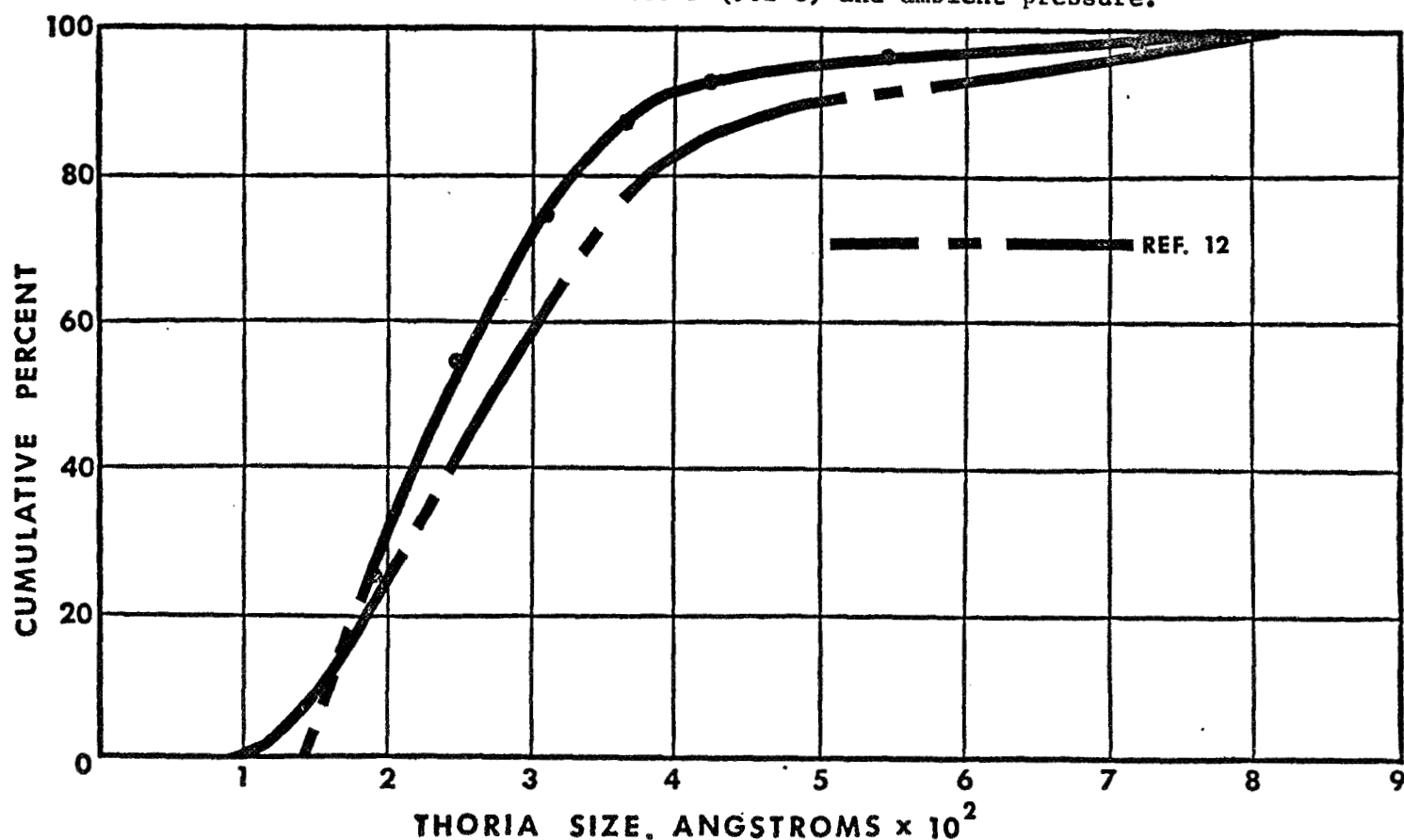


Figure 18. Cumulative particle size distribution of thoria in TD NiCr after 1000 hour exposure at 2000 F (1093 C) and ambient pressure. A particle size distribution for as-received material for the same alloy analysis and manufacturer adapted from ref. 12 is included.

from the same manufacturer is also given in figure 18.

The particle size distribution for TD Co after 1000 hours at 2000 F (1093 C) and ambient pressure is shown in figure 19. Figure 20 is a plot of the particle size distribution for TD Co+ after 1000 hours at 2000 F (1093 C) and 8 Torr.

