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MODIFICATION AND CONTROL OF OXIDE STRUCTURE ON METALS
AND ALLOYS: (PHASE V)

Robert C. Svedberg

Westinghouse Astronuclear Laboratory

Prepared for:

Naval Air Development Center

May 1974

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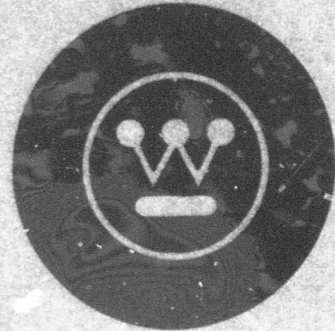
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Westinghouse Astronuclear Laboratory



**MODIFICATION AND CONTROL
OF OXIDE STRUCTURES
ON METALS AND ALLOYS: (PHASE V)
FINAL REPORT**

2 MARCH 1974 - 2 MARCH 1975

"Approved for Public Release - Distribution Unlimited"

by
R. C. Svedberg

Prepared Under Contract N62269-74-C-0289
Naval Air Development Center
Warminster, Pennsylvania 18974

For
Naval Air Systems Command
Department of the Navy
Washington, D. C. 20361

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13 ABSTRACT An indepth analyses of over 50 x-ray diffraction patterns of oxides grown on niobium based oxidation resistant alloys are presented. The oxides analyzed were grown in air on niobium based alloys containing Cr, Ti, Al, Co, Ni, and/or Fe in various amounts and compositions at temperatures between 800 and 1200°C. The analysis of the x-ray diffraction data has shown the oxidation protection of these alloys to be associated with a rutile (tetragonal) oxide of the form $MNbO_4$ where $M = Al, Cr, Fe,$ and/or Co . In most of the oxidation resistant alloys, a spinel related structure such as $CoAl_2O_4$ ($CoO-Al_2O_3$) was detected. Various powder metallurgy and thermomechanical processing techniques were used to attempt to fabricate useful alloys with the compositions 73.4Nb-15Fe-11.6Al and 80Nb-5.6Co-13.9Al. Both alloy compositions were processed by various powder metallurgy techniques from elemental, intermetallic, and arc-melted alloy powders. Powder compacts were densified by a combination of cold isostatic pressing and sintering, high impact rate extrusion or conventional extrusion. None of these techniques produced suitable samples of the alloys for additional characterization.			

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Westinghouse Electric Corporation - P. O. Box 10864 - Pittsburgh, Pennsylvania 15236

FOREWORD

The work described herein was performed at the Astronuclear Laboratory of the Westinghouse Electric Corporation under Navy Contract No. N62269-74-C-0289. This work is a continuing effort started under Navy Contract N00019-70-C-0148 and continued under Contracts N00019-71-C-0089, N00019-72-C-0132, and N62269-73-C-0361. Mr. I. Machlin of the Naval Air Systems Command served as Program Consultant; Program supervision at Westinghouse was by Mr. R. W. Buckman, Jr., Manager, Materials Science.

The author wishes to acknowledge additional personnel contributing to this program. These are Mr. A. Filippi and Mr. J. Sundin for alloy fabrication; Mr. S. Laciak for metallography; and Mr. H. Ebner for oxidation testing.

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1.0 INTRODUCTION

An indepth analysis of over 50 x-ray diffraction patterns of oxides grown on niobium based oxidation resistant alloys and an effort to fabricate Nb-Al-Co and Nb-Al-Fe alloys using various powder metallurgy and thermal-mechanical processing techniques are discussed in this final report for the Naval Air Development Center under Contract No. N62269-74-C-0289.

The oxides analyzed were grown in air on niobium based alloys containing Cr, Ti, Al, Co, Ni, and/or Fe in various amounts and compositions at temperatures between 800 and 1200°C. The analysis of the x-ray diffraction patterns has shown the oxidation protection of these alloys to be associated with a rutile (tetragonal) oxide of the form $MNbO_4$ where M = Al, Cr, Fe, and/or Co. In the most oxidation resistant alloys, a spinel related structure such as $CoAl_2O_4$ ($CoO-Al_2O_3$) was detected.

In addition, the Nb-Co-Al and Nb-Fe-Al alloys, which were successfully fabricated during this program, were oxidized in air at 1200°C to determine the effects of composition and fabrication procedures on the oxidation rate. These alloys showed the most promise for oxidation resistant applications because of the low oxidation rate and minimal subsurface interstitial contamination noted during exposure to air. Two alloy compositions (73.4Nb-15Fe-11.6Al and 80Nb-5.6Co-13.9Al) were processed by various powder metallurgy techniques from elemental, intermetallic, and arc-melted alloy powders by pressing and sintering, high impact rate extrusion processes, and conventional extrusion processes. None of these techniques produced suitable samples of the alloys for additional characterization.

This program was initiated under Contract No. N00019-70-C-0148⁽¹⁾ and continued under Contract Nos. N00019-71-C-0089⁽²⁾, N00019-72-C-0132⁽³⁾, and N62269-73-C-0361⁽⁴⁾

to investigate the feasibility of modifying oxide structures to enhance oxidation protection of elevated temperature structural materials.

Improvement of the oxidation resistance of Nb alloys has been the subject of many investigations. However, there have not been many detailed studies or characterizations of the oxides which form on the more oxidation resistant alloys nor has there been much systematic characterization of the structure of the oxides with composition of the niobium based alloys. The approach to this program therefore has been primarily to investigate the structures of the equilibrium oxides which form on oxidation resistant niobium based alloys and to attempt to categorize these oxide structures and compositions with the composition of the parent metal alloys. Ideally one would like to improve oxidation resistance of a structural alloy without altering its mechanical properties. Early in the program⁽¹⁾, preoxidation treatments to form protective oxides at elevated temperature and modifications to the oxide structure by utilizing ultra-high pressures were studied. During Phases II⁽²⁾ and III⁽³⁾, the diffusion rates of oxygen through various oxides were measured to determine which alloying elements added to Nb would form the most protective oxides. Then these alloy compositions were fabricated and oxidized, and the structures of these oxides were determined and correlated with the alloy compositions during Phase IV⁽⁴⁾. The oxide structures associated with improved oxidation performance of some niobium alloys and intermetallic compounds were identified, and the alloy compositions required to support these structures have been investigated.

1.1 PROGRAM SUMMARY

The Phase I⁽¹⁾ study has shown that high pressure high temperature exposure of Nb_2O_5 produces a denser oxide phase which maintains its characteristics after quenching to room temperature. However, the stability of the quenched phases and the transport properties of the quenched phases could not be investigated. Pre-exposure of alloy B-1 (Cb-15Ti-10W-10Ta-2Hf-3Al) in 20 Torr oxygen at 650°C resulted in a decrease in the subsequent

oxidation rate in air at 1040°C when compared to untreated B-1 alloys. Another treatment technique involved an exposure of the B-1 alloy to air at 1360°C for 1 hour. This improved the oxidation resistance during exposure at 1204°C in air. These experiments have shown that modification of the oxide structure is possible.

During Phase II⁽²⁾, the study of the rate of oxygen transport through mixed niobates was initiated. Thermogravimetric techniques were employed to determine weight changes in the oxides as a function of the partial pressure of oxygen in a reacting gas mixture. Results from this work indicated that mixed oxides of Nb₂O₅-TiO₂ and Nb₂O₅-HfO₂ would not form protective oxide layers based on limiting the transport of oxygen through the scale and protecting the parent metal. The NiO-Nb₂O₅ binary oxides exhibited a stoichiometric behavior, i. e., no weight loss as a function of oxygen pressure until a partial pressure equivalent to that of the dissociation pressure of NiO is reached. At that point, a reduction reaction is apparently triggered, and large weight losses begin.

As a result of efforts during Phase III⁽³⁾, the rutile structure family for oxide compounds of the type Nb(B)O₄ where B = Cr, Al, or Fe were identified as being the primary oxide phase in the scales formed on oxidation resistant Nb intermetallic compounds and Nb-Ti-Cr-Al, Nb-Fe-Al, Nb-Cr-Al-Co, and Nb-Cr-Al-Ni alloys. Along with this oxide, small amounts of either (B)₂O₃ where B = Cr, Al, or Fe or a CoAl₂O₄ spinel in cobalt containing alloys were detected. Oxygen transport rates through Nb₂O₃-Cr₂O₃, Nb₂O₅-TiO₂, Nb₂O₅-ZrO₂, and Nb₂O₅-Al₂O₃ were also determined using thermogravimetric techniques. Of the oxide compounds evaluated, only oxygen transport through Nb₂O₅-Cr₂O₃ was slow enough to warrant its classification as a protective scale. In addition to oxidation rate data, metallographic studies and electron microprobe studies were conducted on the Nb intermetallic compounds and alloys.

The Phase IV⁽⁴⁾ study included a continuation of the oxygen transport rate measurements in the binary niobate $\text{Nb}_2\text{O}_5\text{-Co}_3\text{O}_4$ and the investigation of the oxidation kinetics and oxide structure formed on 37 different Nb based alloys containing Co-Fe-Al-Cr-Ni-Y and/or Y_2O_3 . The experimental results, used to select the alloys to scale up for additional oxidation behavior and mechanical studies, were the oxidation kinetics, the oxide structure formed, and the depth of substrate contamination which resulted during oxidation. These results indicate that certain Nb-Al-Fe and Nb-Co-Al alloys give good oxidation behavior and that scales formed on these oxides become more protective as oxidation proceeds. In addition, the substrate contamination of the alloys by oxygen is very low. The protective oxide appears to be a rutile-type NbAlO_4 oxide.

The final phase of the program has been devoted to achieving a better understanding of the oxides responsible for the improved oxidation behavior of the Nb-Fe-Al and Nb-Co-Al alloys and to the manufacturing of a suitable alloy for further evaluation. The results of the characterization of the oxides have shown that a rutile MNbO_4 structure where $M = \text{Fe}, \text{Al}, \text{Cr},$ and/or Co is required to achieve good oxidation protection. Other oxides such as CoAl_2O_4 spinels and M_2O_3 structures where $M = \text{Fe}, \text{Cr},$ and/or Al are also present in many of these scales. The "Search" computer program from the Joint Committee on Powder Diffraction Standards was utilized extensively in this effort.

Although various techniques have been attempted, the brittle nature of these alloys has frustrated all attempts to fabricate anything but button melts. Attempts to extrude and consolidate 1 kg powdered billets produced unsatisfactory material.

This program has led to the identification of a class of oxides which provides improved oxidation resistance on niobium alloys at 1200°C. Additional efforts can be made to determine the limits for the conditions under which the protective scales can be successfully maintained in a high temperature oxidizing environment. The limits of alloy composition, additions of secondary getters and/or coating substrates which would support these structures in a high temperature equilibrium environment should be determined. Additional phase relationship data is required to evaluate the possibility of forming directional eutectic alloys from some of these compositions with suitable mechanical and oxidation resistant properties.

This program has demonstrated the advantages of studying the oxide structure of alloys deemed unsuitable for structural applications. The identification of the NbCrO_4 (rutile) type scale had been proposed by Mayo⁽⁵⁾ based on dilatometric considerations; but because of the poor mechanical properties of the alloys, work was not continued. A direction for future work has been defined by this program with the recognition that the Nb-Al-Co and Nb-Al-Fe systems possess both oxidation resistance and do not suffer greatly from substrate contamination.

2.0 ALLOY FABRICATION

Test rods of three oxidation resistant compositions were prepared by powder metallurgy techniques. Processing involved blending powders of the alloying constituents and effecting densification by cold isostatic pressing followed by extrusion and swaging. Figure 1 is a summary of the fabrication sequence. The compositions examined were 80Nb-13.9Al-5.6Co and 73.4Nb-15Fe-11.6Al (w/o). Both were prepared as rods by processing blends of the elemental powders. In addition, the Nb-Fe-Al alloy was also processed to rod from a powder blend of 60Nb+15Fe+25NbAl₃. A photograph displaying the as-pressed state of the three powder metallurgy blends is given in Figure 2. A machined pressing and extrusion can components and an assembled and welded extrusion billet are shown in Figure 3. Typical extruded and swaged rods are shown in Figure 4. The all metal blends were extruded at room temperature and swaged at 538°C. Extrusion of the 60Nb-15Fe-25NbAl₃ composition was performed at 538°C and swaging at 816°C. Densification to levels of 98 and 100 percent of theoretical were obtained, respectively, for the 73.4Nb-15Fe-11.6Al and 80.5Nb-13.9Al-5.6Co blends. The density achieved for the 60Nb-15Fe-25NbAl₃ alloy was on the order of 90 percent of theoretical.

These alloys were prepared from powders, the characteristics of which are presented in Table 1. The various powders were weighed, blended, and isostatically pressed into billets at ~30,000 psi. These billets were machined to fit inside the extrusion cans. After placing the pressings inside the cans, the cans were welded shut and sealed. Extrusion was done using a high deformation rate Dynapak extrusion press to achieve a 5:1 area reduction ratio. Swaging was done on the extruded rod with the cladding still intact using a Fenn rotary swager.

