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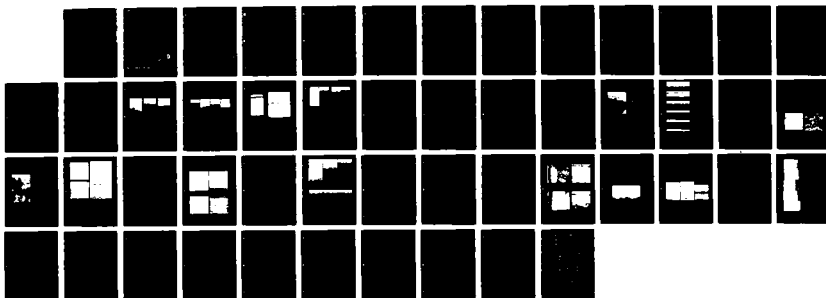
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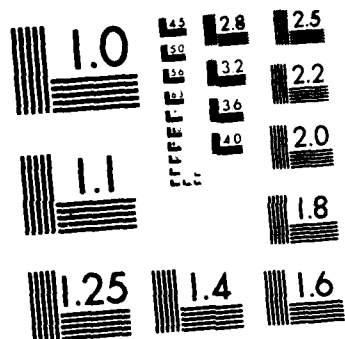
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ENVIRONMENTAL RESISTANCE  
OF NIOBIUM

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EFFECT OF ALLOYING, RAPID  
SOLIDIFICATION, AND SURFACE  
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ENVIRONMENTAL RESISTANCE  
OF NIOBIUM



by  
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prepared for  
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## REPORT DOCUMENTATION PAGE

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| FIELD                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                         | GROUP  | SUB-GROUP                                                           | niobium; oxidation; mechanisms: niobium-aluminum alloys; alumina formation; niobium-titanium-aluminum alloys   |                                                 |                                 |
| 21                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                            | 06     |                                                                     | <i>(Sub AL Crit)</i>                                                                                           |                                                 |                                 |
| 21                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                            | 05, 08 |                                                                     | <i>(Niobium-Aluminum)</i>                                                                                      |                                                 |                                 |
| 19. ABSTRACT (Continue on reverse if necessary and identify by block number) <b>(Aluminum)</b><br>An improved understanding of factors governing the selective oxidation of <b>Al</b> to form continuous alumina scales on modified <b>Nb-Al</b> alloys has been established. It has been demonstrated that highly protective alumina scales can be formed on <b>Nb-Ti-Cr-V-Al</b> alloys without transient oxidation products at temperatures of 1400 to 1600°C in air. Aluminum content has been identified as the critical factor controlling single layer alumina formation. It also has been shown that the <b>N<sub>Al</sub>crit</b> for the formation of a continuous alumina scale is 0.375 - 0.38 at 1400°C, decreasing slightly with increased Nb-Ti ratio in the alloy. A fourth element must be added to <b>Nb-Ti-Al</b> alloys for effective alumina formation. It has been established that this element should be from a group that can reduce the solubility-diffusivity product of <b>O</b> in the alloy. An addition of 2-4% Cr and/or V is effective at 1400-1600°C. Alumina can be formed at 1400°C by substituting V for Ti but a liquid transient oxide is produced. A high rate of transient oxidation relative to alumina (continued) |        |                                                                     |                                                                                                                |                                                 |                                 |
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Vanadium, Rhenium, Ruthenium, Molybdenum  
formation has been identified as the major factor precluding growth of continuous alumina scale at 800 and 1100°C. Elements such as V, Re, Ru, and Mo selected to reduce oxygen permeability and enhance alumina formation in this range accelerated transient oxidation and precluded alumina growth instead. Incorporation of Nb as a major element in transient oxide has been shown to preclude alumina formation above 1550°C by forming a liquid oxide layer. Major attention must be devoted to the control of the transient oxidation process for effective alumina formation. Factors that govern the composition, structure, and growth of transient oxides must be identified.

## EXECUTIVE SUMMARY

### Objectives

The specific goals of the study are to

- 1- derive a model for the selective oxidation of aluminum from niobium to form protective alumina scales
- 2- define the factors in composition and structure that govern the selective oxidation of aluminum from niobium alloys
- 3- establish the feasibility of alloying niobium to produce compact, adherent alumina scales
- 4- determine the limiting kinetics of oxidation of alumina-forming Nb base alloys as a function of temperature and atmosphere composition.

The research will be conducted over a three-year period starting in January, 1986. Results of the first years work have been presented in an LMSC Report (1). Results of the second years work are presented in this report.

### Status

Research during the second year has established a better understanding of factors governing the selective oxidation of Al to form alumina scales on Nb alloys. The formation of external alumina scales without transient oxidation has been shown to be feasible. It has been demonstrated that the amount of transient oxidation that occurs before a continuous alumina scale is formed decreases with both increasing  $N_{Al}$  and temperature. Alumina scales without an external layer of transient oxide were formed on Nb-Ti-Al-Cr-V alloys in air at 1400°C with  $N_{Al}$  between 0.528 and 0.578. Alloys with an  $N_{Al}$  of 0.477 formed single layer alumina in air a temperature between 1550 and 1600°C.

Studies of the transition from internal oxidation of Al to formation of continuous alumina scale under a layer of transient oxide show a similar effect of  $N_{Al}$  and temperature. At 1400°C, the transition occurred at an  $N_{Al}$  of 0.375-0.39. At 1100°C, the transition occurred slightly above an  $N_{Al}$  of 0.578 while at 800°C, concentrations considerably above 0.578 will be required to form continuous alumina scales. The transition at 1400°C was slightly dependent on the Nb:Ti ratio and relatively independent of the Cr

and V contents above an addition of 3-4%.

The formation of continuous alumina scales also was found to be dependent on both oxygen permeability in the alloy and scaling characteristics of the base metal components (transient oxidation). As temperature is reduced, the high activation energy for the formation of external alumina greatly reduces the rate of nucleation and growth. As a result, the transient oxidation process becomes a controlling factor. The nature and kinetics of transient oxidation have been found to be particularly important at 800 and 1100°C. At 800°C, the rate of oxidation was relatively insensitive to Al content but based on limited test data, showed a tendency to increase with increasing  $N_{Al}$ . At 1100°C, the rate of oxidation decreased significantly with increasing Al content as a result of transient oxidation being cut off by more rapidly growing alumina scales.

In both cases, the growth of external alumina and/or reduced transient oxidation was enhanced by the addition of elements that could reduce the solubility-diffusivity product of  $O_2$ . Vanadium was found to be effective and alumina was formed on a Nb-25V-10Cr-40Al alloy in air at 1400°C. Unfortunately, V was taken into the transient oxide and formed a liquid oxide phase at 1400°C. Titanium was marginally effective and partial alumina scales were formed on a Nb-27.6Ti-42.0 Al alloy. Titanium was a major component of most transient oxides, forming liquid oxides with Nb at 1600°C. Chromium was found to be most effective and was required to be present in all alloys to form continuous alumina scales. Only a trace of Cr was detected in the transient oxide formed on Nb-Ti-Cr-V-Al alloys at 1400°C. Small additions of Cr + V (3-4% each) or Cr (without V) in the range of 8-10% to Nb-Ti-Al alloys with a Nb:Ti ratio of 0.8-1.4 offered the best balance of behavior.

The large additions of Ti, Cr, and Al required to form external alumina scales reduced alloy melting points to the range of 1600-1650°C. Melting point was found to be very dependent on Al content. Alloys with 48% Al melted at 1600°C while those with 58% Al melted at 1550°C. Niobium alloys that melt in this temperature range will be of little value as structural materials and research must be directed to mechanisms for further reduction of  $N_{Al}^{crit}$ . Oxygen permeability and rate of transient oxidation relative to that of alumina formation appear to be key factors that require an increased understanding for affecting further reductions in  $N_{Al}^{crit}$ .

It has been found that high e/a elements such as Re, Ru, and Mo which are known to reduce the solubility of  $O_2$  in Nb to near zero do not enhance the formation of Al. Instead, moderate level additions (10-30%) result in the formation of liquid or non-protective transient oxides that greatly accelerate surface recession and preclude alumina formation. These additions do prevent internal oxidation of Al, most likely by reducing the solubility-diffusivity product of O. However, this effect is masked by a high rate of surface recession. Other approaches to reduce permeability of O in the alloys must be examined.

Research during the past year also demonstrated that the composition of the transient oxide as governed by base alloy composition is a very important consideration. The basic oxides formed as transients on Nb-Ti-V-Cr-Al alloys were found to be  $\text{TiO}_2$  and  $\text{NbAlO}_4$ . The latter melts at  $1530^\circ\text{C}$  and forms a low melting eutectic ( $\sim 1400^\circ\text{C}$ ) with  $\text{Nb}_2\text{O}_5$ . Titania ( $\text{TiO}_2$ ) also forms a low melting eutectic with  $\text{Nb}_2\text{O}_5$ . Melting of the transient oxide was observed between  $1550$  and  $1600^\circ\text{C}$ , resulting in a very rapid rate of transient oxidation that precluded formation of alumina scales. The ideal transient oxide would be in the  $\text{TiO}_2$ - $\text{Al}_2\text{O}_3$  system where no melting occurs below  $1700^\circ\text{C}$ . It has been demonstrated that such a scale can be formed as an initial oxidation product (outer scale layer) but its growth cannot be sustained. Low melting niobates of Al and Ti are formed underneath. More attention must be devoted to the transient oxidation process as a significant contribution to the formation of alumina on Nb. Factors that govern the composition, structure, and growth kinetics must be identified. Significant reduction in  $N_{\text{Al}}$  for alumina should be possible through control of transient oxidation.

#### Publications

The following technical manuscript was submitted to Scripta Metallurgica for Publication:

R.A. Perkins, K.T. Chiang, and G.H. Meier, "Formation of Al on Nb-Al Alloys."

#### Professional Personnel

The following professional personnel have participated in the program during the past year:

##### LMSC

Mr. R.A. Perkins  
Dr. K.T. Chiang  
Dr. J.S. Lee

##### UNIVERSITY OF PITTSBURGH

Prof. G.H. Meier  
Mr. R.A. Miller (Graduate Research Assistant)

#### Coupling Activities

- (1) The program now supports and will be the basis for a thesis by a masters candidate, R.A. Miller at the University of Pittsburgh.
- (2) A contract from DARPA has been awarded to Pratt and Whitney for "Development of High Temperature Metallics for Structural Aerospace Applications" (N00014-87-C-0862) as a result of the advanced understanding of Nb alloy oxidation that was obtained during the first year of research on this project. The demonstration of technical feasibility for oxidation resistant Nb-based alloys convinced DARPA that the design of effective alloys would be possible. Lockheed will be a

subcontractor to Pratt and Whitney with prime responsibility for design of the oxidation resistant alloy. Mr. Perkins will be the Task leader for this effort and Prof. Meier of the University of Pittsburgh will be a consultant for the program. As the understanding of oxidation behavior and mechanisms is improved during the second and third years of research on the AFOSR project, results will be factored into the P&W program to provide technical guidelines for alloy design. P&W in turn will supply limited amounts of RSP powders of selected alloys for use in the third year of the AFOSR project.

(3) The following presentations based on results of work during the first year have been made:

- (a) Invited presentation to NMAB committee on Advanced High Temperature Composites- "Oxidation of Refractory Metals", R.A. Perkins, Feb. 1987.
- (b) Invited presentation at Gordon Research Conference on Corrosion, Panel on Oxidation Resistance of Reactive Materials, R.A. Perkins, July 1987.
- (c) Presentation to J. Stevens and Structural Materials Group at NASA-LRC, R.A. Perkins, Aug. 1987.
- (d) Presentation to F.H. Froes, NASP Materials Committee, Sept. 1987.

(4) The following presentations based on result of work during the first and second year have been committed:

- (a) Invited review of Nb oxidation behavior to DARPA/URI Research Groups, Santa Barbara, CA, G.H. Meier, Jan. 1988.
- (b) Invited presentation on oxidation of Nb alloys to NASA-LRC Symposium on Oxidation of Intermetallics, R.A. Perkins, Sept. 1987.
- (c) Invited lecture on "Oxidation of Refractory Metals", Spring '88 Meeting of the Materials Research Society, Reno, NV, R.A. Perkins, April 1988.
- (d) Invited research seminar presentation on "Oxidation of Refractory Metals", Rensselaer Polytechnic Institute, Troy, NY, R.A. Perkins, March 1988.

## FOREWORD

This report covers research performed under contract F49620-86-C-0018 for the period 1 January, 1987 to 1 January, 1988. The project was administered by the Air Force Office of Scientific Research with Dr. A.H. Rosenstein as project manager. The report was prepared by Mr. R.A. Perkins of Lockheed Missiles & Space Co., Palo Alto, Ca. and Prof. G.H. Meier of the University of Pittsburgh, Pittsburgh, Pa.

The program was conducted as a joint research investigation by the Research and Development Division of the Lockheed Missiles & Space Co. (LMSC) and the Materials Science and Engineering Department of the University of Pittsburgh with LMSC as the prime contractor. Mr. R.A. Perkins of Lockheed and Prof. G.H. Meier of the University of Pittsburgh were co-principal investigators. The following personnel assisted in conducting the experimental work:

### LMSC-

Dr. K.T. Chiang  
Dr. J.S. Lee  
Mr. L.R. Iosty  
Mr. R.N. Hall  
Mr. A.H. Heynen

### University of Pittsburgh-

Mr. R.A. Miller  
Mr. K.F. Andrew  
Mr. E. Hewitt

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## INTRODUCTION

Alloys of Niobium are among the most logical materials in terms of mechanical properties, producibility, cost, and availability for use in aerospace propulsion and thermal protection systems at temperatures of 800-1500°C. The major deterrent to effective use of these materials in advanced gas turbines, rocket engines, and thermal protection systems is the lack of adequate resistance to oxidation. Commercially available alloys have high rates of oxidation above 650°C and are embrittled by dissolution of oxygen, carbon, and nitrogen.

Niobium alloys can be coated with oxidation resistant intermetallic compounds of Nb with Si and as such, find limited use in rocket and propulsion applications. Most notable among these are thrust deflectors for aircraft gas turbines and the combustion chambers and exit cones for liquid propellant rocket engines. Useful life is limited, particularly under cyclic use conditions, and random coating failures can lead to rapid attack of the alloy. Coating performance and reliability are not adequate for extended use in advanced gas turbines, spacecraft engines, and thermal protection systems. Niobium alloys with improved resistance to oxidation are needed for use as structural alloys or as coatings for structural alloys of niobium.

A review of the current status of technology for oxidation resistant alloys indicates that major advances in the oxidation behavior of Nb-base alloys may now be possible. Advanced metal processing, such as rapid solidification, offers the ability to produce compositions and structures that have not been attainable by conventional processing. New technology and fundamental knowledge of the formation of protective oxide scales on complex alloys in mixed oxidants coupled with a wide range of new and sophisticated surface analysis techniques can provide a new insight into how to control the oxidation behavior of niobium. The feasibility of providing a technical basis for the design of improved alloys by basic research on the mechanisms by which protective oxide scales can be formed on niobium is considered to

be good.

A fundamental study has been initiated under this contract to provide such a technical basis. The research is directed to develop an understanding of the mechanisms by which protective alumina scales can be formed on niobium by the selective oxidation of aluminum. The specific goals of the study are to

- 1- derive a model for the selective oxidation of aluminum from niobium to form protective alumina scales
- 2- define the factors in composition and structure that govern the selective oxidation of aluminum from niobium alloys
- 3- establish the feasibility of alloying niobium to produce compact, adherent alumina scales
- 4- determine the limiting kinetics of oxidation of alumina-forming Nb base alloys as a function of temperature and atmosphere composition.