The distribution curves are plotted on the basis of equal volume (area) since the observed number of the smallest particles depends greatly on response to etching.

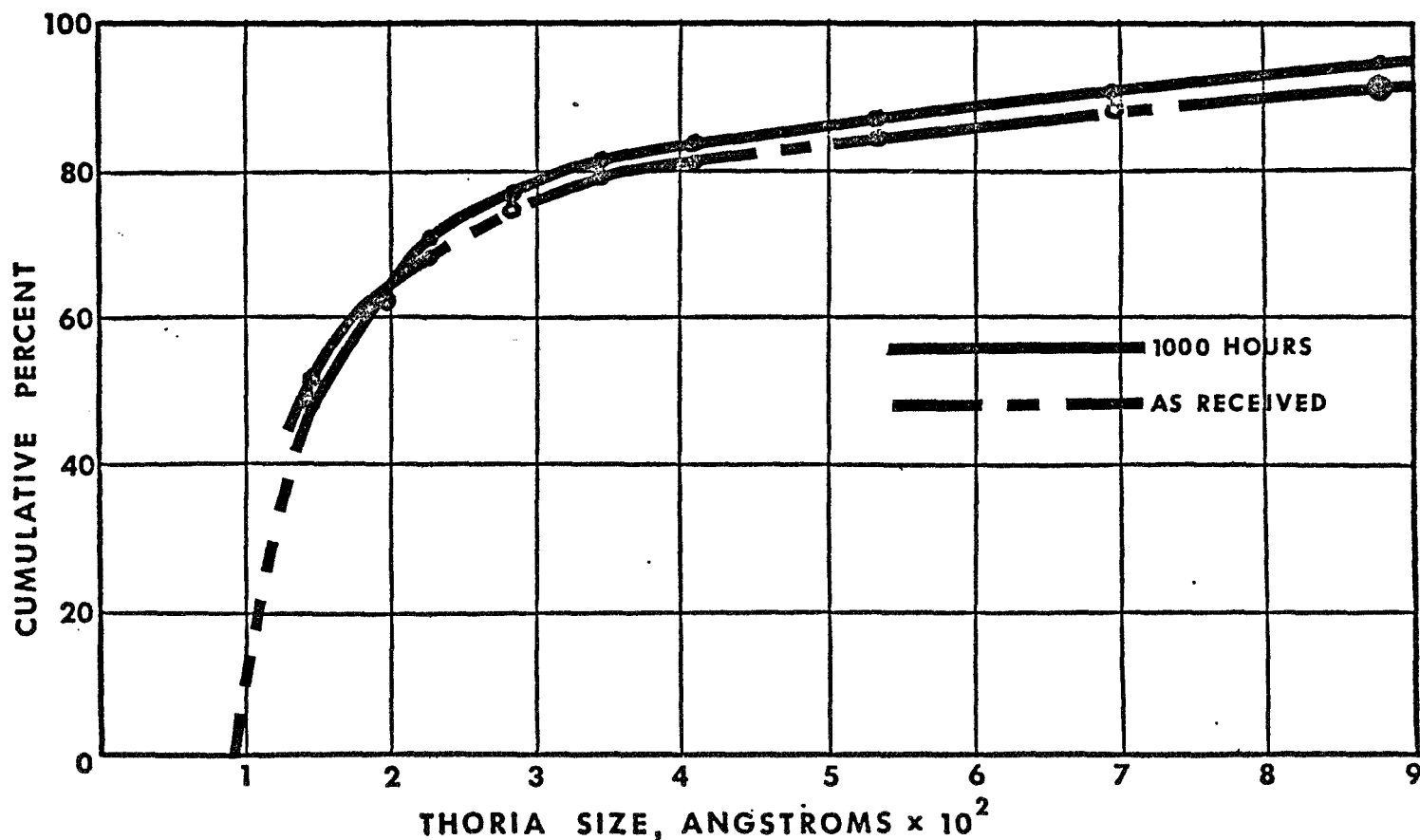


Figure 19. Cumulative particle size distribution of thoria in TD Co after 1000 hours at 2000 F (1093 C) and ambient pressure, together with the as-received distribution.