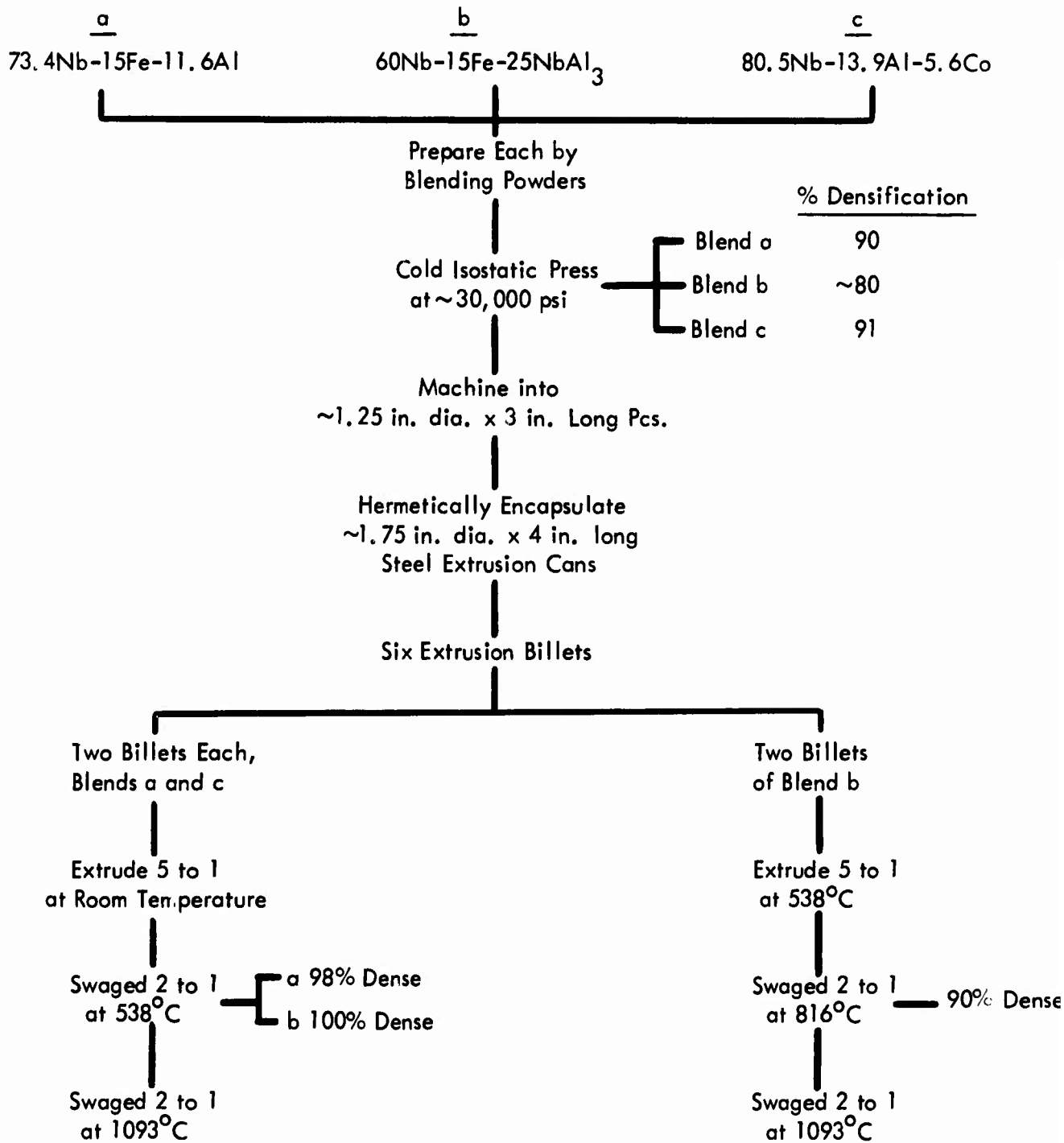


Figure 1. A Summary of Fabrication Data

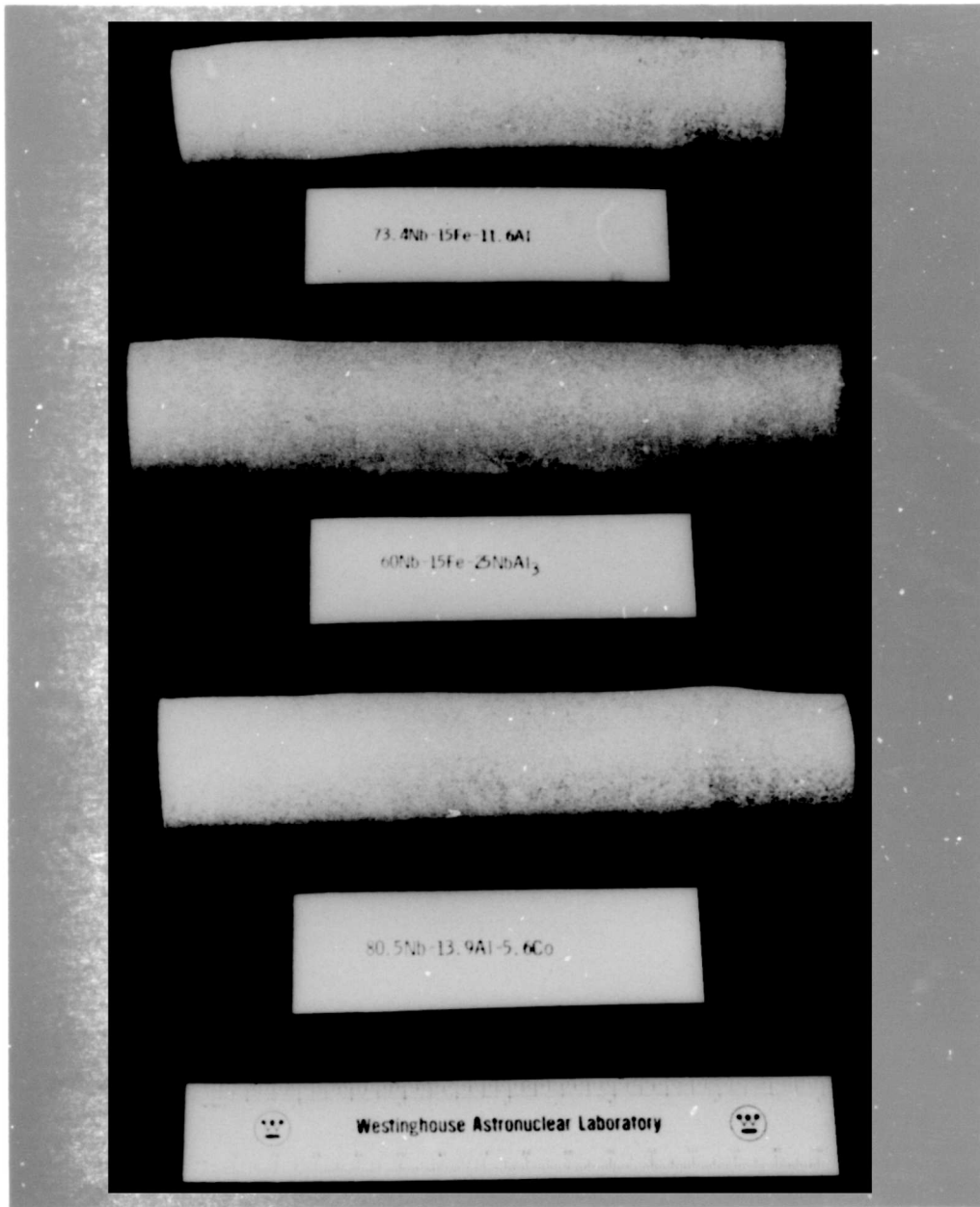


Figure 2. As-pressed Billets of the Three Experimental Blends

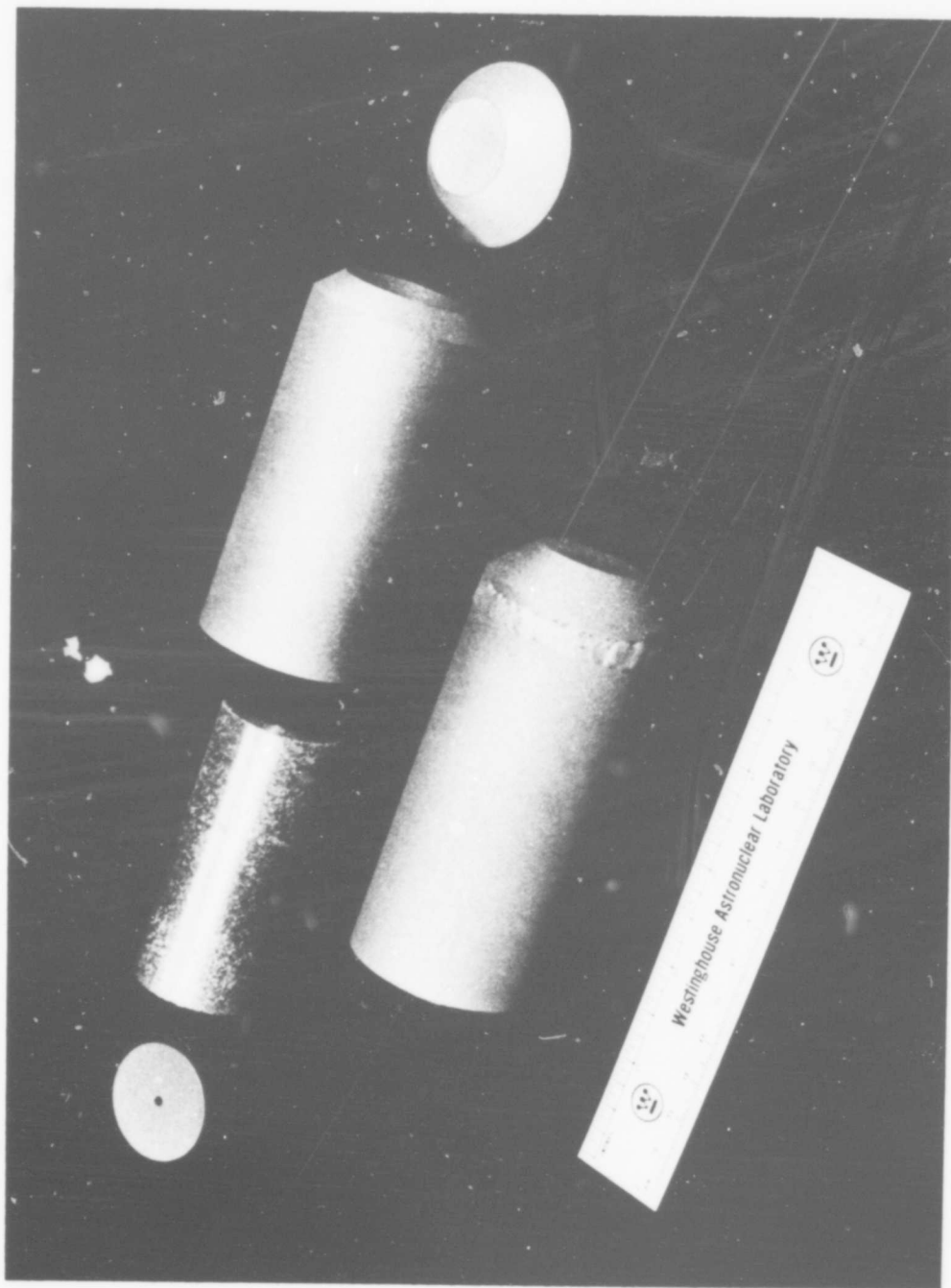


Figure 3. An Exploded View Showing a Machined Pressing with Extrusion Can Components (Top), and an Assembled and Welded Extrusion Billet (Bottom)

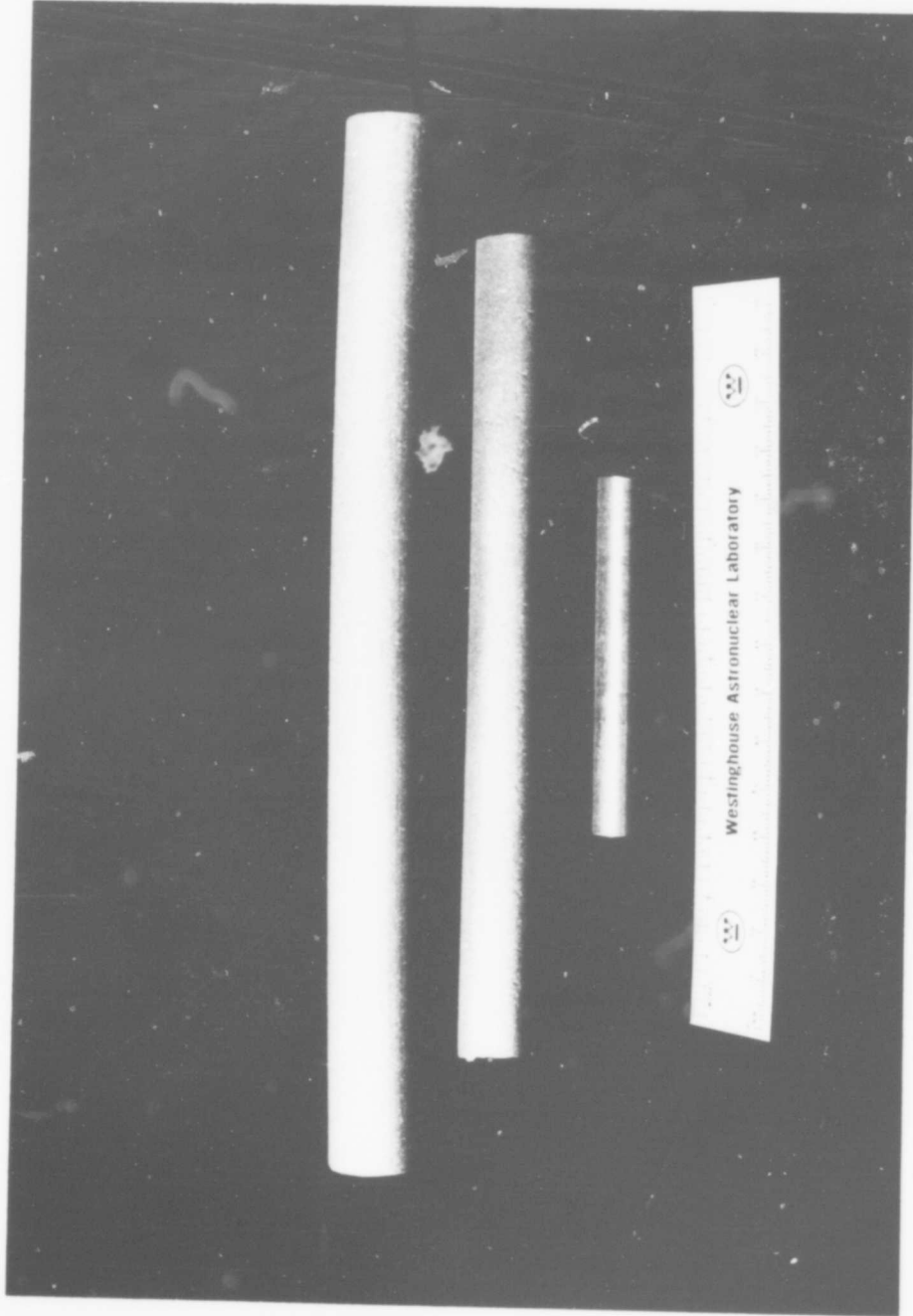


Figure 4. Typical Extruded and Swaged Bar.
Top: As-extruded; Middle: As-swaged; Bottom: Finished Material
After Removal of the Steel Cladding by Machining

Table 1. Powders Used for Test Alloys

Element or Compound	Mesh Size	Purity (%)	Major Impurities (ppm)
Niobium	-20 to +270	99.5	40 C, 670 O, 40 N, 8 H, 100 Zr, 50 Hf, 625 Ta, 50 Fe, 20 Al, 20 Mo, 50 Ti, 20 W
Iron	-325	99.9	1000 C, 1000 Si, 1000 Mn, 100 Ni, 10 Cu, 10 Al, 10 Mg, 100 Mo
Cobalt	-325	99.6	1130 Ni, 50 C, 180 S, 10 Cu, 30 Fe.
Niobium Aluminide NbAl ₃	-325	99	200 Ta, 500 Ti, 500 Fe, 10 Mn, 500 Si, 100 Ni, 100 V, trace - Cu, Cr, Sn, Sb, Mg, W, Mo, Al, Zr, Co, and B.
Aluminum	-50 to -325	99.4	3000 Al ₂ O ₃ , 1500 Fe, 700 Si

The microstructures of as-extruded and as-swaged material are shown in Figure 5. Fabrication through extrusion produced microstructures composed of simple mechanical mixtures of the alloying constituents. Some porosity was also apparent in the as-extruded 60Nb-15Fe-25NbAl₃ blend. Swaging at 538°C produced some intermetallic compound formation in the Nb-Fe-Al and Nb-Fe-Co blends, with porosity also developing in the former material. Swaging did not produce a significant change in the microstructure of the Nb-Fe-NbAl₃ blend from that of the as-extruded state. (A difference in the amount of porosity apparent in the microstructures shown for this material is believed due to differences in the amount of intermetallic phase lost during metallographic preparation.)