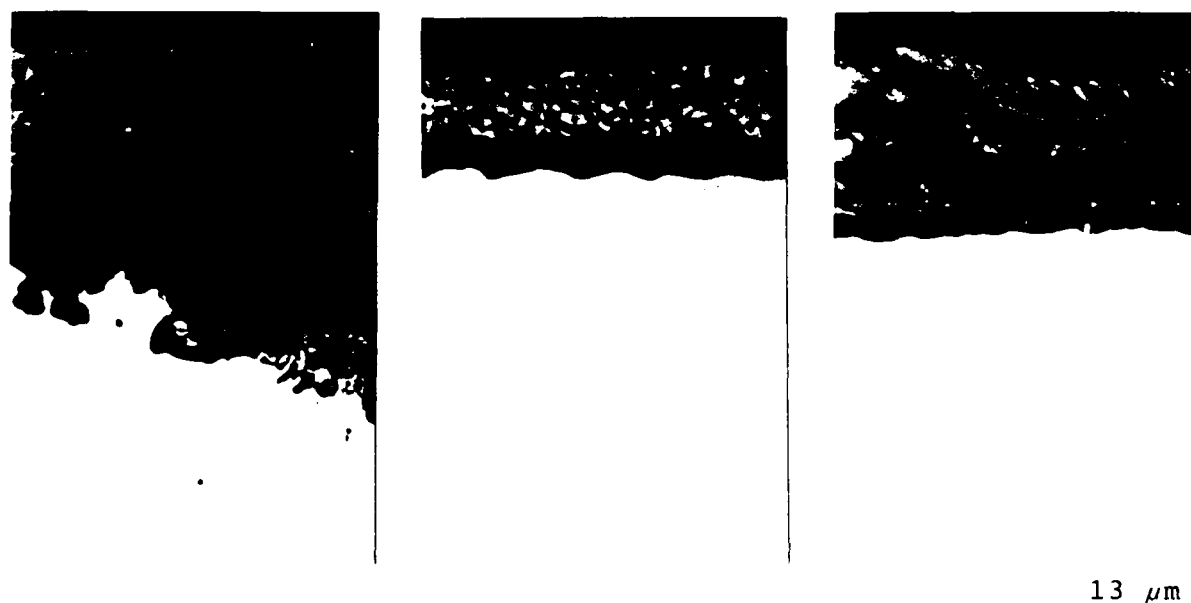
The research will be conducted over a three year period starting in January, 1986. Results of the first years work have been presented in an LMSC Report (1). Results of the second years work are presented in this report.

## TECHNICAL BACKGROUND

### FIRST YEAR PROGRESS SUMMARY

A model derived from first principles for the transition from internal to external oxidation of an active metal in an alloy was tested and found to be applicable to the transition from internal to external oxidation of Al in complex Nb-Al alloys containing 3-5 elements. Calculations and oxidation test results indicated that alloy modifications to affect significant reductions in the solubility-diffusivity product for oxygen and a major increase in the diffusivity of Al in the alloy are required for the selective oxidation of Al to form external alumina scales on Nb-Al alloys. The overriding controlling factor is the diffusivity of Al which must be increased by several orders of magnitude over that in Nb-aluminides to form external alumina scales above 800°C.

The most effective modifications to promote selective oxidation of Al in Nb were found to be the addition of Ti, Cr, and V. Titanium was added in a 1:1 ratio with Nb (on an at.% basis) on the assumption that this would stabilize a phase with a cubic structure in which the diffusivity of Al would be high. External alumina scales were formed on Nb-Ti-Al alloys in air at 1400°C with as little as 42 at.% Al in the alloys (Fig.1A). The Nb-Ti-



A- 27.6 Ti-42.0 Al B- 26.3Ti-4.3Cr-41.6Al C- 29.3Ti-3.6V-38.4Al  
 (29-14), +4.7mgcm<sup>-2</sup> (29-15), +2.0mgcm<sup>-2</sup> (26-3), +4.3mgcm<sup>-2</sup>

Fig. 1 Effect of Cr and V on Transient Oxides, 1h-1400°C, Air

Al alloys were considered to be marginal alumina formers and a large amount of transient oxidation occurred before the slower growing alumina scale was sufficiently continuous to cut off growth of the transient oxide. Further modification with elements that will decrease the solubility-diffusivity product of O in the alloy was found to be needed.

With the addition of as little as 3-4 at.% of either Cr or V to a Nb-Ti-42%Al alloy, continuous alumina scales were formed as shown in Fig.1B,C. The alumina scale formed in 1h at 1400°C in air was about 5μm thick and was covered with a 10-15μm thick outer layer of a transient oxide. This oxide was a complex mixture of Al, Ti, and Nb oxides and most likely grows with linear or other non-

parabolic kinetics. The transient oxide formed on the Cr-modified alloy was much thinner than that formed on the Ti-Nb-Al ternary or the V-modified ternary alloys. The amount of transient oxide was reduced further either by adding 3-4% each of Cr and V together or by increasing the Cr content to 8.3% (Fig.2A). The amount of transient oxidation increased when the Al content was decreased from 42 to 39% (Fig.2B).

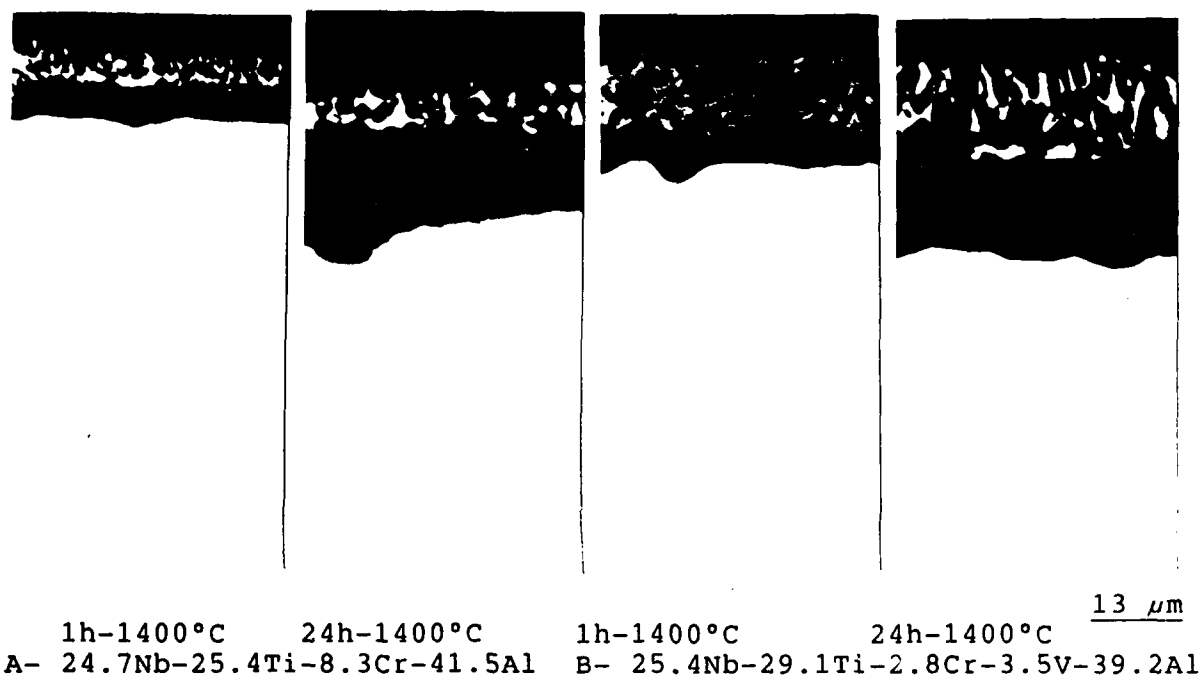


Fig. 2 Effect of Cr and V on Growth of Alumina and Transient Oxides at 1400°C

Kinetic data obtained at 1400°C by heating multiple samples and removing from test at different time intervals from 1 to 24h revealed that the alloys exhibited parabolic kinetics with a  $k_p$  of  $5.3 \times 10^{-2} \text{ mg}^2 \text{cm}^{-4} \text{m}^{-1}$  ( $8.83 \times 10^{-10} \text{ g}^2 \text{cm}^{-4} \text{s}^{-1}$ ). This is close to that of NiAl [ $k_p = 3 \times 10^{-3} \text{ mg}^2 \text{cm}^{-4} \text{m}^{-1}$  ( $5 \times 10^{-11} \text{ g}^2 \text{cm}^{-4} \text{s}^{-1}$ )] which forms a single layer alumina scale. The higher  $k_p$  for the Nb alloy most likely is due to the transient oxidation that occurs before the alumina scale becomes continuous. As shown in Fig.2, the thickness of the alumina inner scale increased 2-3 times while the thickness of the transient oxide was largely unchanged on increasing time of exposure from 1 to 24h. The microstructure of the transient oxide was coarsened but its growth was cut off

effectively by the alumina scale. As shown in Fig.3, the major phase in the transient oxide was a complex niobate containing large amounts of Al and Ti. A trace of Cr but no V also was present in the oxide.

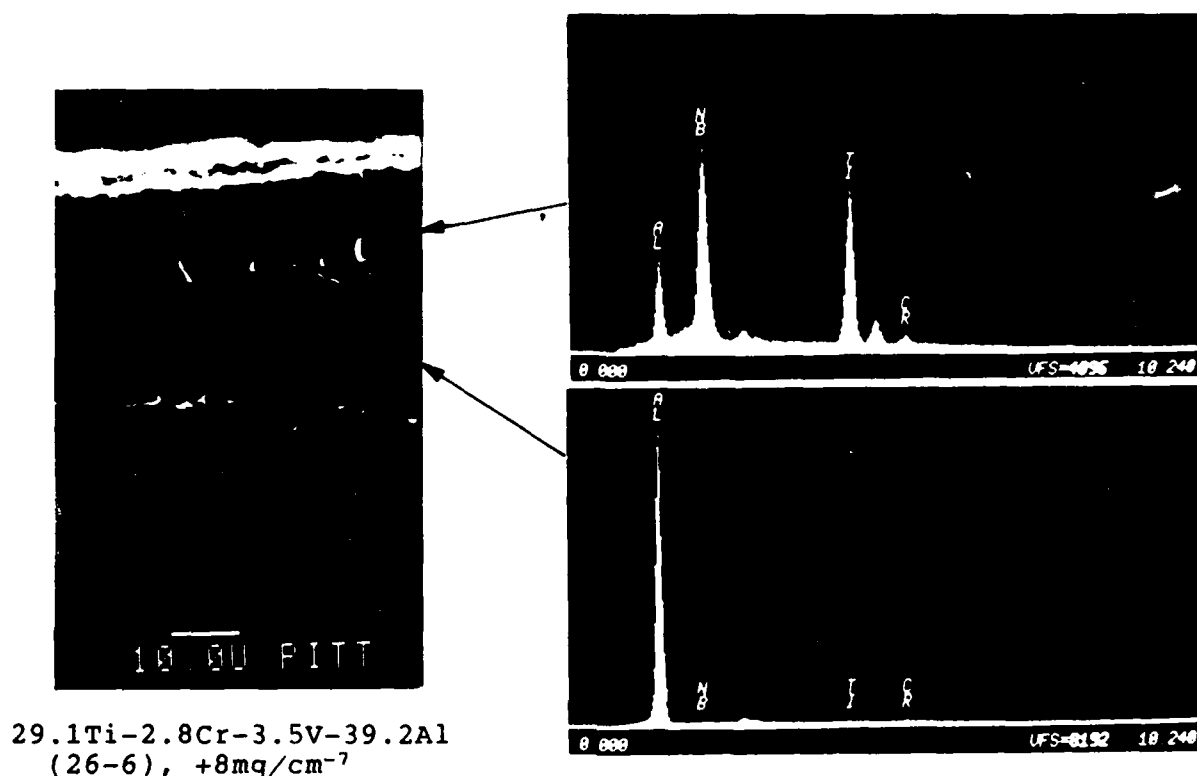


Fig. 3 Elements in Oxide Scale of Nb-Ti-Cr-V-Al Alloy After 24h at 1400°C in Air

These elements appear to function more in the base alloy than in the products of oxidation, most likely by reducing the solubility-diffusivity product of O in the alloy. This was predicated from the model on the basis of the smaller atomic diameter of Cr and V (compared with that of Nb) resulting in oxygen trapping.

The formation of alumina on Nb-Ti-Cr-V-Al alloys became more difficult as temperature was reduced and protective external alumina scales were not formed in air or O<sub>2</sub> at 1100°C. Aluminum was oxidized internally at this temperature, and a thick, non-protective oxide scale was formed (Fig.4A). The high activation energy for alumina formation coupled with the rapid non-parabolic

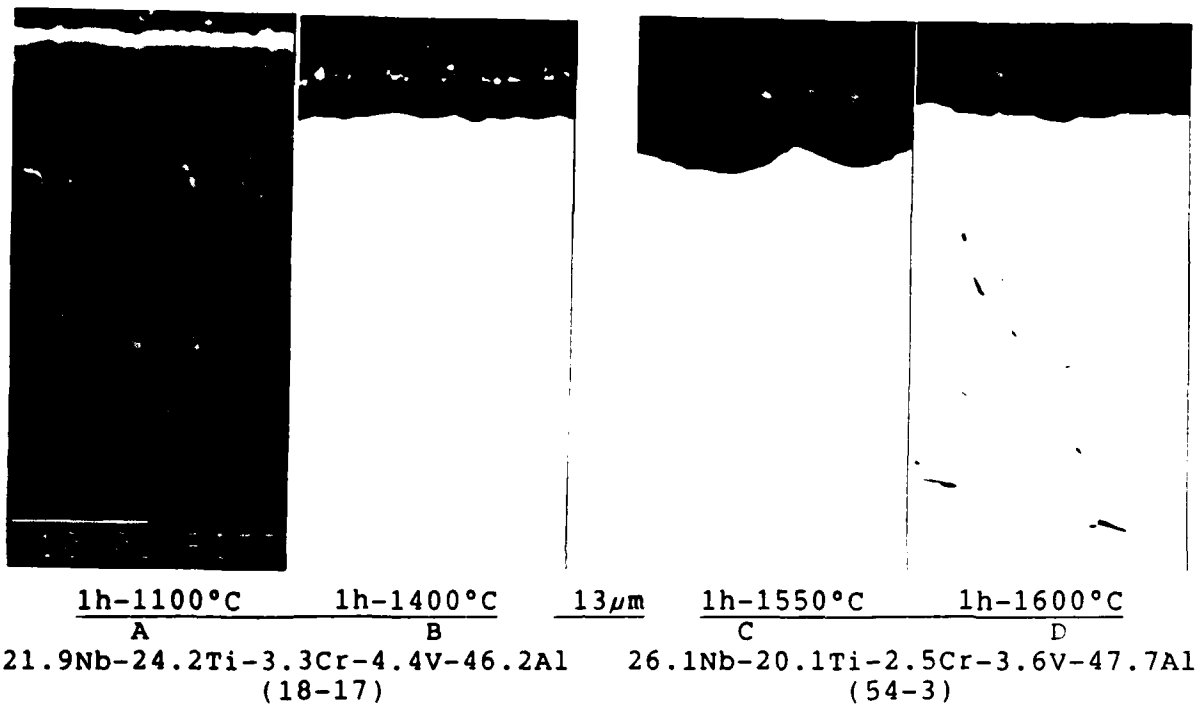


Fig. 4 Effect of Increasing Temperature on Formation of Alumina

kinetics of the transient oxidation process is considered to be responsible for this behavior.

#### SECOND YEAR RESEARCH ACTIVITIES

Research during the second year was directed largely to gaining an improved understanding of the factors controlling the transition from internal to external oxidation of Al in Nb-Ti-Cr-V-Al alloys over a wider range of temperatures. The effect of the Nb:Ti ratio and the  $N_{Al}$  of the alloy on the transition at 1100 and 1400°C was studied in more detail. The effect of temperature on the transition for fixed compositions also was investigated. Oxidation kinetics and the microstructure and composition of transient oxides was studied at 800 to 1600°C as a function of Ti, Cr, and V in the alloy to develop an understanding of the role of transient oxidation in the selective oxidation of Al.