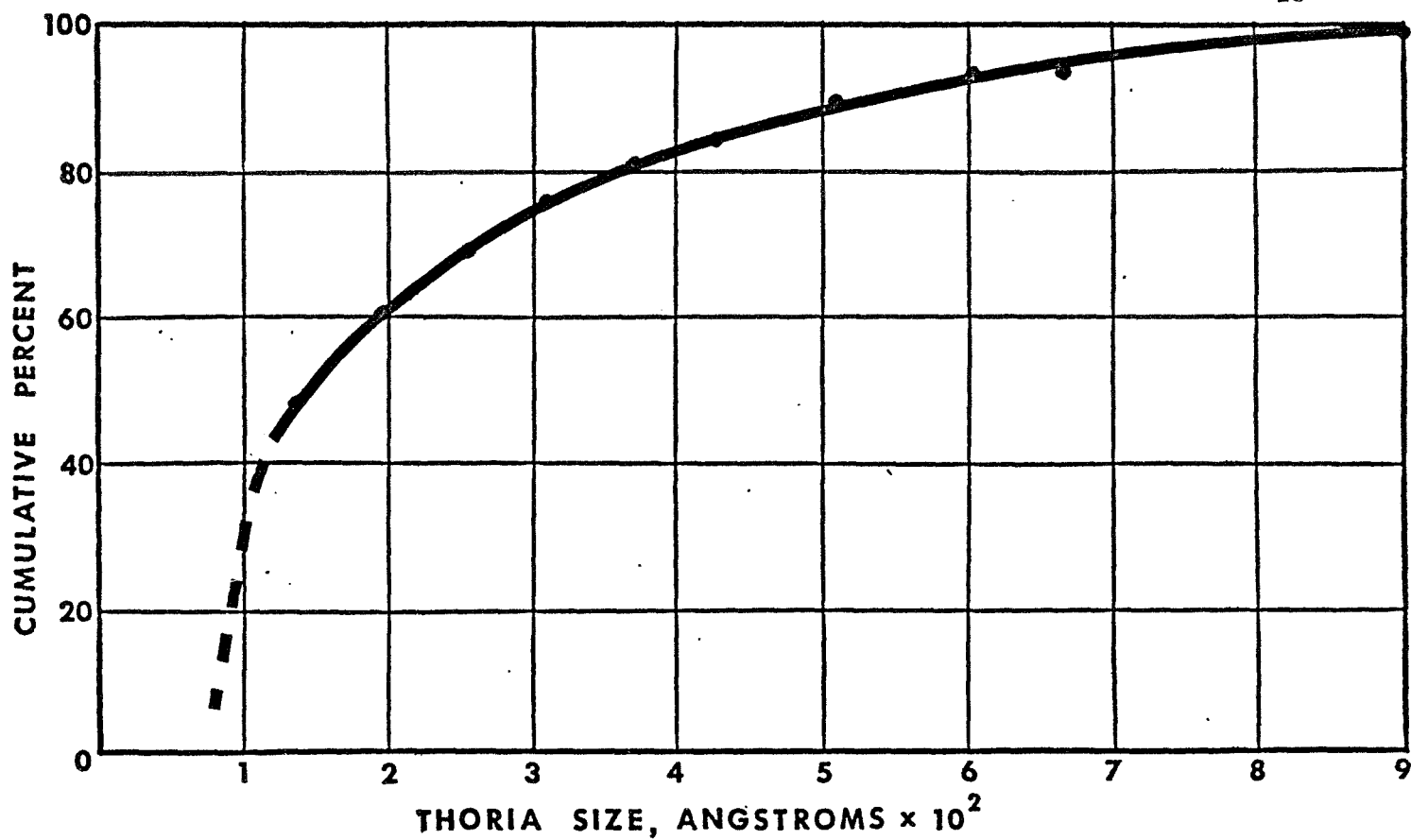


Figure 20. Cumulative particle size distribution of thoria in TD Co+ after 1000 hours at 2000 F (1093 C) and 8 Torr.

DISCUSSION

The oxidation rate data were about as expected. The TD Ni oxidized nearly ten times faster than the TD NiCr and TD cobalt alloys. The TD Ni is hampered by scaling at every cool-down from all temperatures.