Homogenization heat treatments were performed on sample coupons, as per the schedule in Figure 6, of each material in a resistance heated vacuum furnace for 1 hour at 800, 1000, and 1200°C. Major dimensional changes and cracking occurred in the heat treated coupons of the two all-metal blends, presumably due to density changes associated with intermetallic compound formation. Heat treatment of the 60Nb-15Fe-25NbAl₃ material caused only a slight change of dimensions. A pictorial documentation of the influence that thermal treatment had on coupons of each blend is presented in Figure 7. The change of coupon diameter is related to heat treatment temperature in Figure 8 for each study material and illustrates the relative dimensional stability of the 60Nb-15Fe-25NbAl₃ in comparison to the all-metal blends. In addition, the dimension changes of the 60Nb-15Fe-25NbAl₃ alloy heat treated at 1200 and 1300°C for 6 hours are also shown in Figure 8. These data indicate little if any further change resulting from sintering for longer time periods at higher temperatures for this alloy.

Figure 9 (top) shows the microstructures of the 60Nb-15Fe-25NbAl₃ alloy in the as-annealed condition. The annealing soaks were not effective in producing a homogeneous structure. Much of the dark area is due to loss of material as a result of grinding and polishing.

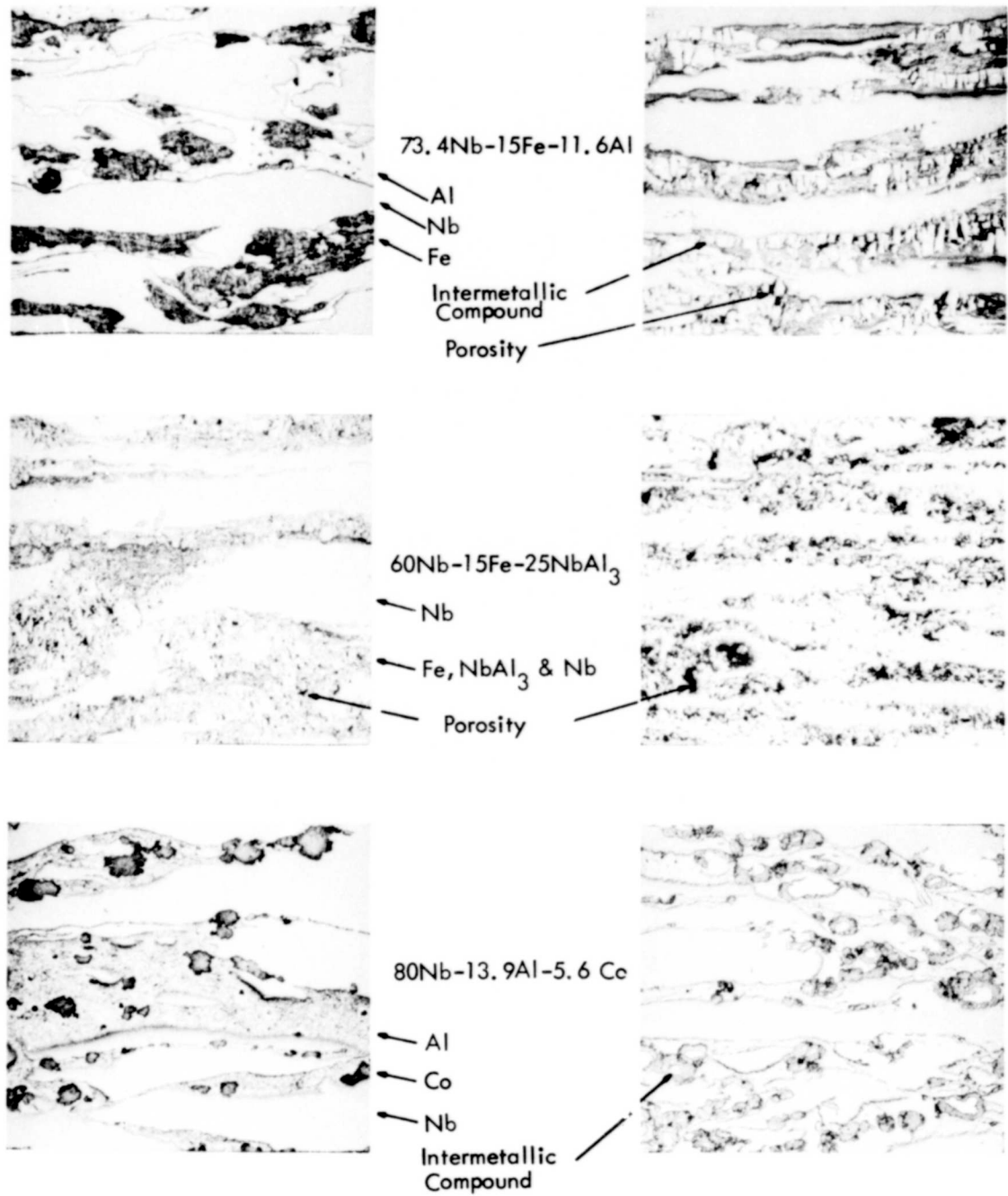


Figure 5. The Longitudinal Microstructure of Each Experimental Blend After Extrusion and Swaging (100X). Left: As-extruded; Right: As-swaged.

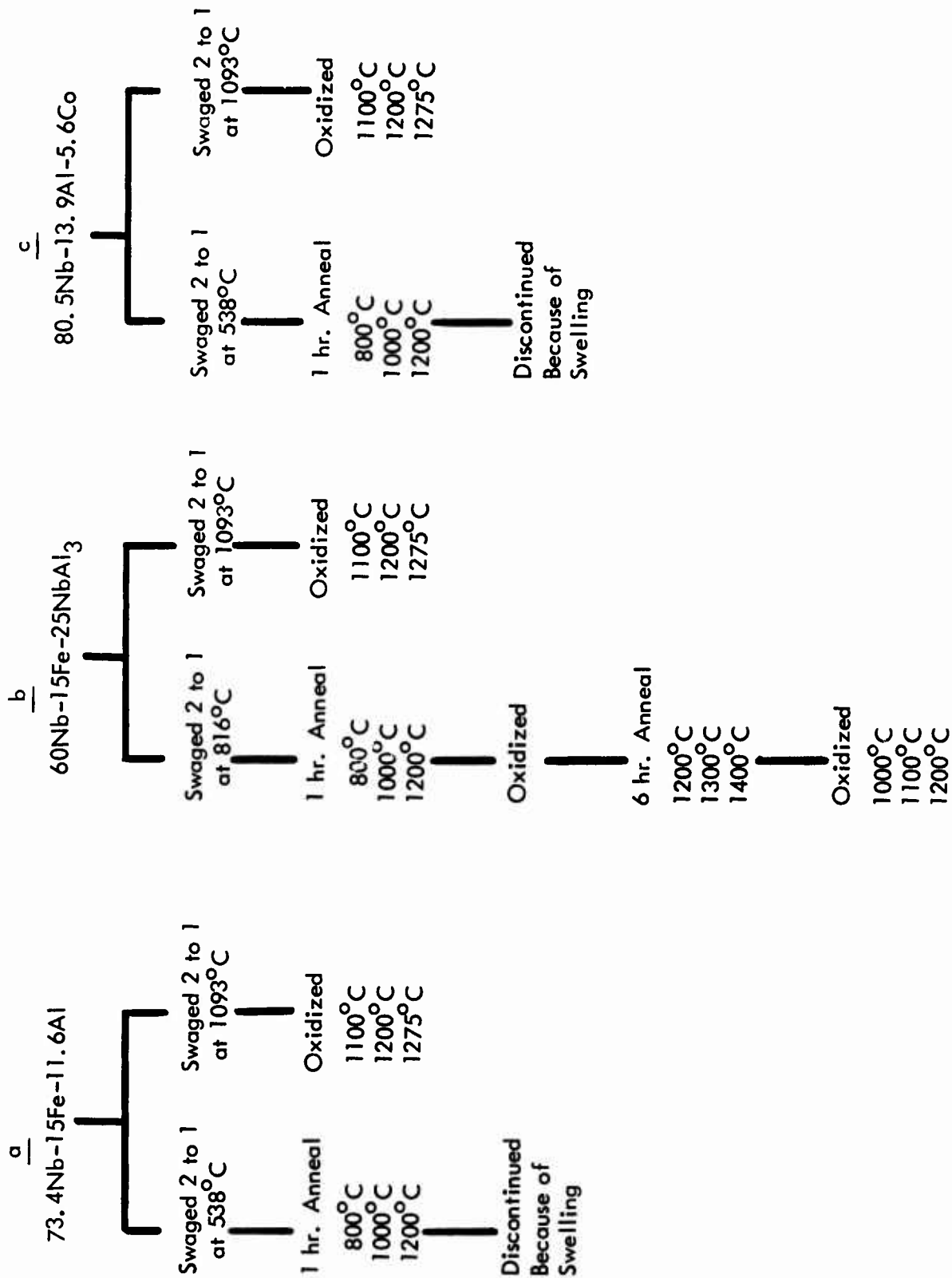


Figure 6. Summary of Heat Treatment and Oxidation Testing



Figure 7. The Influence of Heat Treatment on the Quality and Dimensions of Each Study Blend. Major Increases in Dimensions and Gross Cracking Developed in Both All-Metal Blends.

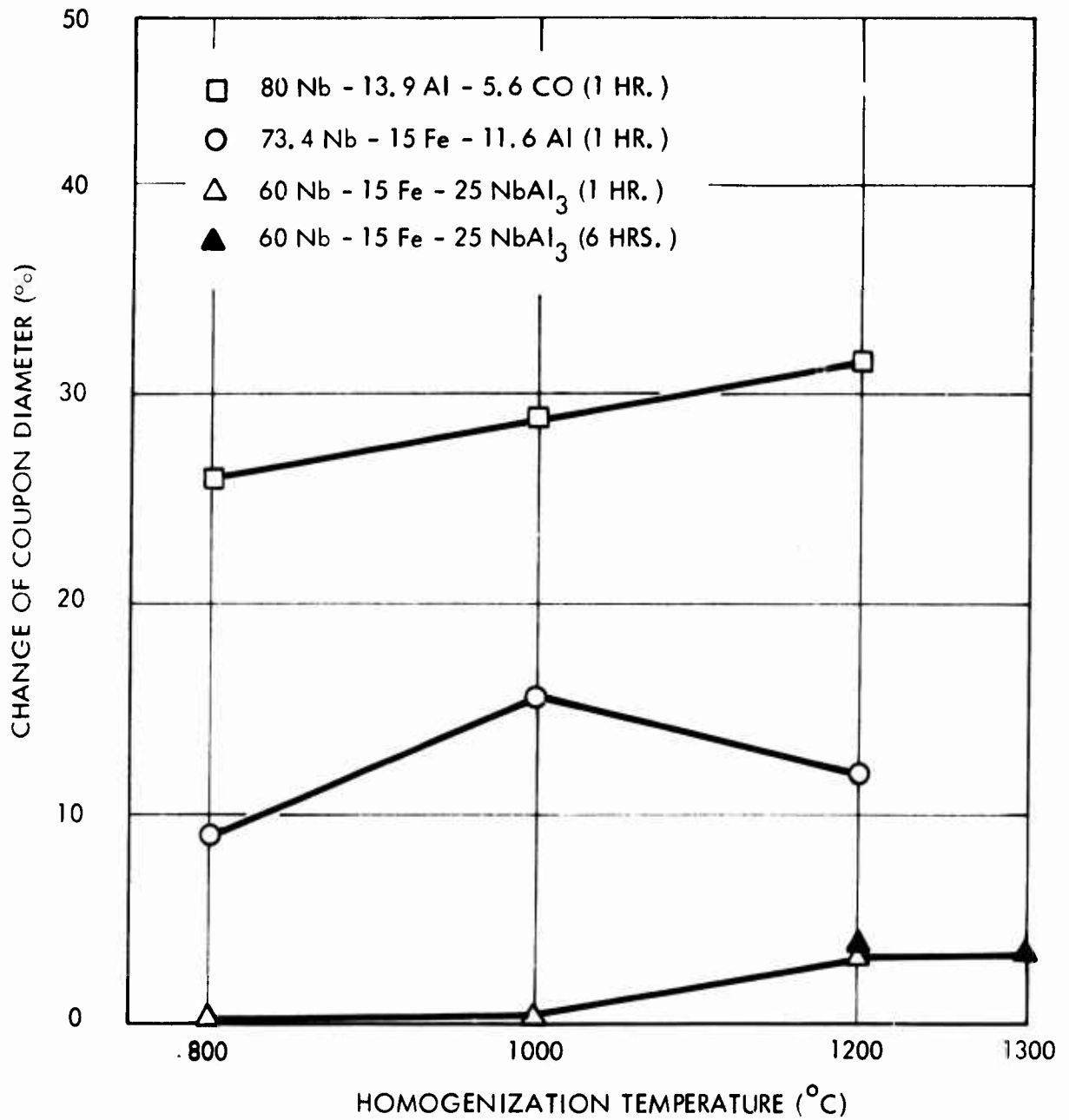


Figure 8. Dimensional Changes Resulting from Thermal Treatment

The volume change on forming intermetallic compounds, the inherent stability of these intermetallic compounds, and the possible formation of a protective oxide film on the separate phases all contributed to preventing homogenization by interdiffusion. A subsequent 6 hour anneal at 1400°C showed the same structure noted for the 1300°C anneal.

The exposed ends of a remaining length of the clad extrusions were resealed, and alloys a, b, and c were swaged at 1093°C. Test coupons were cut from these alloys and oxidized in air at 1100, 1200, and 1275°C without a subsequent anneal. The microstructures of these as-swaged samples are shown in Figure 10. Only the Nb-15Fe-11.6 alloy pictured at the top of Figure 10 appeared to achieve any degree of structural integrity. When compared to the as-swaged microstructure in Figure 5 for this composition, the elevated temperature swaging operation did reduce the areas where the intermetallic compounds formed. Because of the difficulties encountered with sintering after swaging, the alloys swaged at 1090°C were not given an annealing treatment but were oxidized in air.

Success was achieved in forming these mixtures through the swaging operation. The swaged alloys were machinable and were readily cut into oxidation test discs. However, homogenization by annealing was not successful.

Although not all combinations of powder size, powder constitution, or processing temperatures for forming homogeneous alloys from powder mixtures and homogenization by annealing have been tried, it appears unlikely that these techniques would be suitable for forming these alloys without further work on the effects of particle size and annealing temperature.