The high concentrations of Ti, Cr, and Al required to form

alumina at 1400°C have the undesirable effect of depressing the melting point of the alloys to about 1600°C. Approaches to reduce the concentrations required were evaluated by determining if other alloy elements may be effective. The effectiveness of V as a substitute for Ti to stabilize a cubic Nb-Al alloy with a high solubility for Al was evaluated. Lowering oxygen permeability by adding elements such as Mo, Re, and Ru which have a high electron to atom ratio as substitutes for Ti and Cr also was evaluated as an approach to enhance the formation of an external alumina scale. Research was initiated on rapid solidification processing to produce more homogeneous materials with metastable or ultra fine microstructures.

## EXPERIMENTAL

### PREPARATION OF ALLOYS

All experimental alloys were prepared by low pressure argon arc-melting and drop casting. A 20-30 gm charge of high purity elemental alloy additions was premelted on a water-cooled copper hearth with a non-consumable tungsten electrode. The furnace was evacuated to  $10^{-5}$  torr and back filled with high purity argon to 1/2 atm. for melting. The button ingots were melted four times and were turned over after each melt. The flat hearth was then replaced with a water cooled copper drop cast hearth. The casting cavity was 14mm x 14mm deep. The button ingot was placed over the cavity and melted with the arc until the metal dropped into the mold.

Good quality castings of most of the Nb-Ti-Cr-V-Al alloys investigated in both the first and second year were produced by this technique. However, when these alloys were modified by other elements as replacement in part or whole for the Ti and Cr, severe problems with thermal stress cracking were encountered. Drop cast buttons cracked on cooling and often shattered on arc heating to remelt an ingot. This problem was solved by going to a micro-arc melting process in which a small 1-5 gm button ingot was produced without severe cracking. A small mass of the alloys

could be cooled rapidly without cracking.

Unless stated otherwise, all alloy compositions are given in at.% in this report.

#### OXIDATION EXPERIMENTS

Oxidation reactions and kinetics were studied for isothermal oxidation in oxygen at 800 and 1100°C and air at 1400, 1550, and 1600°C. Oxidation coupons were cut from the as-cast ingots using a diamond wafering blade. Holes for supporting the specimen in the weighing mechanism for the 800 and 1100°C kinetic studies were drilled using an electric discharge machine. The coupons were polished through 600 grit SiC paper and cleaned in acetone and methanol immediately prior to oxidation. Thermogravimetric measurements were made in oxygen at 1 atm. at 800 and 1100°C using a Cahn 2000 microbalance. The specimens were placed in the flowing O<sub>2</sub> at room temperature and the reaction was initiated by raising a preheated furnace around the reaction tube. The specimens reached the reaction temperature within 5 minutes. Oxidation runs were terminated by lowering the furnace. Selected specimens were exposed first in tank argon (residual oxygen pressure of about 10<sup>-4</sup> atm) followed by pure O<sub>2</sub> to evaluate the effect of preoxidation at reduced oxygen pressures.

Oxidation behavior was evaluated in static air at 1400-1600°C by exposing samples in a heated box furnace with MoSi<sub>2</sub> elements. Sample preparation was the same as that used for the tests at 800-1100°C in oxygen. The samples were placed in alumina boats and charged into the hot furnace. The temperature of 1400-1600°C was attained in less than 5 min. Samples were held at temperature for 1 to 24 hr and were air cooled to room temperature. Samples were weighed before and after exposure and the weight gain was measured in mgcm<sup>-2</sup>. If surface oxides spalled on cooling, the fragments were collected and weighed with the sample to obtain the total weight gain.

## MATERIALS ANALYSIS

### Chemical Analysis of Alloys

Unless otherwise stated, all compositions are in at.% and are reported as the measured composition of a specific test sample or a sample representative of a lot of samples from the same drop cast ingot. All analyses were done with a Cambridge Stereoscan SEM and a Princeton Gamma-Tech System 4 XES using a standardless quantitative computer program. In a few cases where samples have not been analyzed to date, the compositions are given as nominal at.% added in melting.

### X-ray Diffraction Analysis of Oxide Scales

Experiments to determine the phases present in the oxide scales were performed using a GE XRD 5 diffractometer with Cu  $K_{\alpha}$  radiation. The patterns obtained from most specimens were quite complex and their evaluation is continuing.

### Optical Metallography

Specimens were not cut for mounting in order to preserve the oxide scales. The samples were placed on edge and mounted in a special blend of wet-ground bakelite (Klarmont) specifically designed to aid in edge retention during polishing. The mount was ground by hand on 120 grit SiC paper to reveal the desired cross section of the sample for examination. About 0.125 to 0.25 in. of material was removed. The ground samples were then rough polished with 1 $\mu$ m diamond paste on an automatic polisher with a 300 gm load. The final polish was done on an automatic well-type polisher with a hard surface cotton cloth over a micro cloth. Samples were polished for about 30 min. with a CeO-Al<sub>2</sub>O<sub>3</sub> abrasive using a 240 gm. weight. This technique provided excellent edge retention and permitted metallographic study of the oxide scale and metal interface at magnifications up to 3000X.

### Scanning Electron Microscopy

Selected specimens were examined using a JEOL-JSM35CF scanning electron microscope with energy dispersive x-ray analysis. Observations included the scale/gas interface and, in some cases,

the cross section of the specimen and scale. All analyses were qualitative in nature and were designed to indicate significant but not absolute elemental makeup or changes in composition of the oxide scales and underlying alloy.

## RESULTS

### OXIDATION BEHAVIOR OF Nb-Ti-Cr-V-Al ALLOYS

#### 1400-1600°C Range

Oxidation experiments conducted in air revealed that the amount of transient oxidation of Nb-Ti-Cr-V-Al alloys decreased with increasing temperature. As shown in Fig.4, an  $8\mu\text{m}$  thick transient oxide formed at  $1100^\circ\text{C}$  while a  $4\mu\text{m}$  thick layer formed at  $1400^\circ\text{C}$ . At  $1550^\circ\text{C}$ , the oxide was discontinuous and formed at random spots on the surface while at  $1600^\circ\text{C}$ , no transient was formed and a single layer alumina scale similar to that formed on on NiAl was present. It was found that this alloy was above the solidus at  $1600^\circ\text{C}$  and the alumina scale was formed on a partially molten sample. A distinct grain structure appeared to exist in the alumina but on close examination was found be the result of fragmentation of the oxide as a result of stress induced by the volume change of the alloy during solidification on cooling from the test temperature. The transient oxide formed at random spots on the surface in the  $1550^\circ\text{C}$  test contained Al, Nb, and Ti (Fig.5). It was similar to the transient formed as a continuous layer at  $1400^\circ\text{C}$  (Fig.3). The alumina scale formed at  $1550^\circ\text{C}$  was nearly pure alumina but did contain a trace of Nb as indicated by the SEM-XES scan in Fig.5.

The same transition in oxide scale morphology occurred with increased Al content in the alloy at a fixed temperature of  $1400^\circ\text{C}$  (Fig.6). Aluminum in the alloy was oxidized internally at a level of 38 at.% while a continuous external alumina scale was formed at a level of 44 at.%. The amount of transient oxidation decreased with increasing Al and single layer alumina scale with no transient was formed at a level of 57.8 at.% Al in the alloy. As shown in Fig. 6,  $N_{\text{Nb}}$  and  $N_{\text{Ti}}$  were decreased as  $N_{\text{Al}}$  of the

alloys was increased. Chromium and V remained constant. The ratio of Nb:Ti in the alloys was held constant at 1.3:1.

The transition from internal to external oxidation of Al from Nb-Ti-Al alloys with and without Cr and V in air at 1400°C was

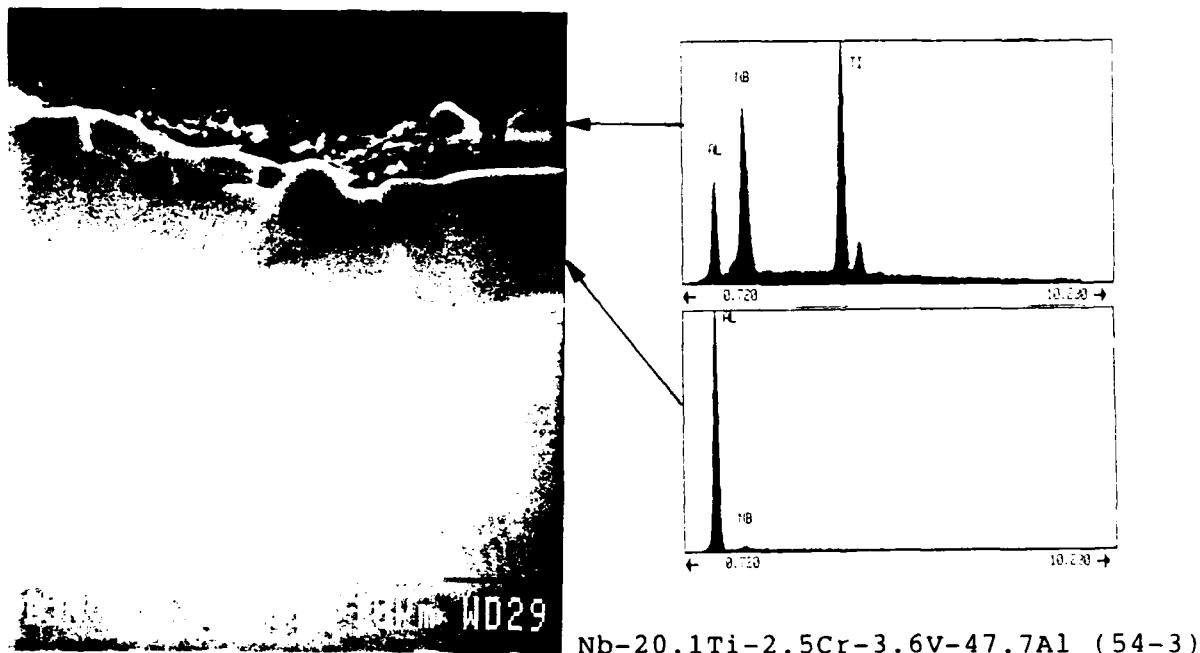
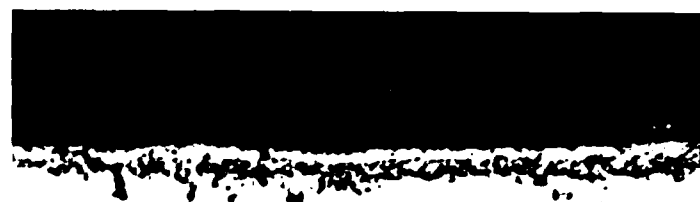
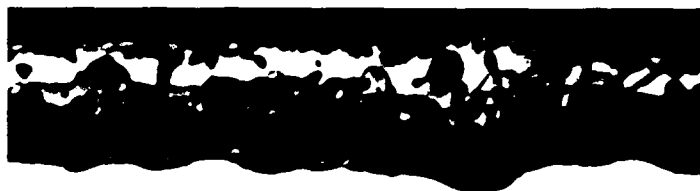


Fig. 5 Elements in Alumina and Transient Oxide Formed in Air at 1550°C

studied as a function Al content and Nb:Ti ratio at 1400°C. As shown in Fig.7, the transition occurred with an  $N_{Al}$  of between 0.375 and 0.39 for a range of Nb:Ti ratios of 0.8 to 1.38. There appears to be a slight trend to a decreasing  $N_{Al}^{crit}$  with increasing Nb:Ti ratio. Higher ratios need to be studied to confirm the trend. Variations in Cr from 3-9% and V from 3-5% had little, if any, effect on the transition. Most of the data are for alloys containing Cr or Cr+V. A Nb-Ti-Al ternary alloy with 37.5% Al was internally oxidized and a second alloy with 42% Al formed a discontinuous alumina scale (Fig.1A), indicating that small additions of Cr and V do have an influence on  $N_{Al}^{crit}$ . More tests are needed with the ternary Nb-Ti-Al alloys to determine the precise effect of small additions of these elements.



| at. % |      |     |     |      | RATIO<br>Nb/Ti |
|-------|------|-----|-----|------|----------------|
| Al    | Ti   | Cr  | V   | Nb   |                |
| 38.0  | 24.1 | 2.4 | 3.4 | 32.1 | 1.33           |



|      |      |     |     |      |      |
|------|------|-----|-----|------|------|
| 44.2 | 21.3 | 2.3 | 3.2 | 29.0 | 1.36 |
|------|------|-----|-----|------|------|



|      |      |     |     |      |      |
|------|------|-----|-----|------|------|
| 47.7 | 20.1 | 2.5 | 3.6 | 26.1 | 1.30 |
|------|------|-----|-----|------|------|



|      |      |     |     |      |      |
|------|------|-----|-----|------|------|
| 49.8 | 19.5 | 2.8 | 2.9 | 25.0 | 1.28 |
|------|------|-----|-----|------|------|



|      |      |     |     |      |      |
|------|------|-----|-----|------|------|
| 52.8 | 17.9 | 2.3 | 3.4 | 23.6 | 1.32 |
|------|------|-----|-----|------|------|



|      |      |     |     |      |      |
|------|------|-----|-----|------|------|
| 57.8 | 15.6 | 2.5 | 3.4 | 20.7 | 1.33 |
|------|------|-----|-----|------|------|

13  $\mu\text{m}$

Fig. 6 Effect of Increasing  $N_{\text{Al}}$  on formation of Alumina in Alloys With Nb-Ti Ratio of 1.3:1, 1h - 1400°C, Air

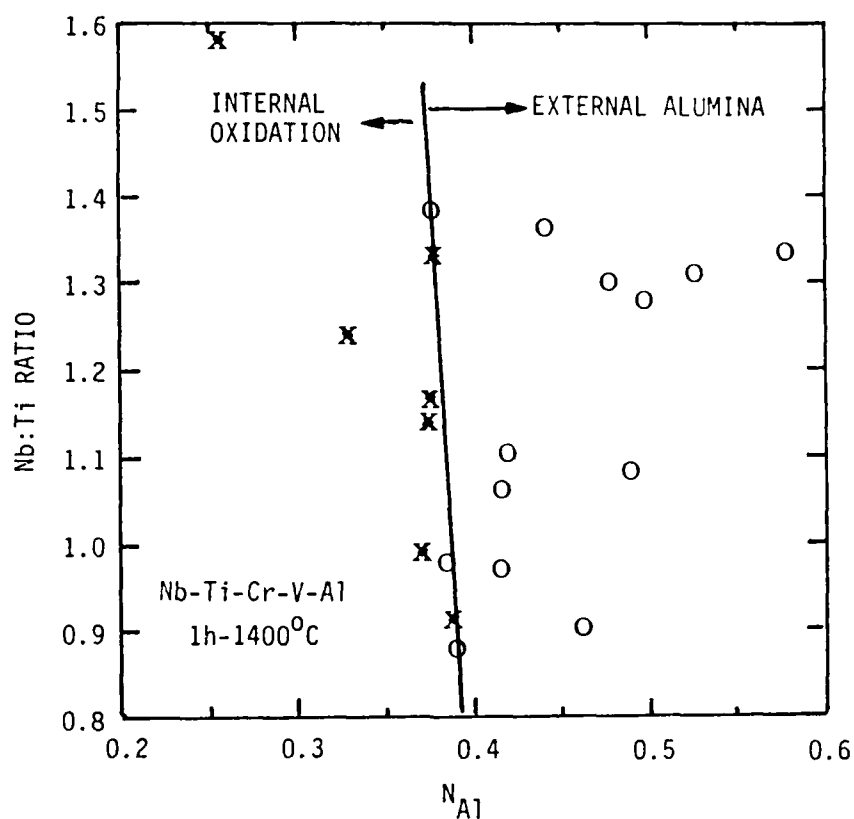


Fig. 7 Effect of Nb/Ti Ratio on  $N_{Al}$  for Transition from Internal to External Oxidation of Al

The effect of increasing Al on the selective oxidation of Al to form an external alumina scale and on reducing transient oxidation is reflected in the oxidation kinetics as measured by weight gain for a fixed time of exposure. As plotted in Fig.8, an abrupt drop in weight gain occurred with the transition to external alumina formation. Weight gain continued to decrease with increasing Al beyond this point as a result of reduced transient oxidation and leveled off to a steady value at the high Al level where only alumina was formed.