Several facts emerged from the oxidation study in regard to the alloyed TD materials. The TD NiCr exhibited about the same thickness of oxide and oxide coloration for 8 Torr specimens at 200 F above those for ambient pressure. The TD NiCr specimens flaked at 1200 and 1400 F (650 and 760 C) at ambient and up to 1600 F (870 C) at 8 Torr. This factor leads to the recommendation given later concerning preoxidation of TD NiCr at 1600 F (870 C) minimum. The TD cobalt alloys were as oxidation resistant as the TD NiCr alloy, but did not scale or flake at any temperature or pressure condition.

The type of oxide scale present on nickel-chromium alloys (80 nickel-20 chromium principally) has been reported to be pure Cr_2O_3 ^{4,9} or NiCr_2O_4 - Cr_2O_3 mixtures^{3,5}. A great many samples of TD NiCr in this study exhibited two phase oxide scale of the type shown in figures 6 and 7. The second phase appears to be a precipitate since it is composed of small cubic particles in the hexagonal Cr_2O_3 matrix. This suggests that the Cr_2O_3 is saturated with NiCr_2O_4 spinel at temperature and that the spinel precipitates upon cooling. This hypothesis would suggest that an explanation for the varying results of previous investigators would lie in examining the cooling rates employed in their studies. A rapid cooling would favor a Cr_2O_3 solution and a slow cool (as employed in this study) would favor the precipitate.

Since the TD cobalt alloys did not scale, the weight loss figures should be explained in some way. Two characteristics of the data can be interpreted to explain the weight loss. First, it should be noted that the 18 percent chromium alloy, TD Co Table VI, did not exhibit as large a weight loss as the 30 percent alloy, TD Co+ Table VII. Second, the weight loss for both alloys is more severe at 8 Torr than at ambient pressure. These two phenomena are interpreted as a preferential loss of chromium because of the high vapor pressure of CrO_3 .

The stability of each of the subject alloys is an important consideration beyond their resistance to material loss through oxidation.

All alloys suffered a small loss in hardness in the first 100 hours of exposure. The long time hardness data were different for each alloy type. TD Ni exhibited a drop from 190 DPH to 180 DPH at 100 and 1000 hours respectively. Particle size analysis (figure 16) did not clearly show any increase in particle size to accompany the drop in hardness. Hardness values and particle size analysis for TD NiCr indicated no significant change for 3000 hours at all test conditions.

Both cobalt alloys suffered a drop in hardness during exposure at 8 Torr for all temperatures. Examination of the alloys in the electron microscope and particle analysis indicated that no change in the dispersion had occurred up to the 1000 hour test mark. This behavior can be explained in the same way as the weight loss during testing, i.e., as a drop in hardness due to chromium loss. The same phenomena also explains why the hardness values are essentially the same for 1600, 1800 and 2000 F (870, 982 and 1093 C) TD Co+ samples after 1000 hours at 8 Torr, Table XV.

The particle size analysis showed that for these manufactured alloys the original particles are larger as the alloy becomes more complex, with

the TD Co exhibiting the largest particle size over the sections examined in this study. The variation in starting particle size did not contribute to instability, however, as all the alloys demonstrated excellent agglomeration resistance. For one example, the TD Co, figure 19, appeared to have a finer particle distribution after exposure, due probably to sample differences from area to area.

CONCLUSIONS AND RECOMMENDATIONS

Material loss rates during oxidation are plotted for TD Ni and TD NiCr. These data can be used as base line estimates for light service requirements. It should be borne in mind that temperature cycling and severity of cool-down might well affect loss rates adversely. The following conclusions are drawn from the present study.

1. TD Ni, TD Co, and TD Co+ show no thoria agglomeration after 1000 hours of exposure between 1200 F (650 C) and 2000 F (1093 C) at ambient or 8 Torr pressures.
2. TD NiCr exhibits no measurable agglomeration after 3000 hours of exposure between 1200 F (650 C) and 2000 F (1093 C) at ambient or 8 Torr pressure.
3. Transport and spheroidization of unreduced chromium oxides occur in TD alloys containing chromium at times under 1000 hours with a resulting structure that is more favorable mechanically.
4. The four alloys examined soften at higher temperatures in a few hours by 10 to 40 points (DPH).