2.1 ARC-MELTING AND EXTRUSION

Continuing the effort to manufacture these alloys in a usable form, the alloy compositions (Nb-5.6Co-13.9Al (ARC-1) and Nb-15Fe-11.6Al (ARC-2)) were arc melted, reduced to



73.4Nb-15Fe-11.6Al

Niobium

Intermetallic Compound



60Nb-15Fe-25NbAl₃



80Nb-13.9Fe-5.6Co

Figure 10. The Longitudinal Microstructure of Each Experimental Blend after Extrusion and Swaging at 1093°C (100X)

powder, pressed into billets, and extruded by conventional extrusion practices on a press.

A trough melting furnace was used to melt the alloys from elemental metals. The alloys were remelted several times by flipping the bars over in the trough after each melting pass. These melts were then broken up by mortar and pestle to -10 mesh size and then ball milled to -100 mesh. These powders were isostatically pressed into billets, similar to those shown in Figure 2, at 50,000 psi. The first two billets were canned in molybdenum extrusion cans and extruded at 1300°C. The sealed molybdenum extrusion can is shown in Figure 11. The second two alloys were canned in 1018 steel extrusion cans of the same size and geometry as the molybdenum cans. Table 2 summarizes the data characterizing all of the billets and these extrusion parameters. Figures 12 and 13 show the as-extruded bar from the molybdenum and steel clad systems, respectively. The alloys extruded in Mo achieved the area reduction desired; however, the difference in the coefficient of thermal expansion between Mo and the Nb alloys most likely caused the cracking and separation of the Nb alloy. Steel has a larger coefficient of thermal expansion and should have eliminated the cracking and separation problem. However, the steel can was extruded off of the pressed alloy billet and ruptured, allowing oxidation of the Nb alloys and yielding no usable alloy for further study.

Attempts to cut the alloy extruded in the molybdenum can were unsuccessful due to the brittle nature of the alloy. Figure 14 shows the transverse macrostructure typical of the alloys extruded in the molybdenum and 1018 steel cans. Figure 15 shows the 100X microstructures of the as-extruded alloys. These structures confirm the consolidation achieved by extrusion in the Mo cans and the porosity remaining because of the poor performance of the 1018 steel clad extrusion.



Figure 11. A Molybdenum Extrusion Can Filled with Arc-Melted and Repowder Nb-15Fe-11.6Al Alloy Prior to Extrusion

Table 2. Extrusion Data

	Billet No. 1	Billet No. 2	Billet No. 3	Billet No. 4
Composition	Nb-5.6Co-13.9Al	Nb-15Fe-11.6Al	Nb-5.6Co-13.9Al	Nb-15Fe-11.6Al
Weight	933.8 g	942.3 g	1060 g	1120 g
Dimensions	4-5/8 in. dia. x 1-13/16 in. dia.	4-9/16 in. dia. x 1-3/4 in. dia.	5 in. dia. x 1-7/8 in. dia.	4-7/8 in. dia. x 1-7/8 in. dia.
Billet No.	6075	6076	6088	6089
Extrusion Ratio	7.4:1	7.26:1	~6:1	7.39:1
Can Material	Molybdenum	Molybdenum	1018 Steel	1018 Steel
Soak Temperature	2400°F	2400°F	2325°F	2325°F
Soak Time	50 min.	51 min.	90 min.	90 min.
Furnace	Induction	Induction	Resistance	Resistance
Load Range	101-119 ksi	92-116 ksi	54-65 ksi	54-59 ksi

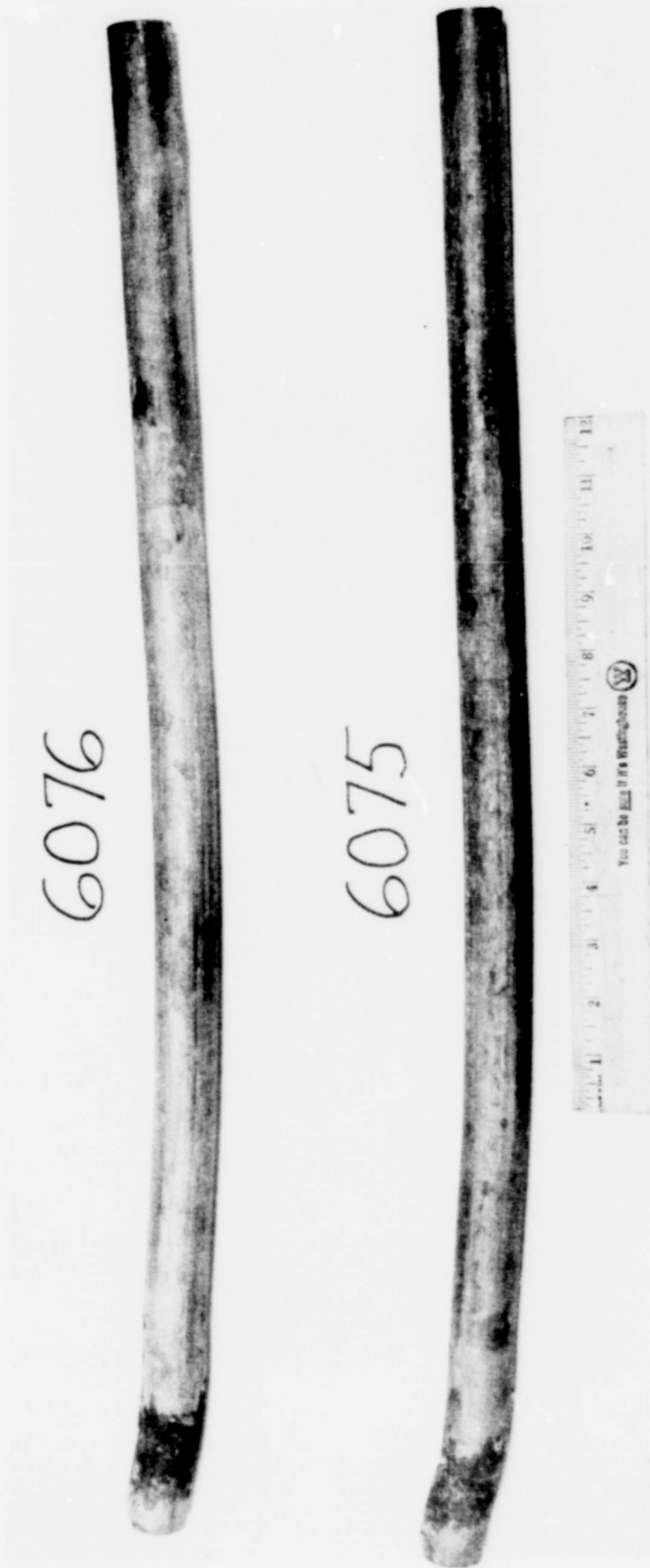


Figure 12. As-extruded Nb-Fe-Al (6076) and Nb-Co-Al (6075) Alloy in the Molybdenum Can

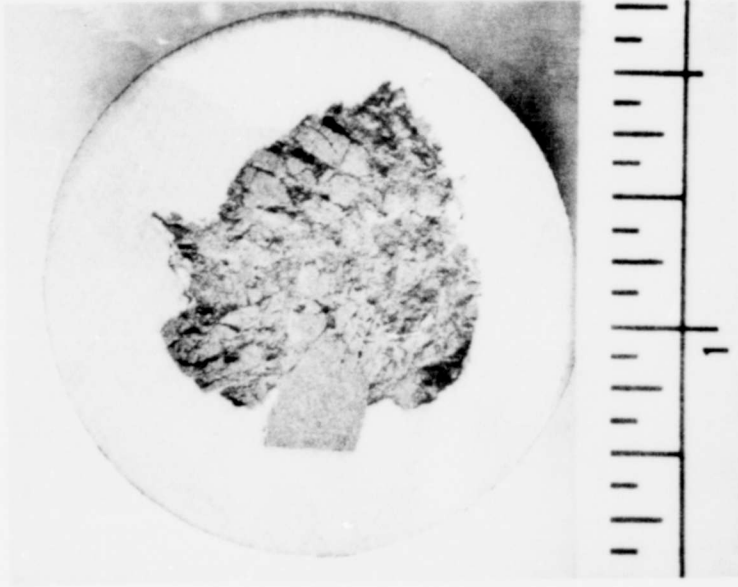
6089



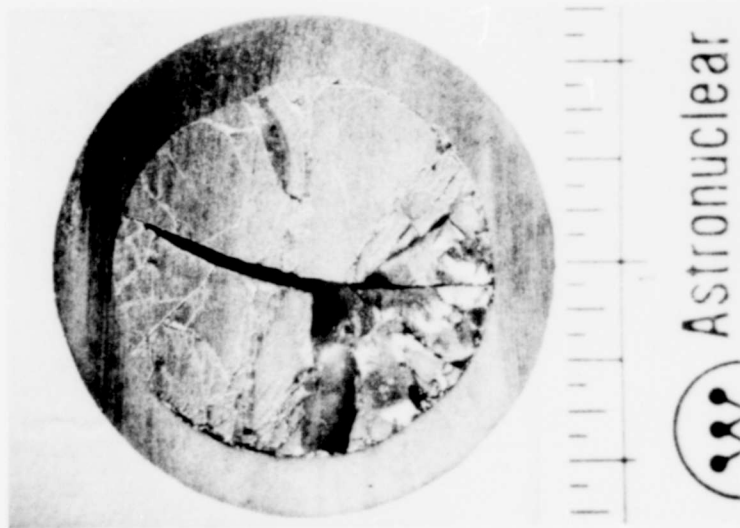
6088



Figure 13. As-extruded Nb-Fe-Al (6089) and Nb-Co-Al (6088) Alloy Canned in 1018 Steel

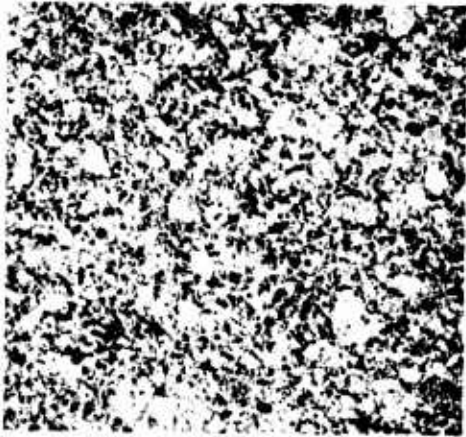


(b) 1018 Steel Extrusion Can

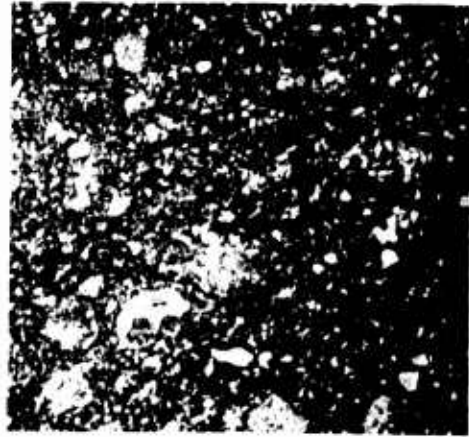


(a) Molybdenum Extrusion Can

Figure 14. Transverse Macro Photos of the As-extruded Alloys in the
(a) Molybdenum and (b) 1018 Steel Extrusion Cans

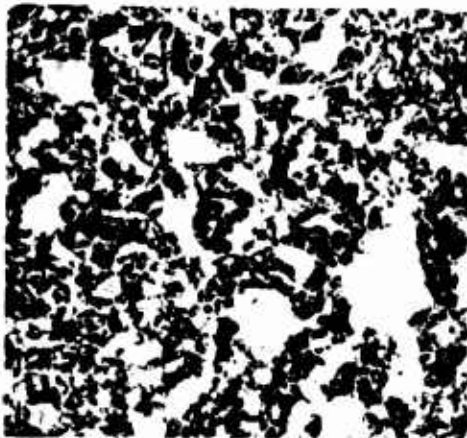


Extrusion No. 6075
Nb-5.6Co-13.9Al

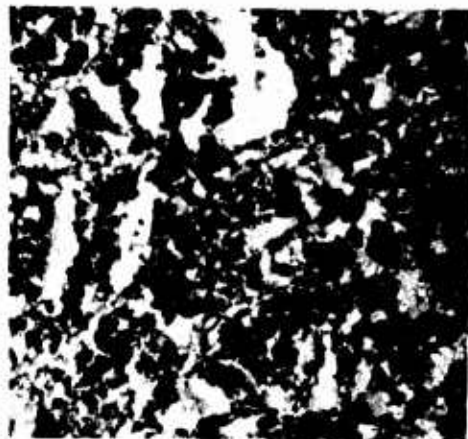


Extrusion No. 6076
Nb-15Fe-11.6Al

(a) Extrusions with Molybdenum Can



Extrusion No. 6088
Nb-5.6Co-13.9Al



Extrusion No. 6089
Nb-15Fe-11.6Al

(b) Extrusions with 1018 Steel Can

Figure 15. Transverse Microstructure of the As-extruded Billets (100X)

3.0 OXIDATION EVALUATION

The oxidation evaluation of the swaged alloys has shown that an oxide can be formed at elevated temperatures ($\sim 1275^{\circ}\text{C}$) which is much more protective at 1100°C than scales formed by oxidation at 1100°C . In addition, the annealing treatments for these alloys had less effect on subsequent oxidation behavior than did the oxidation temperature.

The oxidation apparatus and procedure is as described in a previous report⁽²⁾. All alloys were oxidized in air. Because of the non-homogeneous nature of these alloys, the purpose of the oxidation study was to determine the effects of temperature on the formation of a protective scale for this series of compositions. Rate constants were not determined for these tests because of the inability to determine the surface areas actually in contact with the oxidizing environment. Approximate rates in mils of metal consumption per 100 hours is given; however, these rates are affected grossly by the nonhomogeneous surfaces.

Figures 16 and 17 show the weight gains as a function of time for the Nb-15Fe-25NbAl₃ alloy. Figure 16 compares the oxidation rate at 1100 and 1200°C after a 6 hour anneal at 1300°C. The oxidation rate at 1200°C is initially faster than that measured at 1100°C for several minutes, then the rate abruptly changes. This change in rate indicates the formation of a protective film or oxide. Figure 17 shows the effects of a 1 hour anneal at 1000°C, and a 1 hour anneal at 1200°C on the 1000°C oxidation rate. In this case, the higher temperature anneal resulted in improved oxidation behavior. The two lower curves show that for a 6 hour anneal at 1200°C, the lower oxidation rate occurs at the highest temperature. The other two alloys could not be sintered by annealing as described earlier. As the oxidation temperature increases, the rate of formation of the protective scales increases, and the oxidation rate decreases.