Increasing the Al content to 47.7% with a Nb:Ti ratio of 1.36 to decreased transient oxidation but had the undesirable effect of reducing alloy melting point to about 1600°C (Fig.4D). Increasing Al further to 57.8% lowered the melting point to 1550°C. When the Al content was decreased to 44.2%, the alloy did not melt at 1600°C but the kinetics of transient oxidation at 1550°C were increased greatly. The transient oxide melted between 1550 and 1600°C (Fig.9). The melted oxide was analyzed

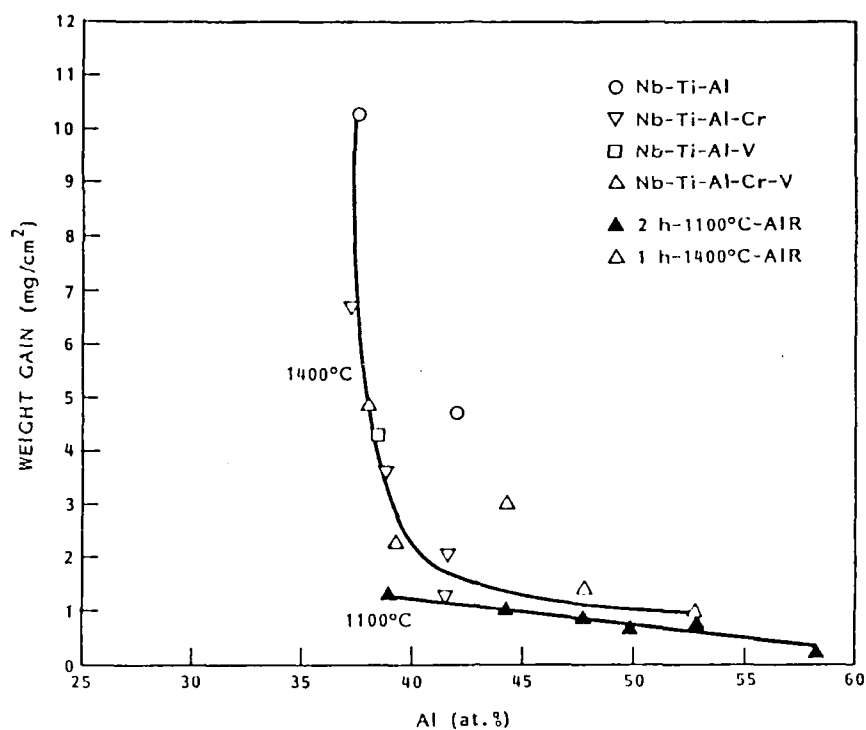


Fig.8 Effect of  $N_{Al}$  on weight Gain

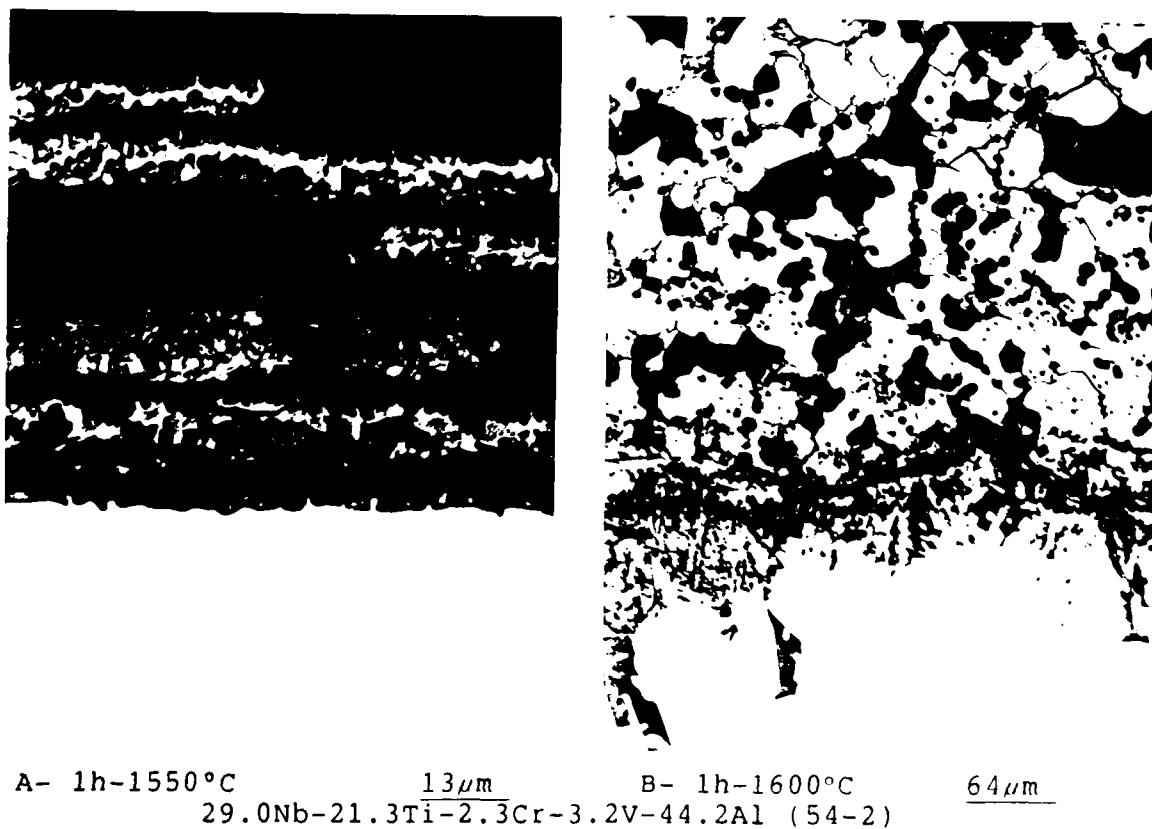


Fig. 9 Effect of Transient Oxide Melting on Formation of Alumina

to determine the composition of phases present (Fig.10). The major phase in the oxide was found to contain 80.2% Nb and 13.3% Ti. The Nb:Ti ratio corresponds to that of  $3\text{Nb}_2\text{O}_5 \cdot \text{TiO}_2$ . The composition of the minor phases in the oxide does not correspond with any identifiable known oxides.

#### 800-1100°C Range

More detailed studies of the transient oxide composition and



25  $\mu\text{m}$

| ELEMENT | WT %   | ATOMIC % |
|---------|--------|----------|
| AL      | 58.35  | 82.23    |
| TI      | 0.26   | 0.21     |
| V       | 0.34   | 0.26     |
| CR      | 1.56   | 1.14     |
| NB      | 39.49  | 16.16    |
| TOTAL   | 100.00 | 100.00   |
| AL      | 1.04   | 3.23     |
| TI      | 7.66   | 13.34    |
| V       | 1.17   | 1.92     |
| CR      | 0.82   | 1.32     |
| NB      | 89.31  | 80.20    |
| TOTAL   | 100.00 | 100.00   |
| AL      | 2.08   | 6.42     |
| TI      | 6.06   | 10.54    |
| V       | 0.92   | 1.50     |
| CR      | 0.00   | 0.00     |
| NB      | 90.95  | 81.55    |
| TOTAL   | 100.00 | 100.00   |
| AL      | 2.37   | 7.48     |
| TI      | 3.12   | 5.54     |
| V       | 0.71   | 1.18     |
| CR      | 0.00   | 0.00     |
| NB      | 93.80  | 85.81    |
| TOTAL   | 100.00 | 100.00   |

Fig. 10 Composition of Phases in Transient Oxide Melted at 1600°C in Air

structure were conducted with samples tested at 1100°C. A high Al alloy (46.2%) formed a 5-10 $\mu\text{m}$  thick scale which was found to be a mixture of  $\text{AlNbO}_4$  and  $\text{TiO}_2$  with small particles that did not have identifiable X-Ray patterns (Fig.11A). As shown in Fig.11B, an alloy with 39.2% Al formed a different scale with three distinct layers on exposure to  $\text{O}_2$  for 2h at 1100°C. The outer layer contained Al and Ti, the middle layer contained Nb and Ti, while the inner layer contained Al and Nb with a small amount of

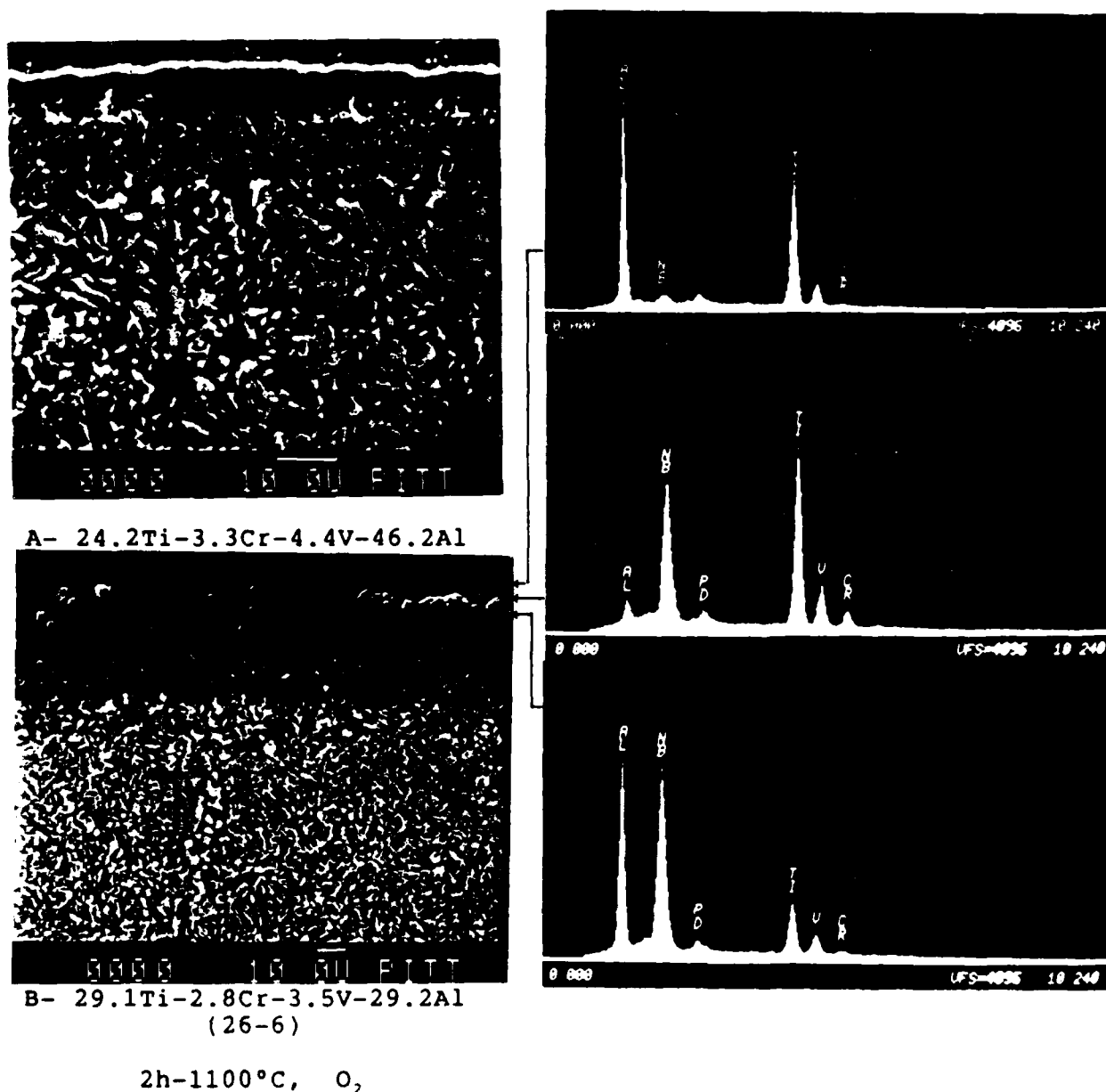


Fig. 11 Distribution of Elements in Transient Oxide Scale Formed at 1100°C

Ti. Vanadium, which was not found in the scales formed at 1400°C, was present in significant amounts in all layers. Vanadium also was found in the melted scale formed at 1600°C at about a 1% level. Chromium, which was present in trace amounts in the transient oxide formed in air at 1400-1600°C (Figs.3,10) was present in higher concentrations in the transient oxide formed in oxygen at 1100°C. It has not been determined if this was the effect of temperature or the result of a change in

oxidizing atmosphere.

The oxidation kinetics of these alloys were studied in  $O_2$  at  $1100^\circ C$  and results of the first series of tests are presented in Fig.12. The alloy with 39.2% Al (26-6) which formed the three layer scale oxidized at a rapid rate. The plot ( $\Delta m/a$  vs.  $t^{1/2}$ ) initially curved upward but then become linear (parabolic behavior) with a  $k_p$  of  $7 \times 10^{-1} \text{ mg}^2 \text{cm}^{-4} \text{m}^{-1}$  ( $1.17 \times 10^{-8} \text{ g}^2 \text{cm}^{-4} \text{s}^{-1}$ ). The alloy with 46.2% Al (18-17) was tested for only 2h but showed parabolic behavior with a  $k_p$  of  $5.3 \times 10^{-2} \text{ mg}^2 \text{cm}^{-4} \text{m}^{-1}$  ( $8.83 \times 10^{-10} \text{ g}^2 \text{cm}^{-4} \text{s}^{-1}$ ). Additional tests will be conducted to verify these results.