5. TD Ni softens slightly with increased time at temperature (10 to 20 points DPH), while TD NiCr is unaffected and TD Co and TD Co+ soften significantly at 8 Torr.
6. Two phase oxidation was observed in TD NiCr and attributed to precipitation of $\text{NiO} \cdot \text{Cr}_2\text{O}_3$ spinel during specimen cooling.

It is recommended that TD Ni be considered suspect in any application that involves cyclic temperature exposure. TD NiCr shows excellent scaling resistance only at elevated temperatures and should be pre-oxidized above 1600 F (870 C) if it is to be used under cyclic conditions at lower temperatures. Cobalt-nickel-chromium alloys appear sensitive to low pressure exposure and should be employed with due care in that kind of service.

Further research is recommended in order to affirm the loss of chromium at low pressure that has been hypothesized in this report. This work might well be done by electron microprobe analysis.

Because these alloys can only be economically applied as long time structures, exposure times should be extended to 10,000 hours or longer.

Finally, other dispersion strengthened alloys should be investigated over the times and temperatures used in this study to determine their respective resistances to agglomeration and to explain agglomeration behavior if it does occur.

APPENDIX

The design of the furnace assembly used for environmental testing was somewhat unique and is therefore described in detail in this appendix.

The apparatus was basically two gradient furnaces arranged in a mirror image symmetry. The furnace chambers were impervious alumina, closed at one end and capped with stainless steel at the other end as shown in figure 1A. Both sides were identical in regard to thermal construction. One side was sealed with silicone at the stainless cap and a small hole provided in the inconel thermocouple protection tube (at H in figure 1A).

A throttled mechanical pump was used to pull a constant 8 Torr vacuum against the leak.

Each zone furnace was individually set using an autotransformer. The 1200 F (650 C) zones were continually monitored using a two pen Varian recorder. Both chambers were traversed with a thermocouple from time to time and the temperature versus distance plotted to compare to the desired gradient. It proved possible to hold the gradient to the desired level for a complete run within ± 15 F and to ± 5 F of the set point over the run.