Figures 18, 19, and 20 describe the effects of oxidation temperature on the oxidation rate for the Nb-15Fe-11.6Al, Nb-15Fe-25NbAl₃, and Nb-5.6Co-13.9Al alloys, respectively,

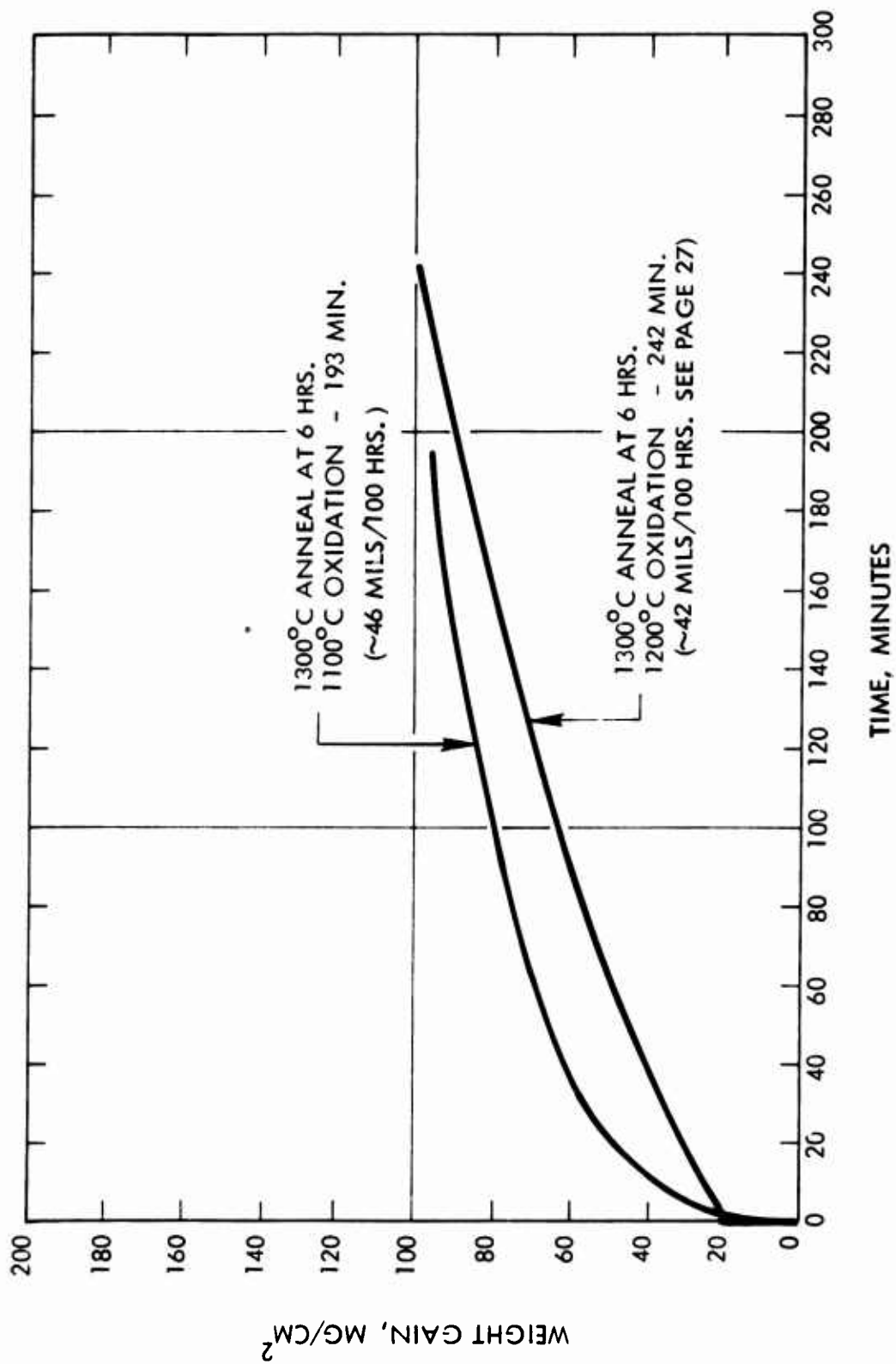


Figure 16. Oxidation Rate Curves for the 60Nb-15Fe-25NbAl₃ Alloy. Swaged at 816°C and Annealed and Oxidized as Stated

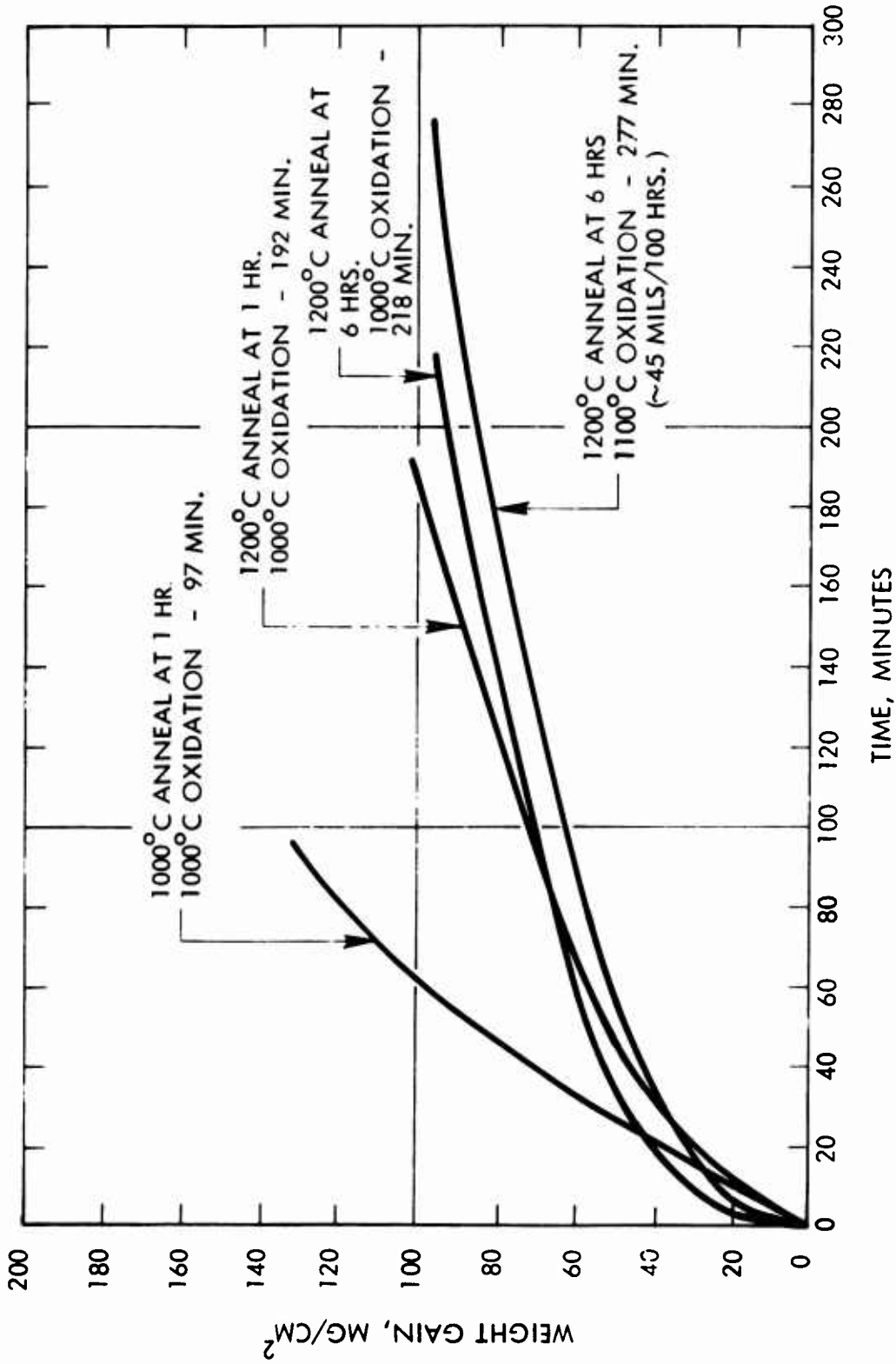


Figure 17. Oxidation Rate Curves for the 60 Nb-15 Fe-25 NbAl₃ Alloy. Swaged at 816°C and Annealed and Oxidized as Stated

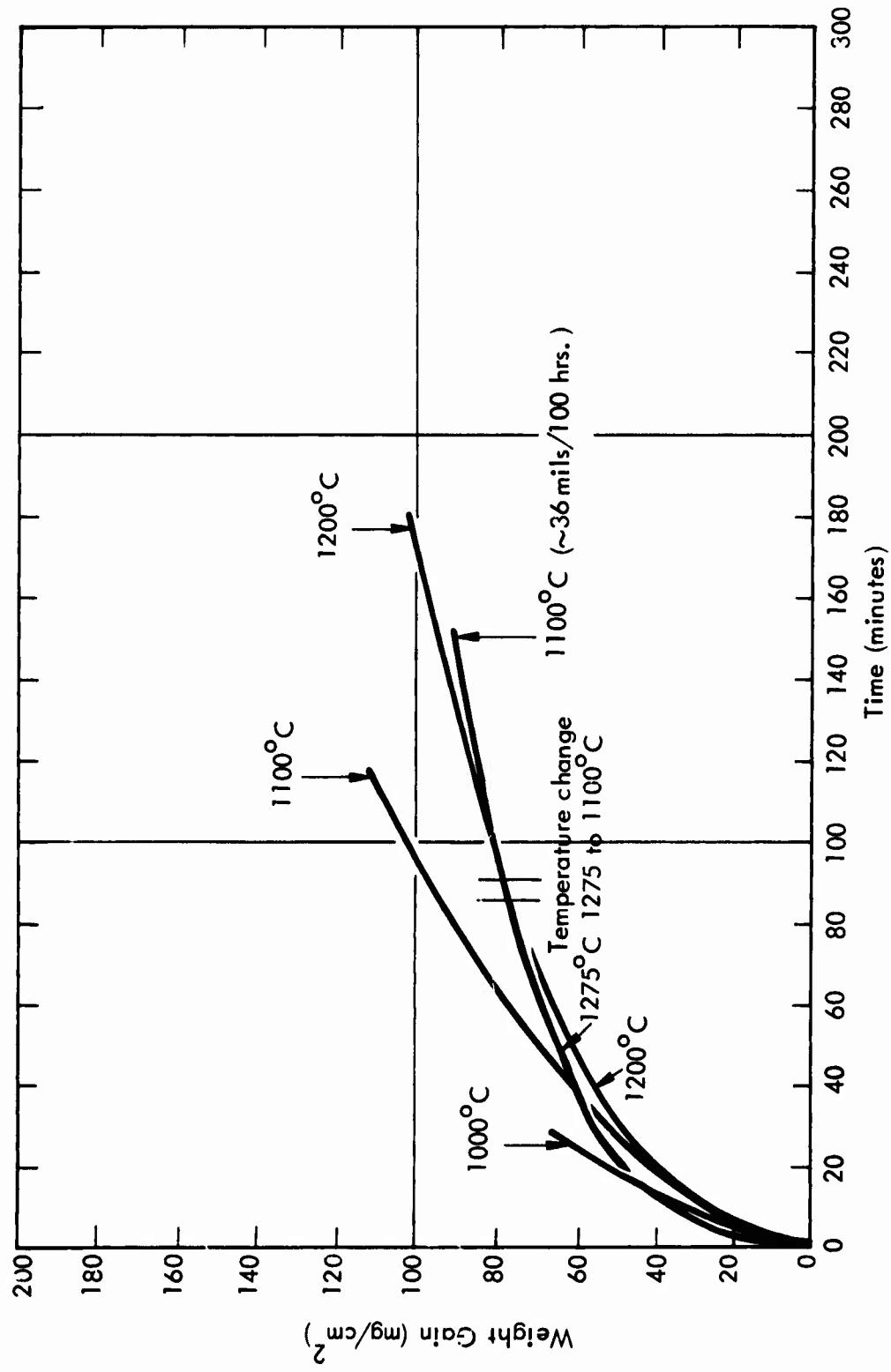


Figure 18. Weight Gain as a Function of Time and Oxidation Temperature for the Nb-15Fe-11.6Al Alloy After 1090°C Swaging

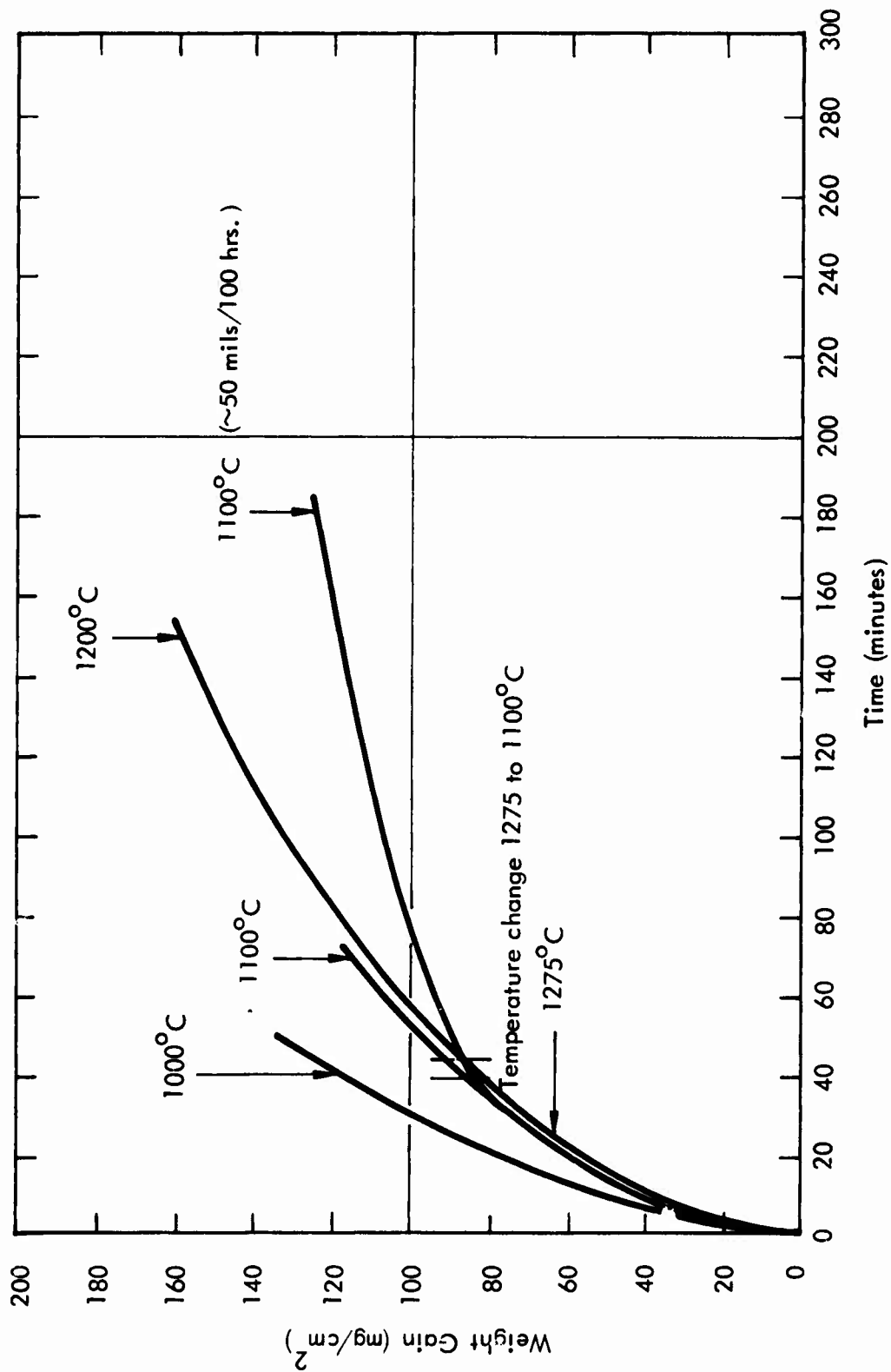


Figure 19. Weight Gain as a Function of Time and Oxidation Temperature for the Nb-15Fe-25NbAl₃ Alloy After 1090°C Swaging