When the lower Al content alloys were exposed for 24-55h at  $1100^\circ C$ , they formed thick scales with a layered structure that spalled on cooling (Fig.13). Major oxides in the scales were identified as  $TiO_2$  (rutile) and  $AlNbO_4$ . Aluminum was internally

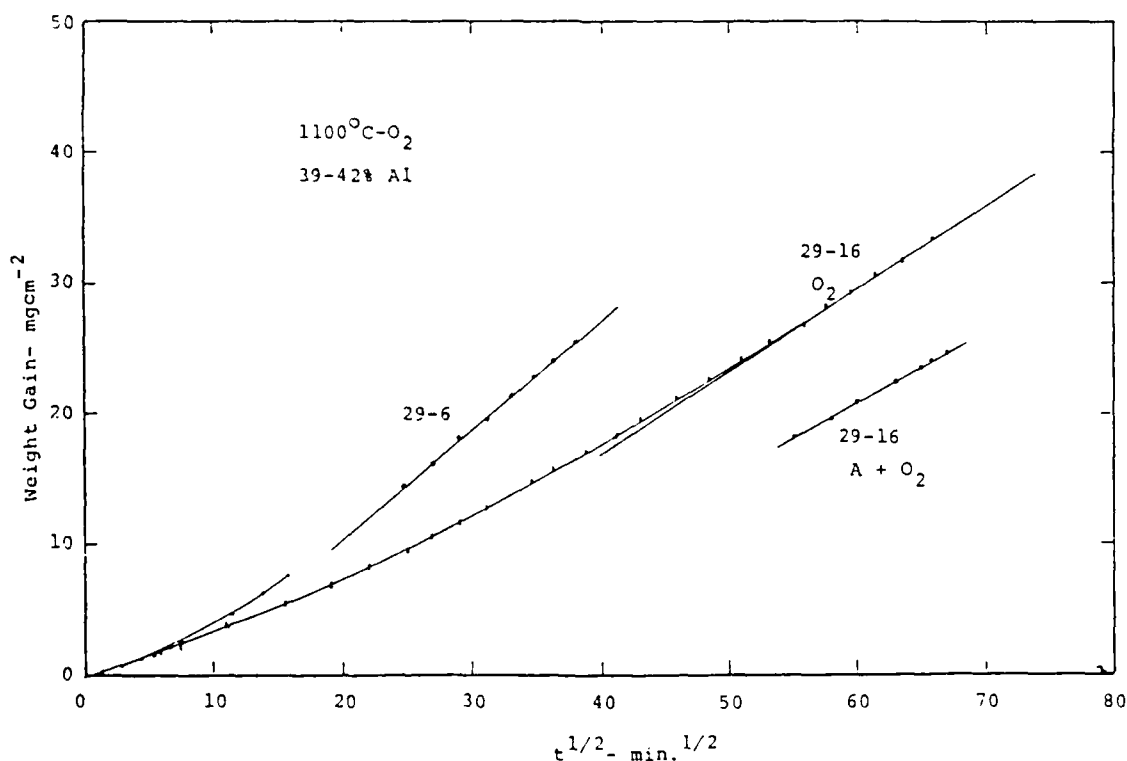
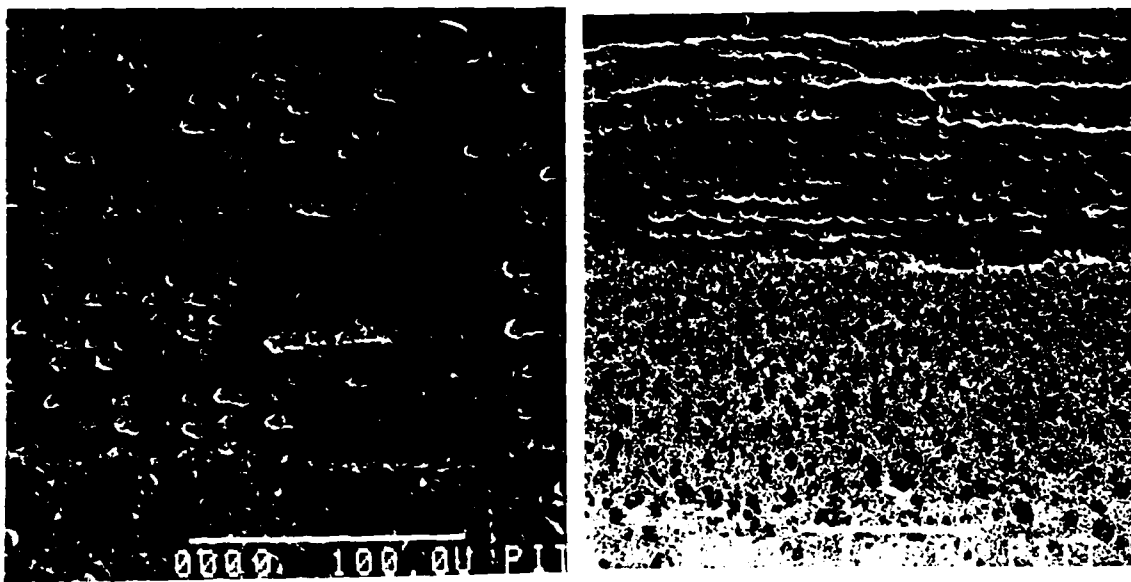


Fig. 12 Oxidation Kinetics at  $1100^\circ C$  in Oxygen

oxidized in the alloys to a depth of over  $150 \mu m$ . Pre-oxidation of a Nb-25.4Ti-8.3Cr-41.5Al alloy by heating for 20h in impure

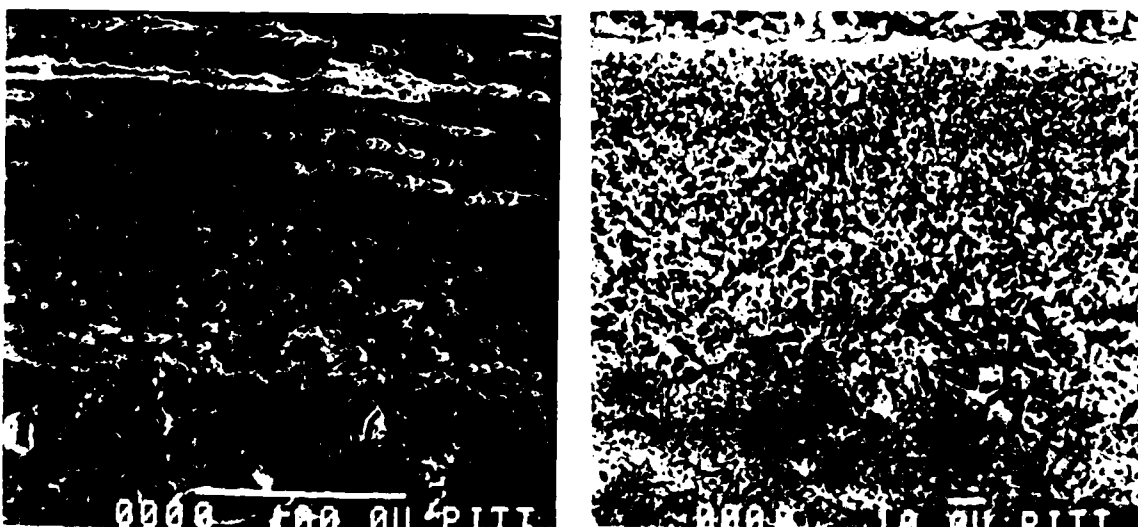
argon (low  $P_{O_2}$ ) did not reduce the rate of oxidation significantly as shown in Fig.12. The final part of the rate curve is parabolic with a  $k_p$  of  $2.87 \times 10^{-1} \text{ mg}^2 \text{ cm}^{-4} \text{ m}^{-1}$  ( $4.87 \text{ g}^2 \text{ cm}^2 \text{ s}^{-1}$ ). The sample without preoxidation had a  $k_p$  of  $3.9 \times 10^{-1} \text{ mg}^2 \text{ cm}^{-4} \text{ m}^{-1}$  ( $6.5 \times 10^{-9} \text{ g}^2 \text{ cm}^{-4} \text{ s}^{-1}$ ) (Fig. 12A).



72.6h -  $O_2$  (SPALLED SCALE)

19.8h - A + 55.5h -  $O_2$   
24h-1100°C,  $O_2$

A- 24.7Nb-25.4Ti-8.3Cr-41.5Al (29-16)



SPALLED SCALE

INTERNALLY OXIDIZED ALLOY  
24h-1100°C,  $O_2$

B- 25.4Nb-29.1Ti-2.8Cr-3.5V-39.2Al (26-6)

Fig. 13 Effect of Cr and V on Metal and Oxide Structures, 1100°C,  $O_2$

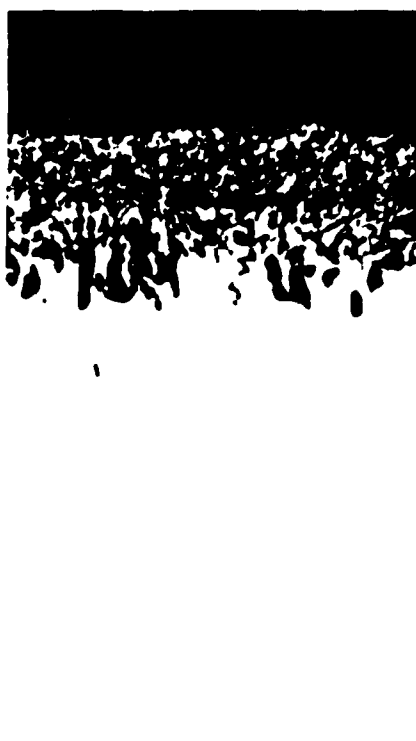
A major reduction in the amount of transient oxidation and oxidation kinetics at 1100°C was achieved only by a large increase in Al content. As shown in Fig.14, the thickness of the transient oxide and the depth of internal oxidation increased steadily with increasing Al from 38 to 57.8 at.%. The alloy with 57.8% Al was very close to forming a continuous alumina scale in air at 1100°C.

Oxidation behavior of the alloys at 800°C was similar to that at 1100°C. The rate curves from tests in oxygen are shown in Figs.15,16. Alloys with 39-48%Al started to oxidize with parabolic kinetics at one rate but shifted to a higher rate after 15-25h (Fig.15). Alloys with 49-58% Al, on the other hand, plotted as upward curves initially but shifted to linear (parabolic kinetics) after ~60h (Fig.16B). The alloy with the highest Al content (57.8%) was of particular interest in that a cyclic behavior was observed. The plot started linear (parabolic kinetics), shifted to upward curving at 6.7h, returned to linear (parabolic kinetics) at 26.7h, and shifted back to curving upward at 60h. (Fig. 16C). The alloy appears to form a protective scale that breaks away, reforms, and breaks away again, much like the behavior of NbAl<sub>3</sub> in tests at 1300°C in air (1).

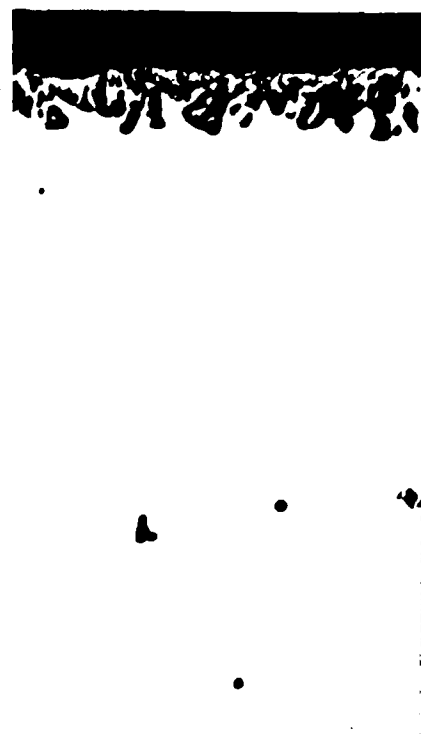
Rate constants for parabolic segments of the curves ranged from 1.7 to 6.4 x 10<sup>-3</sup> mg<sup>2</sup>cm<sup>-4</sup>m<sup>-1</sup> (2.9x10<sup>-11</sup> to 1.1x10<sup>-10</sup> g<sup>2</sup>cm<sup>-4</sup>s<sup>-1</sup>) as shown in Table A2, Appendix. The unusual shape of the 800°C curves requires that the parabolic rate data be qualified. The data are based on segments of plots of  $\Delta m/a$  vs  $t^{1/2}$  that may not be truly linear and may be curving upward at a slow rate. More extensive testing with longer times of exposure will be required to establish sound kinetic data. Results to date should be considered tentative. The parabolic rate constant at 800°C was relatively insensitive to changes in  $N_{Al}$  but tended to increase with increasing  $N_{Al}$  as shown in Fig. 17. This behavior is quite different from that observed at 1100°C. As shown in Fig.17, the  $k_p$  at 1100°C decreased with increasing  $N_{Al}$ . Plots of the total weight gain vs.  $N_{Al}$  for a fixed time of exposure reveal a



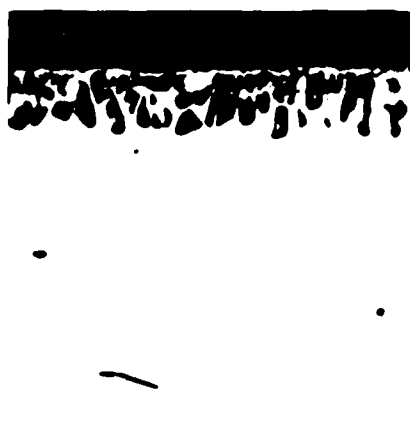
A- 38.0Al-24.1Ti  
24.0Cr-3.4V (54-1)  
+1.25 mg/cm<sup>2</sup>



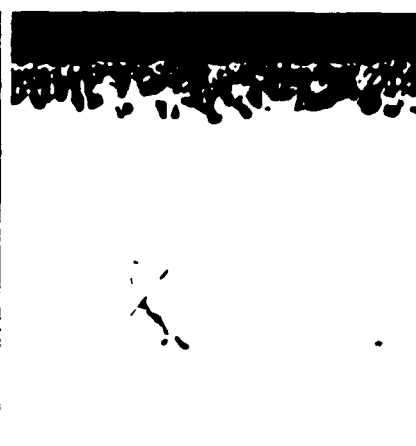
B- 44.2Al-21.3Ti  
2.3Cr-3.2V (54-2)  
+0.97 mg/cm<sup>2</sup>



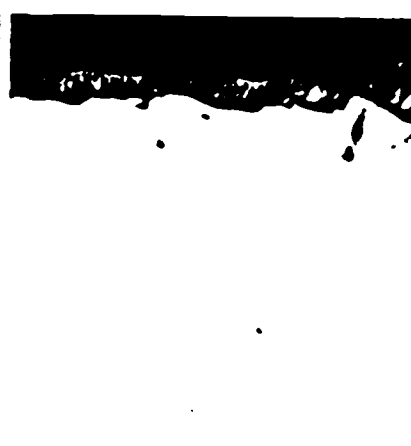
C- 47.7Al-20.1Ti  
2.5Cr-3.6V (59-3)  
+0.87 mg/cm<sup>2</sup>



D- 49.8Al-19.5Ti  
2.8Cr-2.9V (54-17)  
+0.64 mgcm<sup>-2</sup>



E- 52.8Al-17.9Ti  
2.3Cr-3.4V (54-4)  
+0.77 mgcm<sup>-2</sup>



F- 57.8Al-15.6Ti  
2.5Cr-3.4V (54-5)  
+0.18 mgcm<sup>-2</sup>

13  $\mu$ m

Fig. 14 Effect of Increasing N<sub>Al</sub> on Formation of Alumina on Alloys  
With a Nb:Ti Ratio of 1.3:1, 2h-1100°C, Air