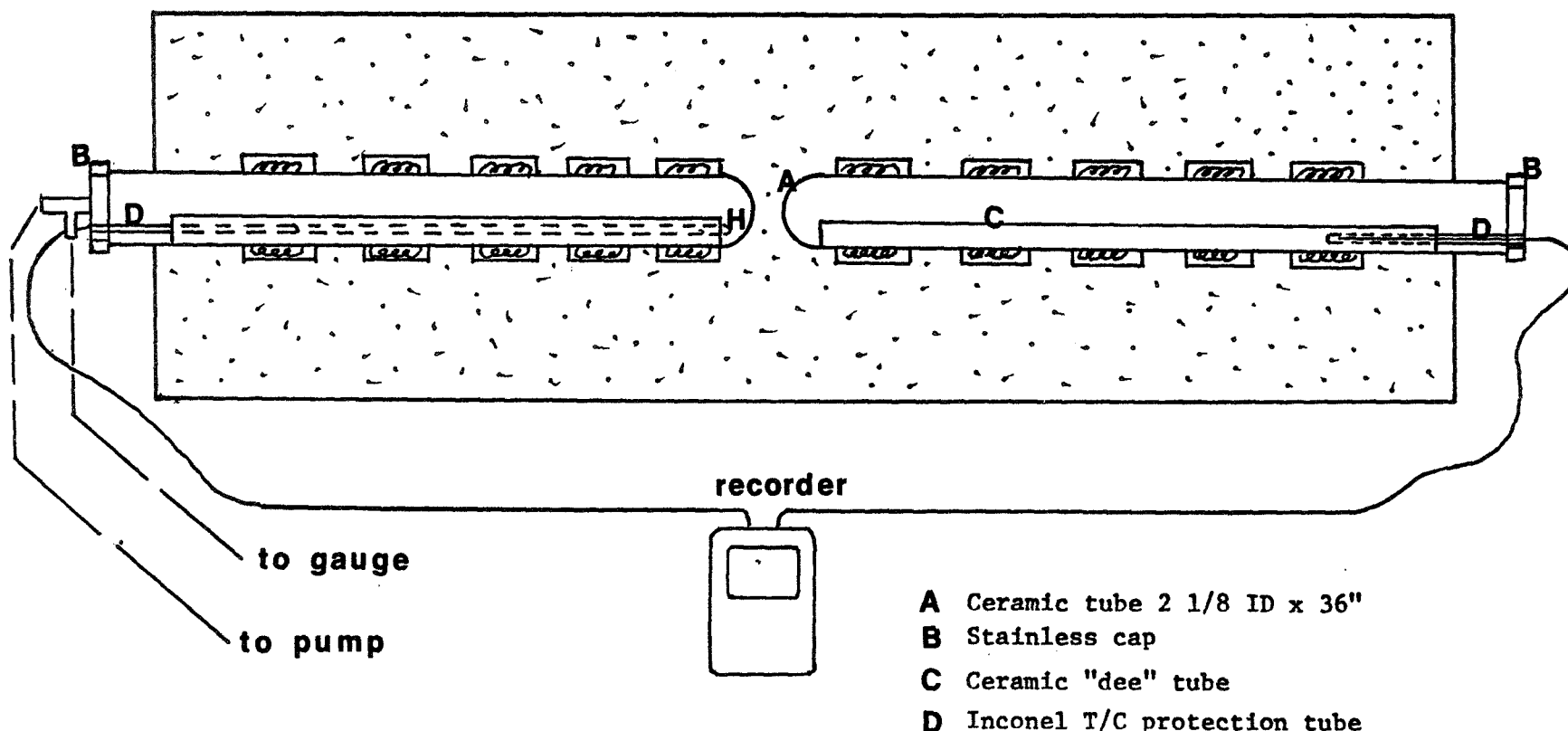


Figure 1A. Schematic of oxidation test apparatus consisting of mirror image furnace tubes with 5 heat zones in each and one side maintained at 8 Torr by pumping against a controlled leak at H.

BIBLIOGRAPHY

1. Hauffe, Karl, "Oxidation of Metals", Plenum Press, New York, 1965.
2. Gulbransen, E. A. and Andrew, K. F., "Rate of Oxidation of Three Nickel-Chromium Heater Alloys between 500° and 900°C, Jour. Electro-chemistry Soc., 101, (4), 163, 1954.
3. Gulbransen, E. A. and Andrew, K. F., "Oxidation Studies on the Nickel-Chromium and Nickel-Chromium-Aluminium Heater Alloys", Jour. Electro-chemistry Soc., 106, (11), 941, 1959.
4. Wood, G. C. and Hodgkiess, T., "Characteristic Scales on Pure Nickel-Chromium Alloys at 800° - 1200°C", Jour. Electro-chemistry Soc., 113, (4), 319 - 327, April, 1966.
5. Ignatov, D. V. and Shamgunova, R. D., "The Structural - Kinetic Investigation of the Process of Oxidation of Nickel, Chrome, and Alloys Based Upon Them.", FTD - TT - 65 - 1275, orig. 1959, 1966.
6. Jones, D. A. and Westerman, R. E., "Oxidation of a Nickel - 2% ThO₂ Alloy and the Logarithmic Rate Law of Oxidation", T1D²- 4500, 1963.
7. Wilcox, B. A. and Clauer, A. H., "High Temperature Deformation of Dispersion Strengthened Nickel Alloys", NAS 3-9413 2/29, 1968.
8. Cole, F. W., Padden, J. B. and Spencer, A. R., "Oxidation Resistant Materials for Transpiration Cooled Gas Turbine Blades", NASA CR-930, Feb., 1968.
9. Burks, N. and Rickert, H., "The Oxidation Mechanism of Some Nickel-Chromium Alloys", J. Inst. Metals, 91, 308, 1963.
10. Worn, D. R. and Marton, S. F., Power Metallurgy, Ed. by W. Lesynski, Interscience, New York, 1961, p. 309.
11. Weeton, J. W. and Quatinetz, M., "Cleaning and Stabilization of Dispersion Strengthened Materials", NASA TM X - 52220°, 1966.
12. Chang, W. H., "Some Observations of the Effect of Aluminum on Thoria Agglomeration in a Ni-20% Cr Alloy", Trans. ASM, 60 (4), 730, 1967.
13. Raymond, L. and Neumann, J. P., "The High Temperature Stability of Thoria-Strengthened Nickel-Chromium Alloys", SAMSO - TR - 68 - 442, 1968.

14. Manning, C. R., Jr., Royster, D. M. and Braski, D. N., "An Investigation of a New Nickel Alloy Strengthened by Dispersed Thoria", NASA TN D - 1944, 1963.