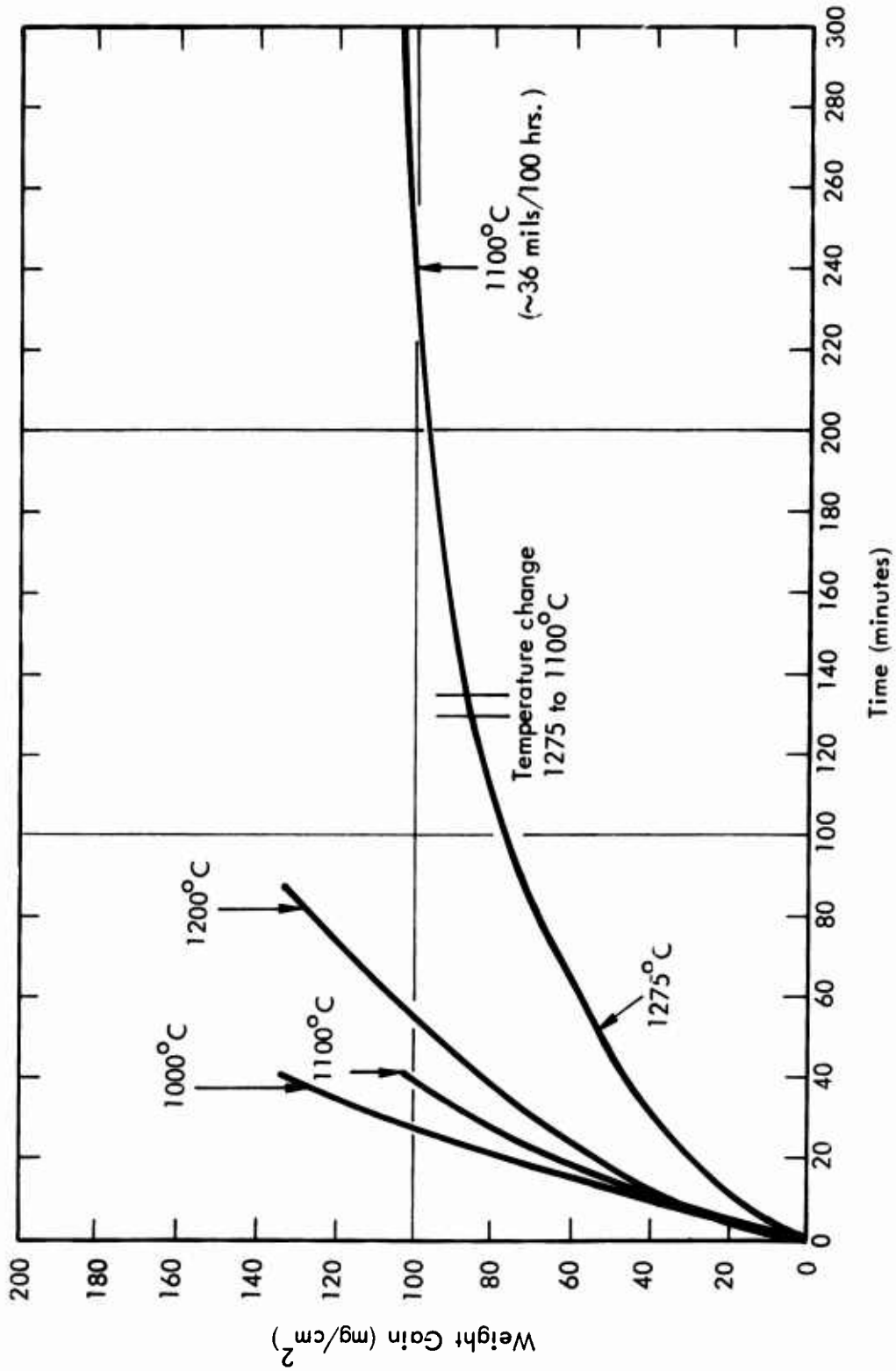


Figure 20. Weight Gain as a Function of Time and Oxidation Temperature for the Nb-5.6Co-13.9Al Alloy After 1090°C Swaging

after the 1090°C swaging with no annealing treatment. Figure 18 shows that the oxidation rate at 1200°C is lower than that at 1100 and 1000°C. The effect of a 1275°C pretreatment for 86 minutes before a 1100°C oxidation run significantly improves the 1100°C oxidation behavior. Figures 19 and 20 show this same behavior, with the exception that the 1275°C preoxidation treatment affords a significant improvement in 1100°C oxidation kinetics for the Co containing alloy.

Figures 21 through 23 show the microstructures of these various alloys after the oxidation exposures indicated. Much of the area shown unfortunately contains large voids where the brittle phases have been removed during sample preparation.

These results indicate that for many alloys, an oxidation pretreatment step is required to form a protective film at a rate which is fast enough to use a minimum of matrix material.



25675

1000°C - 40 minutes



25678

1100°C - 140 minutes



25681

1200°C - 180 minutes



25684

1275°C - 86 minutes then
1100°C - 96 minutes

Figure 21. Longitudinal Microstructures of the Nb-15Fe-11.6Al Alloy After Swaging at 1093°C and Oxidation at the Temperatures and Times Indicated (100X)



25677

1100°C - 71 minutes



25680

1200°C - 195 minutes



25683

1275°C - 40 minutes
1105°C - 178 minutes

Figure 22. Longitudinal Microstructures of the Nb-15Fe-25NbAl₃ Alloy After Swaging at 1093°C and Oxidation at the Temperatures and Times Indicated (100X)



1100°C - 47 minutes

25676



1200°C - 89 minutes

25679

Figure 23. Longitudinal Microstructure of the Nb-13.9Al-5.6Co Alloy After Swaging at 1093°C and Oxidation at the Times and Temperatures Indicated (100X)

4.0 OXIDE STRUCTURES

Many x-ray diffraction patterns have been made during the several phases of this study, dating back to 1971. Annually ASTM updates its file of ASTM Powder Diffraction Standards. Oxide phases grown on the B-1 alloy⁽³⁾, the Solar alloys⁽³⁾, and the Nb-Co-Al, Nb-Fe-Al, Nb-Cr, and other alloys investigated during Phase IV⁽⁴⁾, were identified based on the ASTM Powder Diffraction Standards available during the respective reporting periods. Table 7, pages 54 and 55 in Reference 4, list many lines which were not indexed when that report was written. To make full use of the data generated during this entire program and to further define the structures responsible for oxidation protection, these films were reanalyzed.

The powder films were read twice using a suitable interatomic spacing template. If the D spacing pairs were in agreement, an average was taken, and the new values were used for indexing. When disagreement in the readings was found, a third reading was taken to resolve the discrepancy. The relative intensities were also estimated visually during each reading and recorded. The relative intensities were normalized by using an intensity of 100 for the strongest Bragg reflection.

The data were then screened for K-beta reflections and tungsten and iron radiation reflections that may have been present from possible x-ray tube contamination. The corrected averaged data were then key punched onto IBM cards in the standard format of the "Search" program of the Joint Committee on Powder Diffraction Standards (JCPDS) Program. This data is compiled in Appendix A.

The films were then arranged into groups based upon similarities in the patterns. Several diffraction patterns from each group were analyzed by computer using the JCPDS Search Program (about two dozen total). The bulk of the patterns was analyzed using a microfiche powder diffraction system containing card sets up to set 24 (the latest available).

The results reported here account for all the major and significant phases in the crystalline fraction of the oxides analyzed. In some instances, a few weak or very weak reflections remained after the analysis was terminated. However, we feel as though these unindexed reflections correspond to phases representing a very small volume fraction of the total sample.

It should also be emphasized that many of these patterns are very complex, representing mixtures of oxides. The results reported here are often based on subtle differences between diffraction patterns of phases having similar atomic packing arrangements. The diffraction data were further complicated by the presence of solid solutions in many of the phases present.

4.1 ALLOY SYSTEM Nb-15Ti-10W-10Ta-2Hf-3Al (B-1 ALLOY)

This alloy developed by WANL is a ductile moderately oxidation resistant alloy⁽⁶⁾. Several examples of improved oxidation resistance resulting from oxidation first at 1300°F for 1 hour have been reported⁽⁶⁾. The four films of the oxides grown on alloy B-1 are virtually identical and appear, at first glance, to have diffraction data compatible with the rutile structure. More careful analysis of the patterns, however, indicated that more complex structures were in fact present.

All of the oxides contained Nb₂O₅-TiO₂ (9-229) and Nb₂TiO₇ (9-258) as the predominant phases. Another phase, Nb₃₀WO₇₈, was present in moderate quantities, while traces of AlTaO₄ (12-0407), TiO₂, HfW₂O₈ (21-363), and Al₂O₃-9Nb₂O₅ (16-545) were detected. These results are summarized in Table 3. The parabolic rate constant measured for the B-1 alloy can be expressed by the equation⁽²⁾

$$k_p = (4.26 \pm 1.65) \times 10^7 \cdot \exp\left(\frac{48,100 \pm 9,500}{RT}\right) \text{ mg}^2/\text{cm}^4\text{-min.}$$

Table 3. Oxides Formed on the B-1 Alloy (Nb-Ti-W-Ta-Hf-Al)

Film No.	Elemental Composition	Starting Mat'ls. & Treatment	Oxidation Conditions	Oxidation Products
5524	Nb-15Ti-10W-10Ta-2Hf-3Al-2.2% Al	-	1300°C 1 hr.	S - Nb ₂ O ₅ ·TiO ₂ (9-229) Nb ₂ TiO ₇ (9-258) M - Nb ₃₀ WO ₇₈ T - AlTaO ₄ (12-0407), TiO ₂ HfW ₂ O ₈ (21-363) Al ₂ O ₃ ·9Nb ₂ O ₅ (16-545)
5529	Nb-15Ti-10W-10Ta-2Hf-3Al-3.4% Al	-	1300°C 1 hr.	Same as above
5530	Nb-15Ti-10W-10Ta-2Hf-3Al-2.2% Al	-	1300°C 1 hr. and 1150°C 3 hrs.	Same as above
5537	Nb-15Ti-10W-10Ta-2Hf-3Al-3.4% Al	-	1300°C 1 hr. and 1150°C 3 hrs.	Same as above
5703	-	Nb ₂ O ₅ - TiO ₂ - Arc-melted	1175°C (P _{O₂} ≈ 10 ⁻¹⁴ atms.)	S* (mixture) - TiO ₂ (21-1276) TiO (12-754) Ti ₂ O (11-218) W - Nb ₆ O·NbO _x (15-258) T - NbO (15-535) T - Nb ₂ O ₅ (18-917)
5911	-	Nb ₂ O ₅ - TiO ₂ - Arc-melted	As-melted	S - Nb ₂ TiO ₇ (9-258) T - (Ti, Nb) (17-102) TiO ₂ (21-1272)

S Strong Mixture
M Medium W Weak T Trace

The last two entries on Table 3 present the oxide structures of arc-melted oxides used during Phases II and III^(2,3) for oxygen diffusion rate measurements. Film 5911 shows the Nb_2TiO_7 (9-258) phase as predominant in the as-melted, stoichiometric $\text{Nb}_2\text{O}_5\text{-TiO}_2$ oxide. This is also one of the two predominant phases present in the B-1 alloy oxide scales. Film 5703 identifies the phases in the same oxide, now sub-stoichiometric $\text{TiO}_2\text{-Nb}_2\text{O}_5$ after an oxygen diffusion rate determination at 1175°C at a $p_{\text{O}_2} \approx 10^{-14}$ atm. The effect of removing oxygen from the oxide melt has a decided effect on the oxide phases of the mixture.

4.2 NIOBIUM-ALUMINUM SYSTEM

Three niobium-aluminum intermetallic compositions (NbAl_3 , Nb_2Al , and Nb_3Al , were melted and oxidized⁽³⁾. Although NbAlO_4 (14-494) was common to all of the oxides, only NbAl_3 exhibited low oxidation rates. Berkowitz⁽⁷⁾ and others have demonstrated that the $\alpha\text{-Al}_2\text{O}_3$ (10-173) film is responsible for the improved oxidation resistance of this intermetallic. The Nb_2Al and Nb_3Al exhibited significant quantities of the oxides - $\text{Al}_2\text{O}_3\text{-}25\text{Nb}_2\text{O}_5$ (16-546) and $\text{Al}_2\text{O}_3\text{-}9\text{Nb}_2\text{O}_5$ (16-545) but no Al_2O_3 . The results of the analysis of the oxides of the niobium-aluminum intermetallics is shown in Table 4.