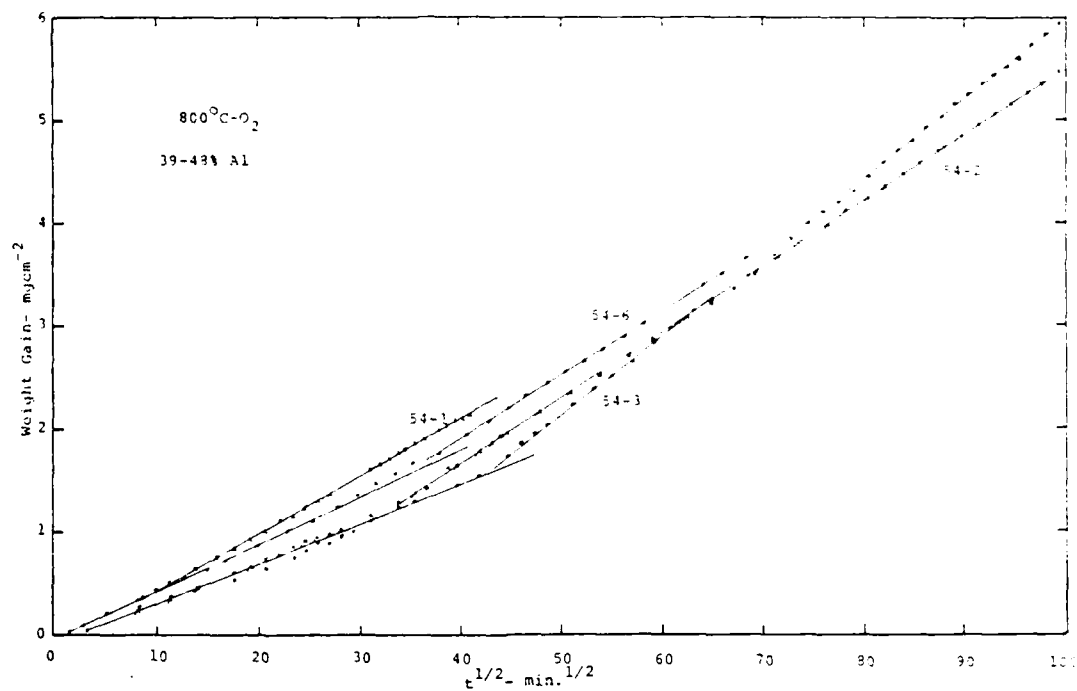


Fig. 15 Oxidation Kinetics for Alloys With 39-48% Al at 800°C in Oxygen

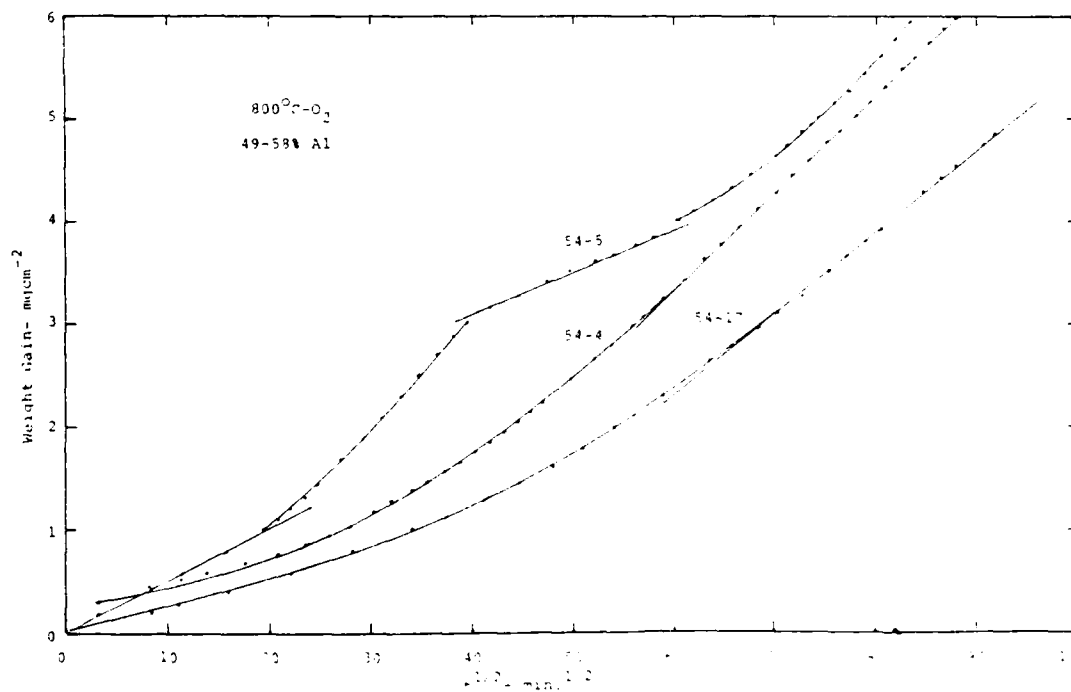


Fig. 16 Oxidation Kinetics for Alloys With 49-58% Al at 800°C in Oxygen

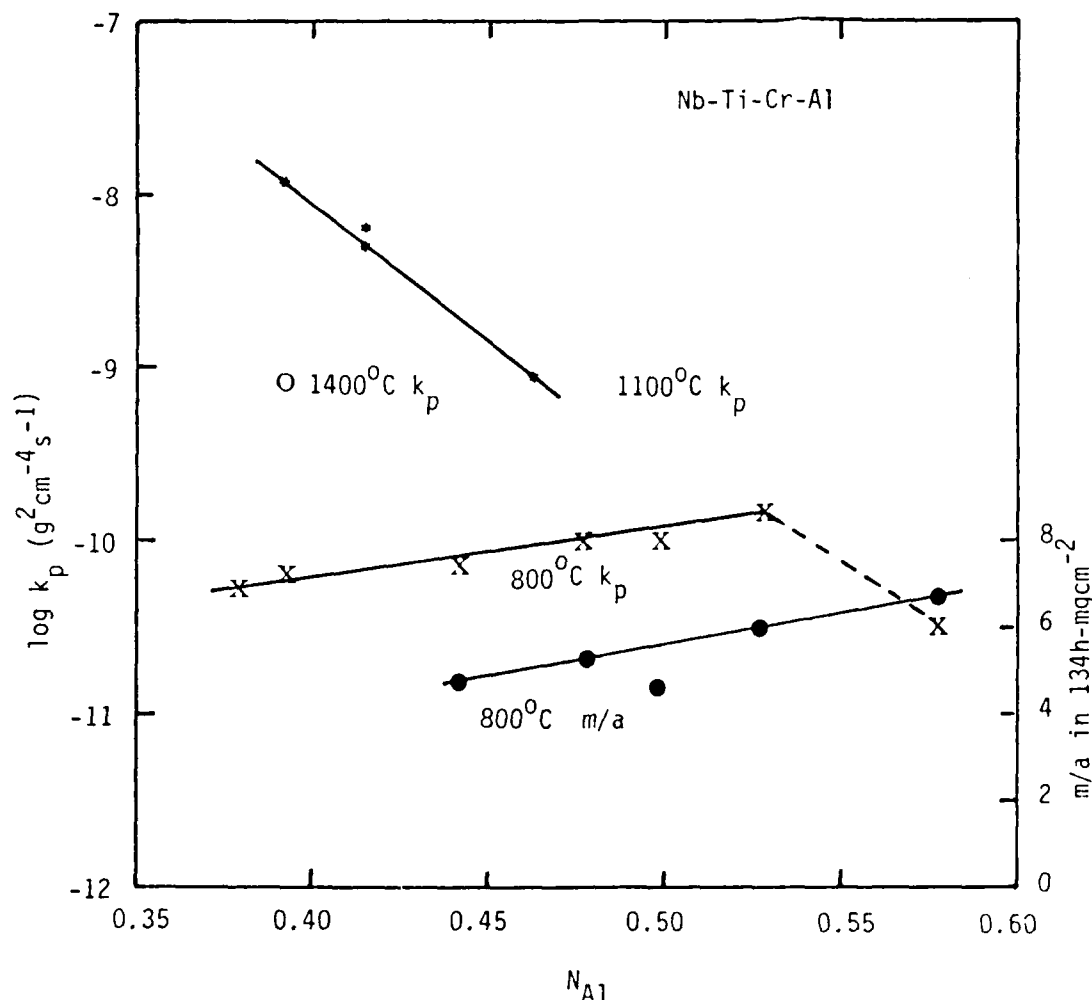


Fig. 17 Effect of Al on Parabolic Rate Constants

similar behavior (Figs. 8, 17). Total  $\Delta m/a$  also is a function of aluminum content, increasing with  $N_{Al}$  at 800°C and decreasing with  $N_{Al}$  at 1100°C.

The reason this behavior was indicated by SEM and metallographic study of the cross section of oxidized samples. A continuous alumina scale was not formed at either temperature, accounting for the large parabolic rate constants relative to those of an alumina former such as NiAl. The  $k_p$  at 1100°C was 3-4 orders of magnitude greater than that of NiAl while at 800°C it was about 5 orders of magnitude greater. As noted in the previous section, the alloys did form continuous alumina at 1400°C and the rate constants were within 1 order of magnitude of the  $k_p$  for NiAl (Table A2, Appendix). When the alloys were oxidized at 1100°C, internal oxidation of Al and formation of a complex Nb-Ti-Al

oxide scale was observed. The scale was more protective as  $N_{Al}$  increased so that both the scale thickness and depth of internal oxidation were decreased (Fig. 14). The result is a decreased  $k_p$  with increased  $N_{Al}$ .

The scale formed on alloys with 44 to 58% Al contained alumina which increased in amount and was more continuous with increased  $N_{Al}$ , becoming a more protective layer. As shown in Fig. 13, the scales formed on alloys with 39-41.5% Al at 1100°C were very thick and had layered structures with bands of Al-rich oxide but no free alumina. XRD patterns showed  $AlNbO_4$  and  $TiO_2$  in the scales. These scales were not protective and deep internal oxidation of Al (100-150  $\mu m$ ) occurred in 24 to 55 h. The most notable change occurred at 44% Al where alumina began to form and the depth of internal oxidation was <15  $\mu m$  in 2h.

Alloys with 38 to 58% Al tested at 800°C all behaved like the alloys with 39-41.5% Al at 1100°C. They formed thick, non-protective layered oxides containing  $AlNbO_4$  and  $TiO_2$  but no  $Al_2O_3$ . The oxide was the same on all alloys regardless of aluminum content. Typical microstructures are shown in Fig. 18A. Aluminum rich bands are dispersed as layers in the structure. The cyclic rate behavior observed with the highest Al content (57.8%) alloy (Fig. 16C) coupled with a significant drop in  $k_p$  is a clear indication that an alumina layer is beginning to form at the highest  $N_{Al}$  evaluated.

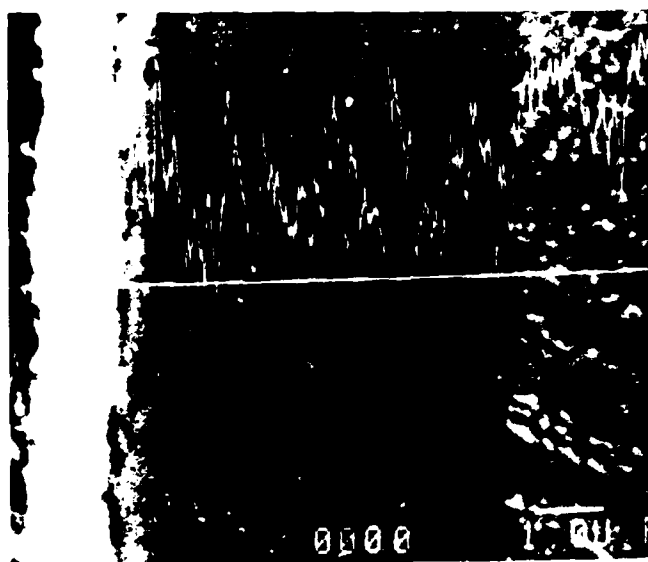
The increased  $k_p$  with increased  $N_{Al}$  at 800°C appeared to be the result of increased internal oxidation. As shown in Fig. 18B, an alloy with 44.2% Al was internally oxidized to a depth of 43  $\mu m$  (1.69 mil) in 164 h at 800°C. The internally oxidized zone was unlike that found at 1100°C where one phase in the alloy is oxidized selectively to form discrete particles of alumina (Fig. 11). Alumina particles in the oxidized zone were not resolved at magnifications up to 3000X (Fig. 18B). The zone appeared to be more like a diffusion hardened zone where O has diffused in,



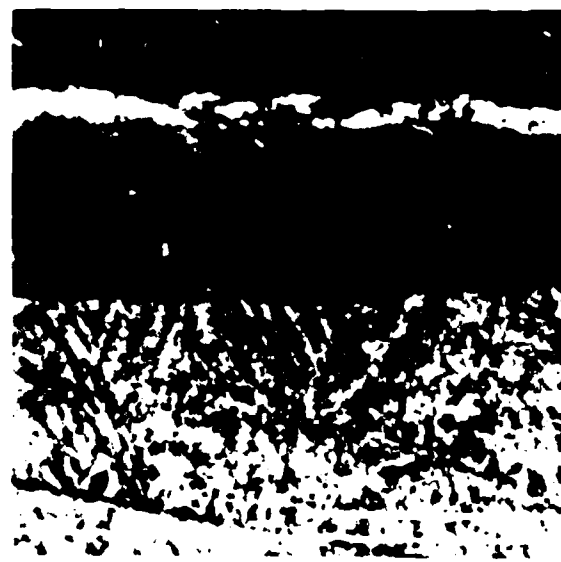
2.5 μm



18 μm



1.3 μm



4.1 μm

A- Nb-29.1Ti-2.8Cr-3.5V-39.2Al  
(26-6)

B- Nb-21.3Ti-2.3Cr-3.2V-44.2Al  
(54-2)

Fig. 18 Oxide Scales Formed in O<sub>2</sub> at 800°C.

forming submicron particles of alumina by internal oxidation. Transmission electron microscopy will be needed to establish the precise nature of the zone. The 800°C samples do reveal, however, that the permeability of oxygen in the alloys is high and that more attention must be given to reducing the solubility diffusivity product of oxygen in the alloy.

#### ALLOYING TO REDUCE PERMEABILITY

Nickel-base alloys that readily form external alumina scales at low values of  $N_{Al}^{crit}$  make effective use of Cr as an oxygen trap to reduce permeability (3). The use of Cr and V as low level additions (2-8%) to NbTiAl alloys has not been as effective. Since higher levels of Cr depress the melting point, increased V content was evaluated as an approach to reduced permeability. As shown in Fig. 19, the addition of 25at%V to Nb-V-Al with 40at.%Al resulted in formation of a continuous alumina scale in 1 h at



Nb-25V-10Cr-40Al (54-13)

Fig. 19 Effect of V as an  $O_2$  Trap on Scale Formation at 1400°C-1h, Air)

1400°C in air. No internal oxidation was observed and the scale is similar to that formed on the Nb-Ti-Al alloys with small additions of Cr and V. The effectiveness of V as an oxygen trap was indicated clearly. The only problem was that the high V content produced a transient oxide that was liquid at 1400°C. While it is likely that the V content could be reduced, the

fluxing characteristics of V-oxides are such that problems with melting of the transient oxide may be encountered over a wide range of compositions.

A second approach to reduced permeability is to add elements that increase the electron/atom ratio ( $e/a$ ). Bryant (4) has shown that the solubility of oxygen in Nb can be reduced to near zero by adding sufficient Mo ( $e/a=6$ ), Re ( $e/a=7$ ), or Ru ( $e/a=8$ ) to Nb ( $e/a=5$ ) to form an alloy with an  $e/a$  of 5.8. A series of Nb-Re-Al alloys was made with a constant ratio of Nb:Re of 1.5:1 to produce a base alloy (disregarding Al) with an  $e/a$  of 5.8. Alloys of this base with 20, 30, and 40at.%Al were oxidized for 1 hr at 1400°C in air. As shown in Fig. 20, the alloys did not form alumina. Very thick, non-protective oxide scales were

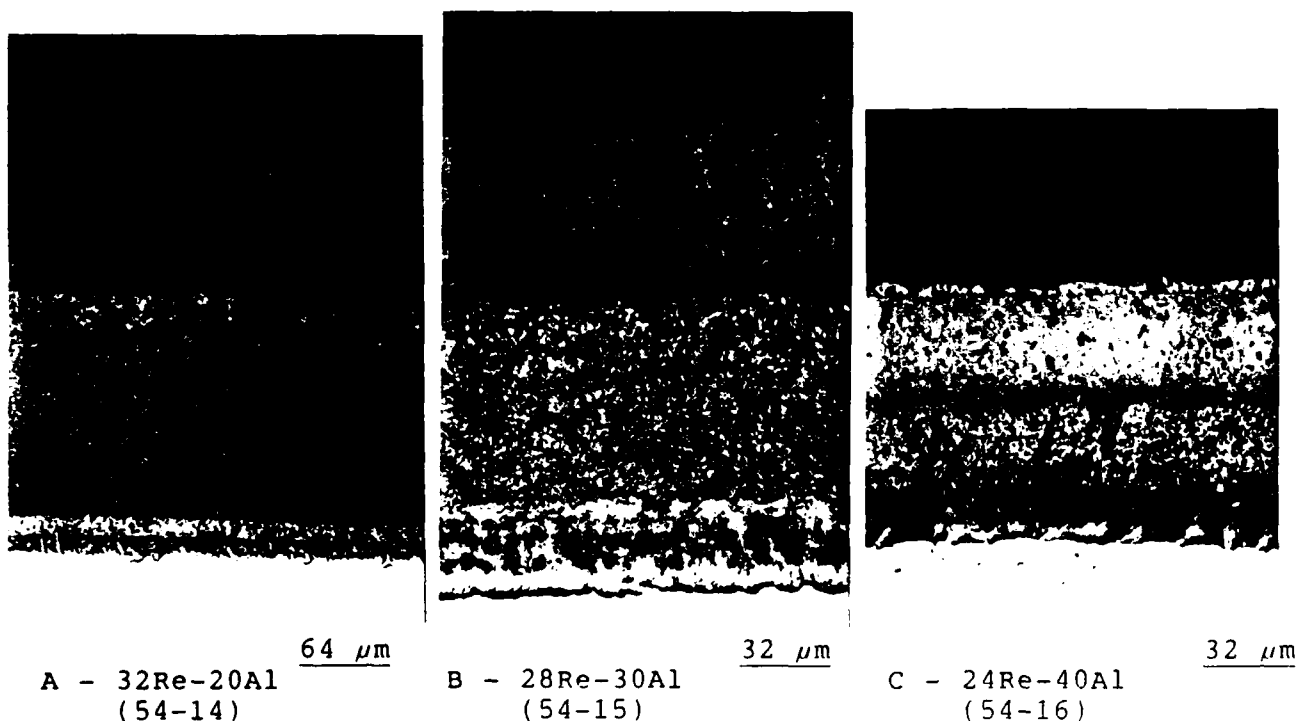


Fig. 20 Effect of Al on Nb-Re ALLOY With a 5.8  $e/a$  on Scale Formation at 1400°C (1 h, Air) formed instead. Oxide thickness decreased with increasing Al from 293  $\mu$ m (11.5 mil) at 20%Al to 96  $\mu$ m (3.8 mil) at 40%. The oxides had complex layered structures and appeared to have been molten or partially molten at 1400°C. Rhenium, like V, forms low melting oxides which behave like fluxes in complex oxide systems.