4.3 NIOBIUM-CHROMIUM SYSTEM

Table 5 lists the oxides formed on various niobium-chromium alloys. The phase CrNbO_4 (20-311) was the major phase found in all of the oxides, whether they were formed on arc-melted or pressed and sintered alloys. Alloy 12-B exhibited good oxidation resistance with a parabolic oxidation constant of $0.25 \text{ mg}^2/\text{cm}^4\text{-min}$ at 1200°C . The NbCr_2 intermetallic oxidized giving a parabolic rate constant of $0.18 \text{ mg}^2/\text{cm}^4\text{-min}$ at 1200°C ⁽⁴⁾. The oxide on the NbCr_2 intermetallic contained a Cr_2O_3 (6-0504) phase while the oxide on Alloy 12-B was almost pure CrNbO_4 with but a trace of $(\text{Fe,Cr})\text{Nb}_2\text{O}_6$ (8-181) (no Fe present in the system). One other phase in some of the oxides, NbO_2 , is associated with the lower chromium

Table 4. Oxides Formed on Nb-Al Intermetallics

Film No.	Elemental Composition	Starting Mat'ls. & Treatment	Oxidation Conditions	Oxidation Products
5719	NbAl ₃	NbAl ₃	1200°C 17 hrs.	S - AlNbO ₄ (14-494) Alpha-Al ₂ O ₃ (10-173)
5723	Nb ₂ Al	Nb ₂ Al	1200°C 13 hrs.	S - AlNbO ₄ (14-494) M - Al ₂ O ₃ ·25Nb ₂ O ₅ (16-546) M - Al ₂ O ₃ ·9Nb ₂ O ₅ (16-545)
5724	Nb ₃ Al	Nb ₃ Al	1200°C 12 hrs.	S - AlNbO ₄ (14-494) M - Al ₂ O ₃ ·25Nb ₂ O ₅ (16-546) M - Al ₂ O ₃ ·9Nb ₂ O ₅ (16-545)
5909	-	Nb ₂ O ₅ ⁻ Al ₂ O ₃ Arc-melted	As-melted	S* (mixture) - Nb ₂ O ₅ (18-917) Nb ₂ O ₅ (18-910) Nb ₂ O ₃ (9-235) NbO (15-535) Al ₂ O ₃ (21-10) Al ₂ O ₃ (10-414) Al ₂ O ₃ (10-425) Al ₂ C ₃ (11-517) T - Al ₃ Nb (13-146) AlNb ₂ (14-458) AlNb ₃ (12-85) AlNbO ₄ (14-494)

S : Strong M Medium W : Weak T Trace
* : Mixture

Table 5. Oxides Formed on Nb-Cr Alloy

Film No.	Elemental Composition	Starting Mat'ls. & Treatment	Oxidation Conditions	Oxidation Products
5721	-	NbCr ₂	1200°C 14 hrs.	S - CrNbO ₄ (20-311) M - Cr ₂ O ₃ (6-0504)
B-1-A	Nb-18Cr	Nb-NbCr ₂ Pressed and Sintered	1200°C -	S - CrNbO ₄ (20-311) S - NbO ₂ (19-859)
1-B	Nb-18Cr	Nb-NbCr ₂ Arc-melted	1200°C 7 hrs.	S - CrNbO ₄ (20-311) S - NbO ₂ (19-859)
5-A	Nb-22Cr	Nb-NbCr ₂ -Cr Pressed and Sintered	1200°C -	S - - M - CrNbO ₄ (20-311) T - Nb ₁₂ O ₂₉ (16-734)
5-B	Nb-22Cr	Nb-NbCr ₂ -Cr Arc-melted	1200°C 7 hrs.	S - - M - CrNbO ₄ (20-311) M - NbO ₂ (19-859) T - Nb ₁₂ O ₂₉ (16-734)
12-A	Nb-31Cr	Nb-NbCr ₂ -Cr Pressed and Sintered	1200°C -	S - CrNbO ₄ (20-311) S - NbO ₂ (19-859)
12-(B)	Nb-31Cr	Nb-NbCr ₂ -Cr Arc-melted	1200°C 7 hrs.	S - CrNbO ₄ (20-311) T - (Cr, Fe)Nb ₂ O ₆ (8-181) (no iron present)
5704	Nb-Cr-O	Nb ₂ O ₅ -Cr ₂ O ₃	As-melted	S - CrNbO ₄ (20-311) T - NbO ₂ (19-859) Nb ₁₂ O ₂₉ (16-734)
5910	Nb-Cr-O	Nb ₂ O ₅ -Cr ₂ O ₃ Arc-melted	1175°C P _{O₂} ≈ 10 ⁻¹⁴ atm.	S - CrNbO ₄ (20-311) W - (Cr, Fe)Nb ₂ O ₆ (8-181) (no iron present)

S = Strong M = Medium W = Weak T = Trace

content. Even in Alloy 12-A the NbO_2 phase was found. This, however, most likely, results from a lack of homogenization of the alloying constituents during the sintering operation. As with NbAl_3 discussed previously, the M_2O_3 - MNbO_4 phases together where $M = \text{Al}$ and Cr in this case, are associated with good oxidation behavior.

Oxide phases in the Nb_2O_5 - Cr_2O_3 oxide mixtures used for oxygen diffusion studies during Phases II and III are described at the bottom of Table 5. The stoichiometric oxide (5704) had some NbO_2 phases present in the oxide. The reduced (sub-stoichiometric) oxide, however, had only the NbCrO_4 (rutile) and $(\text{Cr}, \text{Fe})\text{Nb}_2\text{O}_6$ phases present. These results along with the results present in Table 3 for the Nb_2O_5 - TiO_2 oxides serve to illustrate the complex nature of these oxides. With an oxygen partial pressure gradient existing across an oxide scale, a number of sub-stoichiometric phases could be present in these oxide scales.

4.4 Nb-Ti-Cr-Al-(V) SYSTEMS

These series of alloys represent another family of ductile, oxidation resistant alloys developed for use as a matrix material for a W-Re fiber reinforced composite⁽⁸⁾. The Solar-J alloy and Solar B-IV alloys are similar in composition except that the J alloy contained 9Cr and no vanadium, and the B-IV alloy contained 4Cr and 1V. Both alloys were oxidized as thin sheet samples. As a result, after oxidation, the entire sample was ground for x-ray powder analysis⁽³⁾.

In every oxide mixture sample of this system a major phase compatible with the rutile structure was detected. Care should be taken in using these results since when elemental Nb is present from the matrix, the volume fraction of the oxide phases is reduced. The relative amounts of the remaining phases after subtracting the Nb contribution to the pattern indicate the true oxide concentrations.

It should also be emphasized that the structures of TiO_2 and CrNbO_4 are identical and consequently their respective diffraction patterns are very similar; therefore it is very difficult to unambiguously determine which specific compounds are present. Further, solid solutions in these compounds affect the diffraction patterns in unknown manners. However, subtle differences do exist between the diffraction patterns of these compounds, and it was these differences that were used to distinguish between the rutile compounds.

The NbCr_2 phase, in general, can be expected as an oxidation product in this system.

$\text{Nb}_2\text{O}_5 \cdot \text{TiO}_2$ is also formed at minor concentrations as an oxidation product, but not consistently.

Table 6 lists phases identified in the oxide grown on these alloys at 1000 and 1200°C. Electron beam microprobe work⁽³⁾ has shown coincident Cr-Ti peak in the oxide indicating that both Cr and Ti are in the rutile structure designated as TiO_2 and/or CrNbO_4 . In addition, the Cr and Al atoms could occupy the same lattice sites, since the microprobe data indicate that both Cr and Al are concentrated in the same area close to the air-oxide interface. Both of these elements are apparently oxidized during the initial stages of oxidation.

There was a distinct difference between the oxidation behavior of the J-alloy and B-IV alloy⁽³⁾. The J-alloy oxidized at a slower rate. Based on the phases present in the oxides for both systems, it is difficult to determine why the J-alloy should oxidize at a lower rate. The TiO_2 (21-1276) structure and the solid solution $(\text{Al}, \text{Cr})\text{NbO}_4$ are difficult to separate by x-ray diffraction studies, and it appears that the subtle difference in the chromium content of the alloy must be responsible for the enhanced oxidation behavior. The phase $\text{Nb}_2\text{O}_5\text{-TiO}_2$ (9-258) was evident in three of the four B-IV scales and in only one J-alloy scale. The effect of Cr on stability of this phase could possibly be the factor which improves the oxidation resistance.

Table 6. Oxides Formed on Nb-Cr-Ti-Al-(V) Alloy

Sample No.	Film No.	Elemental Composition	Oxidation Conditions	Oxidation Products
B-IV Solar	5711	Nb-42Ti-4Cr-4Al-1V	1000°C 4 hrs.	S - Nb(Ti) (16-1) W - TiO ₂ (21-1276) T - NbCr ₂ (5-0701) CrNbO ₄ (20-311)
B-IV Solar	5712	Nb-42Ti-4Cr-4Al-1V	1000°C 16 hrs.	S - Nb(Ti) (16-1) S - TiO ₂ (21-1276) S - TiO ₂ (20-311) W - NbCr ₂ (5-0701) Nb ₂ O ₅ ·TiO ₂ (9-258)
B-IV Solar	5713	Nb-42Ti-4Cr-4Al-1V	1200°C 4 hrs.	S - Nb(Ti) (16-1) S - TiO ₂ (12-1276) W - Nb ₂ O ₅ ·TiO ₂ (9-258) T - NbCr ₂ (5-0701)
B-IV Solar	5714	Nb-42Ti-4Cr-4Al-1V	1200°C 16 hrs.	S - TiO ₂ (21-1276) M - Nb(Ti) (16-1) M - Nb ₂ O ₅ ·TiO ₂ (9-258) W - NbCr ₂ (5-0701)
J Solar	5715	Nb-40Ti-9Cr-4Al	1200°C 16 hrs.	S - Nb(Ti) (16-1) M - TiO ₂ (21-1276) M - CrNbO ₄ (20-311) M - NbCr ₂ (5-0701)
J Solar	5716	Nb-40Ti-9Cr-4Al	1200°C 4 hrs.	S - TiO ₂ (21-1276) S - Nb(Ti) (16-1) T - NbCr ₂ (5-0701)
J Solar	5717	Nb-40Ti-9Cr-4Al	1000°C 16 hrs.	S - Nb(Ti) (16-1) W - NbCr ₂ (5-0701) W - TiO ₂ (21-1276) Nb ₂ O ₅ ·TiO ₂ (9-258) T - CrNbO ₄ (20-311)
J Solar	5718	Nb-40Ti-9Cr-4Al	1000°C 4 hrs.	S - Nb(Ti) (16-1) W - TiC ₂ (21-1276) W - TiO ₂ (20-311) T - NbCr ₂ (5-0701)

S Strong M Medium W Weak T Trace

4.5 Nb-Fe-Al SYSTEM

Both the Nb-Fe-Al and the Nb-Co-Al alloys are worth consideration because of minimal surface contamination of the parent metal noted during oxidation. This section will deal with the oxide structures grown on the Nb-Fe-Al alloy. Table 7 lists the oxide phases formed on the various Nb-Fe-Al alloys.

The diffraction patterns of all of the oxide mixtures examined in this system, i. e., samples DU-4, 15-B, 15-C, 16-A, 16-B, 16-C, 14-B, 11-A, and 11-B, except for sample 16-A, contain a major phase of AlNbO_4 (14-494). The diffraction pattern of sample 16-A is compatible (major phase) with the structure of $\text{Al}_{25}\text{Fe}_{25}\text{Nb}_{50}$ (23-1008). During sampling some of the alloy could have been mixed with the oxide.

The FeNbO_4 phase formed appears to be a direct function of iron content and does not appear to be dependent on whether the iron was added elementally or as NbFe_2 .

Either gamma Fe_2O_3 or a mixture of alpha Fe_2O_3 and Fe_3O_4 are present in every sample at levels ranging from trace to minor amounts. It should be emphasized that gamma Fe_2O_3 (maghemite) and Fe_3O_4 (magnetite) have overlapping diffraction patterns. Further, the patterns of all the iron oxides have severe interferences with the other oxidation products identified here. Therefore, the iron-oxide results reported here should be treated with some caution. However, these reported results "best" fit the diffraction data.

The compound $\text{Al}_2\text{O}_3 \cdot 9\text{Nb}_2\text{O}_5$ cannot be generally associated with the oxidation products of this system. Very specific conditions are probably required for its formation. The only alloy in which this phase is present is in the pressed and sintered alloy 11-A and most likely resulted from the oxidation of the individual intermetallic compounds in the unhomogenized alloy.

Table 7. Oxide Formed on Nb-Al-Fe Alloys

Film No.	Elemental Composition	Starting Mat'ls. & Treatment	Oxidation Conditions	Oxidation Products
5738	Nb-10Fe-19Al	Nb-Fe-Al	1200°C 22.8 hrs.	S - AlNbO ₄ (14-494) W - mixture of Fe ₃ O ₄ (11-614) alpha Fe ₂ O ₃ (13-534)
15-B	Nb-30Fe-10Al	Nb-Al-Fe Arc-melted	1200°C 7 hrs.	S - AlNbO ₄ (14-494) M - FeNbO ₄ (16-358) T - gamma Fe ₂ O ₃ (15-615) T - FeNbO ₄ (16-374)
15-C	Nb-30Fe-10Al	Nb-Al-Fe Arc-melted	1200°C 24 hrs.	S - AlNbO ₄ (14-494) M - FeNbO ₄ (16-358) T - gamma Fe ₂ O ₃ (15-615) T - FeNbO ₄ (16-374)
16-A	Nb-15Fe-12Al	Nb-NbAl ₃ -Fe Grd Pressed and sintered	1200°C	S - - M - Al ₁₂₅ Fe ₂₅ Nb ₅₀ (23-1008) W - gamma Fe ₂ O ₃ (15-615) -AlNb ₁₁ O ₂₉ (22-9)- FeNbO ₄ (16-374) AlNbO ₄ (14-494)-Nb (16-)
16-B	Nb-15Fe-12Al	Nb-NbAl ₃ -Fe	1200°C Arc-melted	S - AlNbO ₄ (14-494) W - FeNbO ₄ (16-358) W - Al ₂ O ₃ -9Nb ₂ O ₅ T - gamma Fe ₂ O ₃ (15-615)
16-C	Nb-15Fe-12Al	Nb-NbAl ₃ -Fe Arc-melted	1200°C 24 hrs.	S - AlNbO ₄ (14-494) W - FeNbO ₄ (16-358) T - gamma Fe ₂ O ₃ (15-615) T - FeNbO ₄ (16-374)
14-B	Nb-16Fe-10Al	Nb-NbFe ₂ -Al Arc-melted	1200°C 7 hrs.	S - AlNbO ₄ (14-494) W - alpha Fe ₂ O ₃ (13-534) - FeNbO ₄ (16-374) T - AlNb ₁₁ O ₂₉ (22-9)
11-A	Nb-13.7Fe-11.6Al	Nb-NbAl ₃ -NbFe ₂ Pressed and sintered	1200°C 6.3 hrs.	S - AlNbO ₄ (14-494) M - Al ₂ O ₃ -9Nb ₂ O ₅ (16-545) T - gamma-Fe ₂ O ₃ (24-81)
11-B	Nb-13.7Fe-11.6Al	Nb-NbAl ₃ -NbFe ₂ Arc-melted	1200°C 7 hrs.	S - AlNbO ₄ (14-494) M - gamma Fe ₂ O ₃ (15-615) W - FeNbO ₄ (16-358) - orthorhombic T - FeNbO ₄ (16-374) - monoclinic
5746	-	NbFe ₂	1200°C	S* mixture - FeNbO ₄ (16-357) - tetragonal ** FeNbO ₄ (16-374) - monoclinic *** FeNbO ₄ (16-358) - orthorhombic ** FeNbO ₄ (15-596) M - Fe ₂ O ₃ (24-72) Fe ₂ O ₃ (13-534)
5759	Nb-20Fe-15Ti-5B	Nb-Fe-Ti-B Arc-melted	1200°C 19 hrs.	S - Fe, Ni, Ti C ₃ (21-1276) W - 3Nb ₂ O ₅ -Ti ₂ O ₃ (9-229)

S - Strong M - Medium W - Weak T - Trace
* - Mixture ** - High Temperature Disorder *** - Low Temperature Disorder

The NbAlO_4 phase is expected to form on these alloys. The relative composition of elements such as Ni, Co, and Fe are increased at the oxide metal interfaces because they are more stable relative to Nb and Al with respect to oxygen⁽³⁾. This then changes the relative activities of the alloying elements in the alloy, which affects both the solubility of oxygen into the surface (substrate contamination) and the oxide composition.