It is significant to note that no internal oxidation of Al occurred, even with as little as 20at.%Al in the alloy. This indicates that oxygen permeability has been reduced effectively. On the other hand, the alloys oxidized on a uniform front with a high rate of surface recession. The alloy may have been consumed more rapidly than oxygen could diffuse in or alumina could be formed.

A second series of alloys was made in which Fe was added to increase  $e/a$ . The position of Fe in the periodic table is such that it could act as an element with an  $e/a$  of 8. Svedberg (5) found that iron was an effective addition to reduce the rate of oxidation of Nb and reported that an alloy of Nb-30wt.%Fe-10wt.%Al (34.5at.%Fe, 23.9at.%Al) oxidized with parabolic kinetics at 1200°C. The  $k_p$  was  $4.2 \times 10^{-2} \text{ mg}^2\text{cm}^{-4}\text{m}^{-1}$  ( $7 \times 10^{-10} \text{ g}^2\text{cm}^{-4}\text{s}^{-1}$ ), close to that of NbAl<sub>3</sub>. The ratio of Nb:Fe in the alloy is 1.2:1 ( $e/a=6.4$ ). The alloy formed a protective scale with a rutile structure.

A series of Nb-Fe-Al alloys has been made in which the Nb:Fe ratios were adjusted to  $e/a=5.8$  (series 1) and 4.6 (series 2) and Al was added at levels of 25, 30, and 35at.%. The alloys were extremely sensitive to thermal shock and tended to disintegrate on repeated arc melting. It was found that samples with a minimum of cracking could be produced by micro-melting 1-5 gm pieces of the alloys and a number of samples have been prepared for oxidation tests that will be conducted during the third year.

Another series of alloys containing 40%Al was made in which Re, Ru, and Mo were added to reduce  $e/a$  and Cr and V were added as O<sub>2</sub> traps. Titanium was added to stabilize a cubic phase. The alloy compositions and oxide scales produced in 1 h at 1400°C in air are shown in Fig. 21. Continuous alumina scales were not formed on any of the alloys. A Nb-25Ti-10Re-40Al alloy formed a mixed scale and discontinuous alumina with random fingers of internal oxidation. All the other alloys, in which the Ti had been reduced to 15%, formed thick, non-protective scales. No internal oxidation was observed. Again, this may be the result of rapid

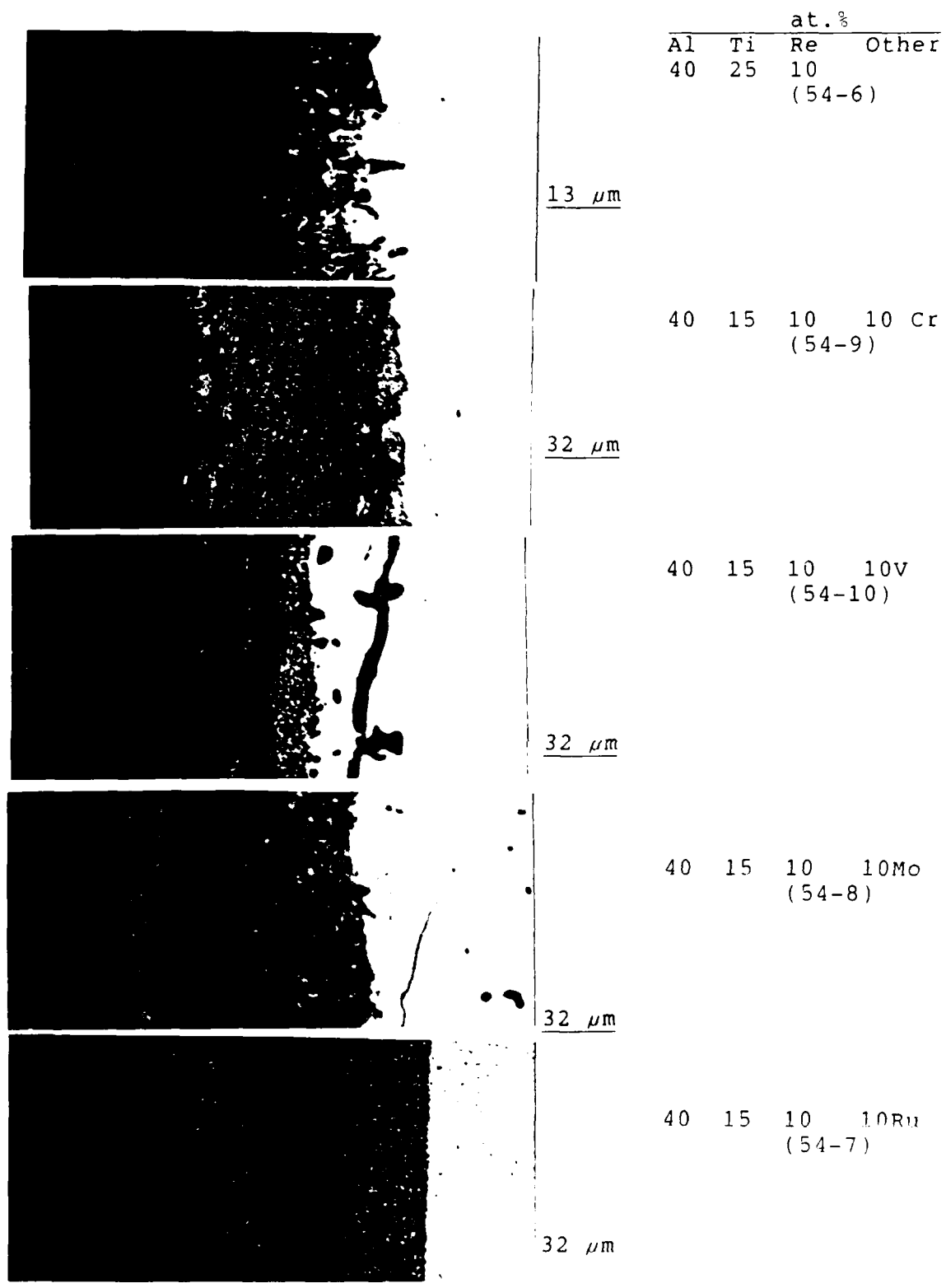


Fig. 21 Effect of Elements With a High electron to Atom Ratio on Scale Formation at 1400°C (1h, Air)

general surface recession which consumes the alloy before O can penetrate to any significant depth. Most of the oxides appeared to have been molten or partial molten at 1400°C.

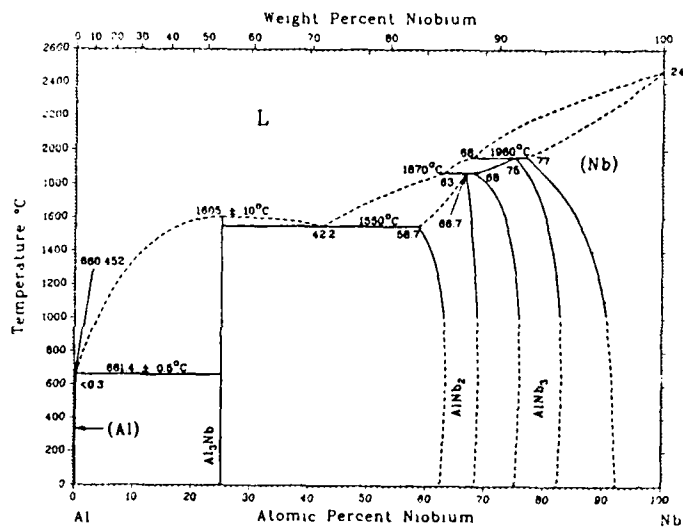
#### ALLOY MICROSTRUCTURES

The Nb-Ti-Cr-V-Al alloys appeared to be single phase in the as-cast condition by optical metallography. Analysis by XRD resulted in patterns for a primitive cubic cell with a B2 superlattice. In the binary Nb-Al system (Fig. 22A), the terminal solid solution has a BCC structure and the Nb<sub>3</sub>Al phase in equilibrium with it has a cubic ( $\beta$ W) structure. The large addition of Ti appears to have resulted in formation of a new phase which at 46at.%Al in the alloy had an ordered cubic structure. The diffusivity of Al should be high in such a phase.

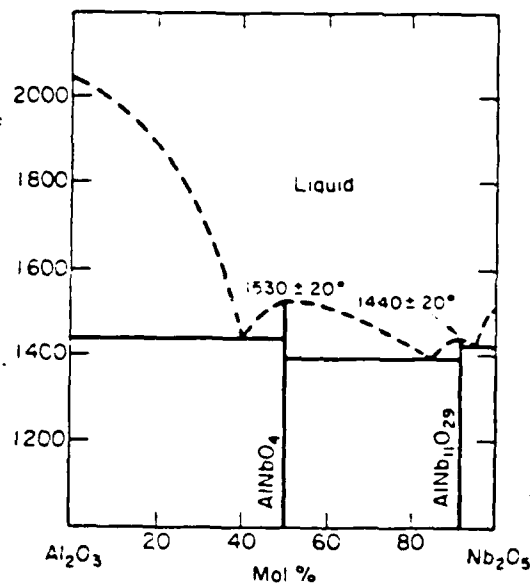
The new phase, however, was metastable and decomposed into a fine two-phase structure on heating at 800 to 1400°C. The nature of the structure varied with temperature at which it was formed. At 1400-1600°C, the microstructure was accicular with the amount of the accicular component decreasing with increased temperature. At 800 and 1100°C, the structure was a fine-grained equi-axed 2-phase mixture with a grain size of about 5  $\mu$ m at 1100°C (Fig. 11A) and <1  $\mu$ m at 800°C (Fig. 18A). An accicular component was still evident at 800°C. Alloy micro-structure after heating was similar for all alloys with a Nb:Ti ratio of 1-1.3:1 and Al contents of 38 to 46 at.%. the composition and structure of the two phases have not been determined to date and detailed studies are continuing.

#### ALTERED MICROSTRUCTURES

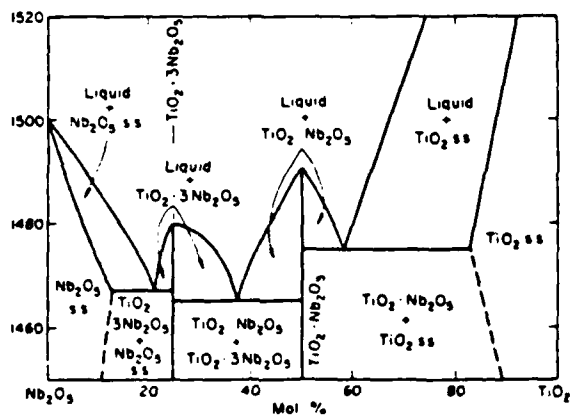
The effect of variations in alloy structure on oxidation behavior is being investigated using several different approaches. The effect of annealing to produce stable coarse and fine-grained stable microstructures will be studied during the third year of the program. Work has been started on two other approaches: rapid solidification processing and oxide dispersions.



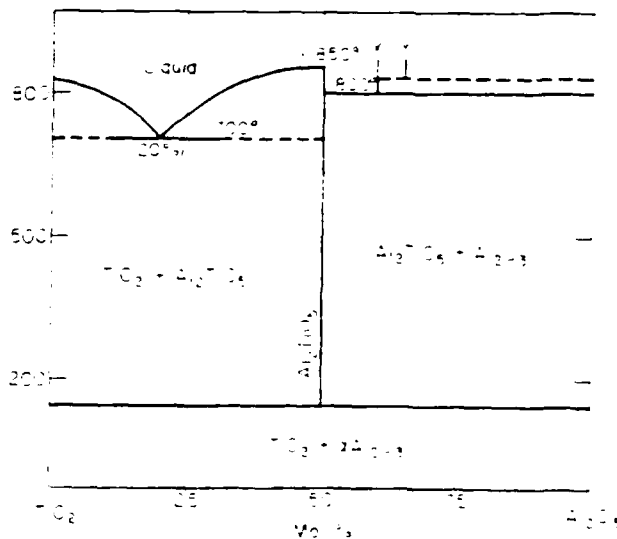
A - Nb-Al SYSTEM



B - Nb<sub>2</sub>O<sub>5</sub>-Al<sub>2</sub>O<sub>3</sub> SYSTEM



C - Nb<sub>2</sub>O<sub>5</sub>-TiO<sub>2</sub> SYSTEM



D - Al<sub>2</sub>O<sub>3</sub>-TiO<sub>2</sub> SYSTEM

Fig. 22 Phase Diagrams for Nb-Al (6) and Binary Systems of Nb, Al, and Ti Oxides (7)

### Rapid Solidification Processing (RSP)

Studies of the effect of RSP on structure, composition, and oxidation behavior have been delayed as a result of the fact that techniques for processing Nb have not been developed to date. Suitable equipment is not available at LMSC or the University of Pittsburgh and project resources are not adequate to fund process development efforts by outside laboratories. Two developments have occurred within the past few month that will alter this situation.

A program to develop oxidation resistant Nb base alloys using rapid solidification processing has been initiated by Pratt & Whitney (8). The following two alloy compositions formulated from the results of the first two years work on the AFOSR project have been selected for preliminary RSP development work on the new contract:

- (1) Nb-23Ti-4Cr-5V-44Al
- (2) Nb-20Ti-8Cr-6V-44Al

A small amount of RSP powder from the first two alloys will be available for evaluation in the AFOSR project.

In the second development, arrangements have been made with Wah Chang Corporation, Albany, OR, and the University of Florida, Gainesville, FL, to prepare a small quantity of RSP splat alloys by levitation melting in a drop tower. Wah Chang will prepare arc melted pancake ingots from which samples will be cut for levitation melting. Two alloys with the following compositions have been melted successfully as 200 gm pancake ingots:

- (1) 25.6Nb-29.1Ti-3.0Cr-4.1V-38.3Al
- (2) 23.6Nb-28.8Ti-9.8Cr-37.8Al

The alloys contained 17 and 360 ppm O<sub>2</sub>, 21 and 60 ppm N<sub>2</sub>, 220 and 100 ppm C, 19 and 21 ppm W, respectively.

Small pieces (1 cm<sup>3</sup>) of alloy 1 have been levitation melted in the drop tower at the University of Florida. One sample was

compressed between cooled anvils for solidification to produce a splat. A second sample was solidified by falling onto a water cooled copper plate. The splat sample was less than 25  $\mu\text{m}$  (1 mil) thick and was suitable for short time oxidation tests. The drop cast sample was flat, about 1000  $\mu\text{m}$  (40 mil) thick, and was suitable for long-time oxidation tests. Additional samples will be prepared for oxidation testing and evaluation.

#### Oxide Dispersions

Oxide dispersions introduced by powder metal processing of RSP powders can provide sites for nucleation of alumina scales and can stabilize fine grains structures at high temperatures. The as-cast Nb-Ti-Cr-V-Al alloys were too difficult to reduce to fine powder in available equipment. As a result, preliminary studies were conducted with a mixture of elemental powders (Nb, Ti, Cr, V, Al) and oxides of Y, Ce, Dy, Zr, Hf, and Th. A baseline mixture with the composition 24.9Nb-30.0Ti-3.0Cr-4.0V-38.1Ti and 0.5-1wt% of the oxides was blended, cold pressed, and vacuum sintered at 1550°C. The pellets delaminated during sintering and lost 4-5% of their weight by evaporation of Al. Further studies will be postponed until the RSP powder from Pratt and Whitney becomes available.

#### SUMMARY AND CONCLUSIONS

Research during the second year has established a better understanding of factors governing the selective oxidation of Al to form alumina scales on Nb alloys. The formation of external alumina scales without transient oxidation has been shown to be feasible. It has been demonstrated that the amount of transient oxidation that occurs before a continuous alumina scale is formed decreases with both increasing  $N_{\text{Al}}$  and temperature. Alumina scales without an external layer of transient oxide were formed on Nb-Ti-Al-Cr-V alloys in air at 1400°C with  $N_{\text{Al}}$  between 0.528 and 0.578. Alloys with an  $N_{\text{Al}}$  of 0.477 formed single layer alumina in air at a temperature between 1550 and 1600°C.

Studies of the transition from internal oxidation of Al to

formation of continuous alumina scale under a layer of transient oxide show a similar effect of  $N_{Al}$  and temperature. At 1400°C, the transition occurred at an  $N_{Al}$  of 0.375-0.38. At 1100°C, the transition occurred slightly above an  $N_{Al}$  of 0.578 while at 800°C, concentrations considerably above 0.578 will be required to form continuous alumina scales. The transition at 1400°C was slightly dependent on the Nb:Ti ratio and relatively independent of the Cr and V contents above an addition of 3-4%.

The formation of continuous alumina scales also was found to be dependent on both oxygen permeability in the alloy and scaling characteristics of the base metal components (transient oxidation). As temperature is reduced, the high activation energy for the formation of external alumina greatly reduces the rate of nucleation and growth. As a result, the transient oxidation process becomes a controlling factor. The nature and kinetics of transient oxidation have been found to be particularly important at 800 and 1100°C. At 800°C, the rate of oxidation was relatively insensitive to Al content but based on limited test data, showed a tendency to increase with increasing  $N_{Al}$ . At 1100°C, the rate of oxidation decreased significantly with increasing Al content as a result of transient oxidation being cut off by more rapidly growing alumina scales.

In both cases, the growth of external alumina and/or reduced transient oxidation was enhanced by the addition of elements that could reduce the solubility-diffusivity product of  $O_2$ . Vanadium was found to be effective and alumina was formed on a Nb-25V-10Cr-40Al alloy in air at 1400°C. Unfortunately, V was taken into the transient oxide and formed a liquid oxide phase at 1400°C. Titanium was marginally effective and partial alumina scales were formed on a Nb-27.6Ti-42.0 Al alloy. Titanium was a major component of most transient oxides, forming liquid oxides with Nb at 1600°C. Chromium was found to be most effective and was required to be present in all alloys to form continuous alumina scales. Only a trace of Cr was detected in the transient oxide formed on Nb-Ti-Cr-V-Al alloys at 1400°C. Small additions of Cr + V (3-4% each) or Cr (without V) in the range of 8-10% to

Nb-Ti-Al alloys with a Nb:Ti ratio of 0.8-1.4 offered the best balance of behavior.

The large additions of Ti, Cr, and Al required to form external alumina scales reduced alloy melting points to the range of 1600-1650°C. Melting point was found to be very dependent on Al content. Alloys with 48% Al melted at 1600°C while those with 58% Al melted at 1550°C. Niobium alloys that melt in this temperature range will be of little value as structural materials and research must be directed to mechanisms for further reduction of  $N_{Al}^{crit}$ . Oxygen permeability and rate of transient oxidation relative to that of alumina formation appear to be key factors that require an increased understanding for affecting further reductions in  $N_{Al}^{crit}$ .

It has been found that high e/a elements such as Re, Ru, and Mo which are known to reduce the solubility of  $O_2$  in Nb to near zero do not enhance the formation of Al. Instead, moderate level additions (10-30%) result in the formation of liquid or non-protective transient oxides that greatly accelerate surface recession and preclude alumina formation. These additions do prevent internal oxidation of Al, most likely by reducing the solubility-diffusivity product of O. However, this effect is masked by a high rate of surface recession. Other approaches to reduce permeability of O in the alloys must be examined.

Research during the past year also demonstrated that the composition of the transient oxide as governed by base alloy composition is a very important consideration. The basic oxides formed as transients on Nb-Ti-V-Cr-Al alloys were found to be  $TiO_2$  and  $NbAlO_4$ . The latter melts at 1530°C and forms a low melting eutectic (~1400°C) with  $Nb_2O_5$ . Titania ( $TiO_2$ ) also forms a low melting eutectic with  $Nb_2O_5$ . Melting of the transient oxide was observed between 1550 and 1600°C, resulting in a very rapid rate of transient oxidation that precluded formation of alumina scales. The ideal transient oxide would be in the  $TiO_2$ - $Al_2O_3$  system where no melting occurs below 1700°C. It has been demonstrated that such a scale can be formed as an initial

oxidation product (outer scale layer) but its growth cannot be sustained. Low melting niobates of Al and Ti are formed underneath. More attention must be devoted to the transient oxidation process as a significant contribution to the formation of alumina on Nb. Factors that govern the composition, structure, and growth kinetics must be identified. Significant reduction in  $N_{Al}$  for alumina should be possible through control of transient oxidation.

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## APPENDIX

TABLE A1

## Experimental Nb-Ti-Al Alloys

## COMPOSITION (SEM/XES)

| COMPOSITION (PERCENT)                            |        |      |      |            |     |          |      |      |                |     |             |
|--------------------------------------------------|--------|------|------|------------|-----|----------|------|------|----------------|-----|-------------|
| ALLOY NO.                                        | ATOM % |      |      |            |     | WEIGHT % |      |      |                |     | CALC. DENS. |
|                                                  | Nb     | Ti   | Al   | Cr         | V   | Nb       | Ti   | Al   | Cr             | V   | gm/cc       |
| FIRST YEAR OF RESEARCH                           |        |      |      |            |     |          |      |      |                |     |             |
| 18-14                                            | 40.8   | 25.8 | 25.6 | 3.2        | 4.4 | 62.0     | 20.2 | 11.3 | 2.8            | 3.7 | 5.92        |
| 18-15                                            | 32.6   | 26.3 | 33.0 | 3.5        | 4.6 | 54.0     | 22.5 | 15.9 | 3.3            | 4.2 | 5.45        |
| 18-16                                            | 31.7   | 23.0 | 37.5 | 2.8        | 4.9 | 54.9     | 20.2 | 18.5 | 2.7            | 3.7 | 5.33        |
| 18-17                                            | 21.9   | 24.2 | 46.2 | 3.3        | 4.4 | 42.1     | 24.0 | 25.8 | 3.5            | 4.6 | 4.76        |
| 29-11                                            | 33.6   | 28.9 | 37.5 |            |     | 56.6     | 25.1 | 18.3 |                |     | 5.28        |
| 29-12                                            | 31.0   | 27.3 | 37.4 | 4.3        |     | 53.2     | 24.1 | 18.6 | 4.1            |     | 5.26        |
| 29-13                                            | 26.9   | 27.2 | 37.2 | 8.7        |     | 47.5     | 24.8 | 19.1 | 8.6            |     | 5.18        |
| 29-14                                            | 30.4   | 27.6 | 42.0 |            |     | 53.5     | 25.0 | 21.5 |                |     | 5.07        |
| 29-15                                            | 27.8   | 26.3 | 41.6 | 4.3        |     | 49.8     | 24.3 | 21.6 | 4.3            |     | 5.05        |
| 29-16                                            | 24.7   | 25.4 | 41.5 | 8.3        |     | 45.4     | 24.0 | 22.1 | 8.5            |     | 5.01        |
| 26-2                                             | 27.9   | 30.5 | 38.8 | 2.8        |     | 49.4     | 27.9 | 19.9 | 2.8            |     | 5.08        |
| 26-3                                             | 28.7   | 29.3 | 38.4 |            | 3.6 | 50.4     | 26.5 | 19.6 |                | 3.4 | 5.11        |
| 26-4                                             | 27.1   | 25.2 | 42.2 | 2.5        | 3.0 | 48.9     | 23.5 | 22.1 | 2.5            | 3.0 | 5.02        |
| 26-6                                             | 25.4   | 29.1 | 39.2 | 2.8        | 3.5 | 45.9     | 27.1 | 20.6 | 2.8            | 3.5 | 5.01        |
| SECOND YEAR OF RESEARCH                          |        |      |      |            |     |          |      |      |                |     |             |
| 54-1                                             | 32.1   | 24.1 | 38.0 | 2.4        | 3.4 | 54.6     | 21.2 | 18.8 | 2.3            | 3.2 | 5.31        |
| 54-2                                             | 29.0   | 21.3 | 44.2 | 2.3        | 3.2 | 51.9     | 19.7 | 23.0 | 2.3            | 3.1 | 5.06        |
| 54-3                                             | 26.1   | 20.1 | 47.7 | 2.5        | 3.6 | 48.6     | 19.4 | 25.8 | 2.6            | 3.6 | 4.89        |
| 54-17                                            | 25.0   | 19.5 | 49.8 | 2.8        | 2.9 | 47.5     | 19.1 | 27.4 | 3.0            | 3.0 | 4.80        |
| 54-4                                             | 23.5   | 17.9 | 52.8 | 2.3        | 3.4 | 45.9     | 18.0 | 29.7 | 2.6            | 3.7 | 4.68        |
| 54.5                                             | 20.8   | 15.6 | 57.8 | 2.5        | 3.4 | 42.5     | 16.5 | 34.4 | 2.9            | 3.8 | 4.47        |
| (THE FOLLOWING ARE NOMINAL COMPOSITIONS- %ADDED) |        |      |      |            |     |          |      |      |                |     |             |
|                                                  | Nb     | Ti   | Al   | Other      |     | Nb       | Ti   | Al   | Other          |     |             |
| 54-6                                             | 25     | 25   | 40   | 10 Re      |     | 35.9     | 18.5 | 16.7 | 28.8 Re        |     |             |
| 54-7                                             | 25     | 15   | 40   | 10Re, 10Ru |     | 33.2     | 10.3 | 15.4 | 26.6Re, 14.5Ru |     |             |
| 54-8                                             | 25     | 15   | 40   | 10Re, 10Mo |     | 33.5     | 10.4 | 15.5 | 26.8Re, 13.8Mo |     |             |
| 54-9                                             | 25     | 15   | 40   | 10Re, 10Cr |     | 35.7     | 11.1 | 16.6 | 28.7Re, 7.8Cr  |     |             |
| 54-10                                            | 25     | 15   | 40   | 10Re, 10V  |     | 35.8     | 11.1 | 16.6 | 28.7Re, 7.9V   |     |             |
| 54-11                                            | 28     | 28   | 40   | 4 Hf       |     | 45.4     | 23.4 | 18.8 | 12.4 Hf        |     |             |
| 54-12                                            | 28     | 28   | 40   | 4 Zr       |     | 48.3     | 24.9 | 20.0 | 6.8 Zr         |     |             |
| 54-13                                            | 25     |      | 40   | 25V, 10Cr  |     | 44.7     |      | 20.8 | 24.5V, 10.0Cr  |     |             |
| 54-14                                            | 48     |      | 20   | 32 Re      |     | 40.7     |      | 4.9  | 54.4 Re        |     |             |
| 54-15                                            | 42     |      | 30   | 28 Re      |     | 39.3     |      | 8.2  | 52.6 Re        |     |             |
| 54-16                                            | 36     |      | 40   | 24 Re      |     | 37.6     |      | 12.2 | 50.3 Re        |     |             |
| 57-1                                             | 41.6   |      | 23.9 | 34.6 Re    |     | 60       |      | 10.0 | 30.0 Fe        |     |             |
| 57-2                                             | 38.2   |      | 30   | 31.7 Fe    |     | 60       |      | 13.2 | 28.9 Fe        |     |             |
| 57-3                                             | 35.5   |      | 35   | 29.5 Fe    |     | 60       |      | 16.0 | 28.0 Fe        |     |             |
| 57-4                                             | 54.9   |      | 25   | 20.0 Fe    |     | 60       |      | 9.8  | 16.2 Fe        |     |             |
| 54-5                                             | 51.3   |      | 30   | 18.7 Fe    |     | 60       |      | 12.2 | 15.8 Fe        |     |             |
| 54-6                                             | 47.6   |      | 35   | 17.4 Fe    |     | 60       |      | 14.9 | 15.3 Fe        |     |             |

Table A2

Parabolic Rate Constants  
for Nb-Ti-Al-Cr-V Alloys<sup>1</sup>

| Alloy              | Nb              | Ti     | Cr  | V   | Al   | Temp.<br>°C | $\frac{k_p}{g^2 cm^{-2} s^{-1}}$ | $\log k_p$ |
|--------------------|-----------------|--------|-----|-----|------|-------------|----------------------------------|------------|
|                    |                 | (at.%) |     |     |      |             |                                  |            |
| NiAl <sup>2</sup>  |                 |        |     |     | (50) | 1400        | $5.00 \times 10^{-11}$           | -10.30     |
| 18-17 <sup>3</sup> | ba <sup>1</sup> | 24.2   | 3.3 | 4.4 | 46.2 | 1400        | $6.33 \times 10^{-10}$           | -9.20      |
| NiAl               |                 |        |     |     | (50) | 1100        | $6.30 \times 10^{-13}$           | -12.20     |
| 18-17              | "               | "      | "   | "   | "    | "           | $8.83 \times 10^{-10}$           | -9.05      |
| 29-16 <sup>4</sup> | "               | 25.4   | 8.3 |     | 41.5 | "           | $4.87 \times 10^{-9}$            | -8.31      |
| 29-16              | "               | "      | "   |     | "    | "           | $6.50 \times 10^{-9}$            | -8.19      |
| 26-6               | "               | 29.1   | 2.8 | 3.5 | 39.2 | "           | $1.17 \times 10^{-8}$            | -7.93      |
| NiAl <sup>2</sup>  |                 |        |     |     | (50) | 800         | $1.00 \times 10^{-15}$           | -15.00     |
| 54-5               | "               | 15.6   | 2.5 | 2.9 | 57.8 | "           | $2.87 \times 10^{-11}$           | -10.54     |
| 54-4               | "               | 17.9   | 2.3 | 3.4 | 52.8 | "           | $1.49 \times 10^{-10}$           | -9.83      |
| 54-17              | "               | 19.5   | 2.8 | 2.9 | 49.8 | "           | $1.07 \times 10^{-10}$           | -9.97      |
| 54-3               | "               | 20.1   | 2.5 | 3.6 | 47.7 | "           | $9.88 \times 10^{-11}$           | -10.00     |
| 54-2               | "               | 21.3   | 2.3 | 3.2 | 44.2 | "           | $6.88 \times 10^{-11}$           | -10.16     |
| 26-6               | "               | 29.1   | 2.8 | 3.5 | 39.2 | "           | $6.33 \times 10^{-11}$           | -10.20     |
| 54-1               | "               | 24.1   | 2.4 | 3.4 | 38.0 | "           | $5.42 \times 10^{-11}$           | -10.27     |

- 1- Cahn Microbalance, O<sub>2</sub> Atmosphere
- 2- Extrapolated Data, Ref. (2).
- 3- Multiple Furnace Exposures in Air
- 4- Preoxidized 19.8h in Tank Argon

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