4.6 Nb-Co-Al

Table 8 describes the oxides formed on the Nb-Co-Al alloys. In general, a mixture of AlNbO_4 and $\text{Al}_2\text{O}_3 \cdot 9\text{Nb}_2\text{O}_5$ can be expected to form as oxidation products in this system. For several compositions, namely, 21-A and 25-A where the aluminum concentration was low, the phase $\text{AlNb}_{11}\text{O}_{29}$ forms at the expense of the aluminum niobate. In addition, minor and trace phases of CoNbO_4 , CoOAl_2O_3 , $\text{Nb}_{12}\text{O}_{29}$, and $\text{AlNb}_{49}\text{O}_{124}$ were formed. This would indicate very strongly that the amount of aluminum in these alloys must exceed 4 percent. Composition 18-A with 9 w/o aluminum does form AlNbO_4 when oxidized, although the x-pattern was somewhat diffused. The only other cases where AlNbO_4 did not form were on the pressed and sintered alloys 17-A, 19-A, and 24-A. These pressed and sintered alloys were not homogeneous, and the various phases from which they were made oxidized individually. All of the arc-melted Nb-Co-Al compositions formed the AlNbO_4 phase during oxidation in air.

4.7 Nb-Al-Cr-(Co, Ni) SYSTEMS

The CrNbO_4 (20-311) structure is present and predominant in all of the arc-melted alloys shown on Table 9. The oxide formed on the pressed and sintered alloy 22-A did not give a diffraction pattern indicative of a well formed oxide structure, indicating that the oxide structure is dependent on the alloy constitution.

Table 8. Oxide Phases Grown on the Nb-Al-Co-(Y) Alloy

Film No.	Elemental Composition	Starting Mat'ls. & Treatment	Oxidation Conditions	Oxidation Products
13-A	Nb-12Al-10Co	Nb-NbAl ₃ -Co Pressed and sintered	1200°C 7 hrs.	S - AlNbO ₄ (14-494) M - Al ₂ O ₃ ·9Nb ₂ O ₅ (16-545) W - Nb ₂ O ₅ (18-917, 18-910) T - AlNb ₄₉ O ₁₂₄ (22-11) T - (Fe, Co)NbO ₄ (16-358) (no iron present)
13-B	Nb-12Al-10Co	Nb-NbAl ₃ -Co Arc-melted	1200°C 7 hrs.	S - AlNbO ₄ (14-494) W - Al ₂ O ₃ ·9Nb ₂ O ₅ (16-545) T - (Fe, Co)NbO ₄ (16-358) (no iron present)
17-A	Nb-15Al-15Co	Nb-Al-Co Pressed and sintered	1200°C 6 hrs.	S - Al ₂ O ₃ ·9Nb ₂ O ₅ (16-545) M - AlNbO ₄ (14-494) T - CoO (9-418) T - Nb ₁₂ O ₂₉ (16-734) T - (Fe, Co)NbO ₄ (16-358) (no iron present)
17-C	Nb-15Al-15Co	Nb-Al-Co Arc-melted	1200°C 24 hrs.	S - AlNbO ₄ (14-494) W - Al ₂ O ₃ ·9Nb ₂ O ₅ (16-545)
18-A	Nb-9Al-11Co	Nb-NbAl ₃ -NbCo ₂ Pressed and sintered	1200°C 8 hrs.	S - - M - AlNbO ₄ (14-494) W - Al ₂ O ₃ ·9Nb ₂ O ₅ (16-545) W - Al ₂ O ₃ (16-435) W - NbAl ₂ (18-13) T - CoO (9-402)
19-A	Nb-10Al-11Co	Nb-Al-NbCo ₂ Pressed and sintered	1200°C 8 hrs.	S - Al ₂ O ₃ ·9Nb ₂ O ₅ (16-545) M - AlNbO ₄ (14-494) T - CoO (9-402) T - (Fe, Co)NbO ₄ (16-358) (no iron present)
19-B	Nb-10Al-11Co	Nb-Al-NbCo ₂ Arc-melted	1200°C 7 hrs.	S - AlNbO ₄ (14-494) M - Al ₂ O ₃ ·9Nb ₂ O ₅ (16-545) T - (Fe, Co)NbO ₄ (16-358) (no iron present)
19-C	Nb-10Al-11Co	Nb-Al-NbCo ₂ Arc-melted	1200°C 24 hrs.	S - AlNbO ₄ (14-494) W - Al ₂ O ₃ ·9Nb ₂ O ₅ (16-545) T - (Fe, Co)NbO ₄ (16-358) (no iron present)
20-A	Nb-7Al-8Co	Nb-NbAl ₃ -NbCo ₂ Pressed and sintered	1200°C 4 hrs.	S - Al ₂ O ₃ ·9Nb ₂ O ₅ (16-545) W - AlNbO ₄ (14-494) T - (Fe, Co)NbO ₄ (16-358) (no iron present)
21-A	Nb-2Al-8Co	Nb-Nb ₂ Al-NbCo ₂ Pressed and sintered	1200°C 2-12 hrs.	S - AlNb ₁₁ O ₂₉ (22-9) M - Al ₂ O ₃ ·9Nb ₂ O ₅ (16-545) W - AlNbO ₄ (14-494) T - (Fe, Co)NbO ₄ (16-358) (no iron present)

Table 8 (Continued)

Film No.	Elemental Composition	Starting Mat'ls. & Treatment	Oxidation Conditions	Oxidation Products
24-A	Nb-14Al-6Co	Nb-NbAl ₃ -NbCo ₂ Pressed and sintered	1200°C -	S - Al ₂ O ₃ ·9Nb ₂ O ₅ (16-545) W - AlNbO ₄ (14-494) T - Nb (16-001) CoO (9-402)
24-B	Nb-14Al-6Co	Nb-NbAl ₃ -NbCo ₂ Arc-melted	1200°C 7 hrs.	S - AlNbO ₄ (14-494) M - Al ₂ O ₃ ·9Nb ₂ O ₅ (16-545)
24-C	Nb-14Al-6Co	Nb-NbAl ₃ -NbCo ₂ Arc-melted	1200°C 24 hrs.	S - AlNbO ₄ (14-494) M - Al ₂ O ₃ ·9Nb ₂ O ₅ (16-545) T - (Fe, Co)NbO ₄ (16-358) (no iron present)
25-A	Nb-4Al-17Co	Nb-NbAl ₃ -NbCo ₂ Pressed and sintered	1200°C	S - AlNb ₁₁ C ₂₉ (22-9) M - Al ₂ O ₃ ·9Nb ₂ O ₅ (16-545) W - AlNbC ₄ (14-494) T - (Fe, Co)NbO ₄ (16-358) (no iron present)
26-A	Nb-11Al-10Co-2Y	Nb-NbAl ₃ -Co-Y Pressed and sintered	1200°C -	S - AlNbC ₄ (14-494) W - Al ₂ O ₃ ·Nb ₂ O ₅ (16-545)
27-A	Nb-11Al-10Co-2Y ₂ C ₃	Nb-NbAl ₃ -Co-Y ₂ C ₃	1200°C -	S - AlNbC ₄ (14-494) S - Al ₂ O ₃ ·9Nb ₂ O ₅ (16-545)
23-A	Nb-7Al-8Co-4Ni	Pressed and sintered (Grd)	1200°C 7 hrs.	S - Al ₂ O ₃ ·9Nb ₂ O ₅ (16-545) S - AlNbO ₄ (14-494) W - NbO ₂ (17-717)
9-B	-	Nb ₂ O ₅ -Co ₃ O ₄ Arc-melted	As-melted	S - CoC·Nb ₂ O ₅ (8-181) M - Co ₂ O ₃ (2-770)
10-B	-	Nb ₂ O ₅ -Co ₂ O ₃ Arc-melted	As-melted	S - Co ₄ Nb ₂ O ₉ (13-464) M - CoNbC ₄ (23-1480)
5745	-	NbCo ₂ Arc-melted	1200°C 4 hrs.	S - Nb ₂ Co ₄ O ₉ (13-464) S*(mixture) - Nb(Co, Fe)O ₄ (16-358) Nb(Co, Fe)O ₄ (16-374) Nb(Co, Fe)O ₄ (15-19) (no iron present)

S Strong M Medium W Weak T Trace
* Mixture

Table 9. Oxide Phases Formed on Nb-Al-Cr-(Co, Ni) Alloys

Film No.	Elemental Composition	Starting Materials & Treatment	Oxidation Conditions	Oxidation Products
5742	Nb-19Cr-10Al-15Co	- Arc-melted	1200°C 24 hrs.	S - CrNbO ₄ (20-311) S - CoAl ₂ O ₄ (10-458) W - Nb ₂ O ₅ (12-104)
22-A	Nb-7Al-8Co-5Cr	Nb-NbCr ₂ -NbAl ₃ -NbCo ₂ Pressed and sintered	1200°C -	S - - M - Al ₂ O ₃ ·9Nb ₂ O ₅ (16-545) M - AlNbO ₄ (14-494) W - NbO ₂ (19-859)
22-(B)	Nb-7Al-8Co-5Cr	Nb-NbCr ₂ -NbAl ₃ -NbCo ₂ Arc-melted	1200°C 7 hrs.	S - CrNbO ₄ (20-311) M - AlNbO ₄ (14-494) M - Al ₂ O ₃ ·9Nb ₂ O ₅ (16-545)
5740	Nb-9Cr-10Al-25Ni	- Arc-melted	1200°C 27 hrs.	S - (Cr, Ni)NbO ₄ (20-311) W - AlNbO ₄ (14-494)
5741	Nb-10Cr-10Al-15Ni	- Arc-melted	1200°C 23 hrs.	S - CrNbO ₄ (20-311) M - AlNbO ₄ (14-494)
5743	Nb-10Cr-10Al-15Ni	- Arc-melted	1200°C 23 hrs.	S - (Cr, Ni)NbO ₄ (20-311) M - AlNbO ₄ (14-494)
5720	-	NbNi	1200°C	S - NiNb ₂ O ₆ (15-159) M - Nb ₁₂ O ₂₉ (16-734)

S Strong M Medium W Weak T Trace

With the exception of film No. 5742, the AlNbO_4 phase (14-494) was also identified in the oxide scale. Film 5742 showed a strong spinel phase CoAl_2O_4 (10-458) in addition to the CrNbO_4 (20-311) phase. The Al_2O_3 - $9\text{Nb}_2\text{O}_5$ phase is present in both 22-A and 22-B. The oxides grown on the NbNi intermetallic compound (film 5720) are shown with this series of alloys. The addition of chromium and aluminum to the Nb-Ni mixture stabilized the rutile phase AlNbO_4 and CrNbO_4 at the expense of the NiNb_2O_6 columbite phases. In fact, Ni reacts as a noble metal in these systems and is rejected back into the metallic substrate where it apparently changes the elemental activities at the alloy substrate.

5.0 DISCUSSION OF RESULTS

The analyses of the x-ray diffraction patterns have definitely established the rutile oxide phase $NbMO_4$, where $M = Al, Cr, Fe,$ and/or Ni , as the scale formed on these oxidation resistant niobium alloys. The most oxidation resistant alloys or compounds evaluated, $NbAl_3$ and the Nb-19Cr-10Al-15Co (DU-1) alloy also had Al_2O_3 and $CoAl_2O_4$ phases in their oxide scales. The iron based oxidation resistant alloys, 14 (73.6Nb-10Al-16.4Fe); 15 (60Nb-10Al-30Fe); and 16 (73.4Nb-11.6Al-15Fe) had $AlNbO_4$ and $FeNbO_4$ and either $\alpha\text{-Fe}_2O_3$ (hematite) or $\gamma\text{-Fe}_2O_3$ (maghemite) present in the oxide scale. The $FeNbO_4$ (16-374) shown on Table 7 is the low temperature phase which is formed on cooling at about $1085^\circ C$ from the $FeNbO_4$ (16-358) high temperature phase.

According to Goldschmidt⁽⁹⁾, the evolution of the hemitites (M_2O_3) is closely linked, for some of the transition metals, to that of the spinels. The $Fe_3O_4 (=Fe^{++}O \cdot Fe_2^{+++}O_3)$ is considered to be the most prominent example of this behavior. The $CoAl_2O_4$ spinel phase in the Nb-19Cr-10Al-15Co (DU-1) alloy and the $MO \cdot M_2O_3$ spinel class could be inter-related. Defects in the spinel structure such as metal and oxygen vacancy sites are common. Occurrence of $\gamma\text{-Fe}_2O_3$ and $\gamma\text{-Al}_2O_3$, still of the spinel types, are examples of how far this defect lattice can extend. Within this framework then, the $NbAl_3$, DU-1, and Nb-Fe-Al alloys can be classed as a family of alloys which form a rutile-spinel oxide system as a protective scale. On considering the Nb-Co-Al alloys, Goldschmidt⁽⁹⁾ states that the Co_3O_4 spinel is the last stable spinel along the First Long Period. This spinel Co_3O_4 becomes unstable at elevated temperatures. As one moves farther along the First Long Period to Ni, no Ni type " Ni_2O_3 " spinel can exist.

Examining the scales formed on the Nb-Co-Al alloys, even in the most oxidation resistant alloys of this family 80.5Nb-13.9Al-5.6Co (24), 90Nb-15Al-15Co (17), and 78.8Nb-10Al-11.2Co(19) none of the spinel type oxides were present as expected from the preceding discussion. Only the AlNbO_4 (14-494) and $\text{Al}_2\text{O}_3\text{-9Nb}_2\text{O}_5$ (16-542) phases were found in the oxides in any significant concentrations. Traces of CoNbO_4 were found in some of the oxides, this being isostructural with FeNbO_4 (16-358).

The nonexistence of the Ni spinel types noted above are consistent with the oxide phases reported for some of these alloys containing nickel. Only the rutile NbCrO_4 and AlNbO_4 phases were detected in the oxides (see Table 9).

Formation of more protective oxides by an initial oxidation exposure at temperatures of 1300°C which aid in the development of a stable, protective phase before excessive metal consumption is realized, has been illustrated during this program. However, this technique is applicable only for phases which do not exhibit phase transformation as a function of temperature. This is possibly why the Nb-Fe-Al alloys did not respond as well to pre-treatment as did the Nb-Al-Co alloys. According to the ASTM x-ray diffraction files, a phase transformation for FeNbO_4 occurs at approximately 1085-1100°C.

Stringer⁽¹⁰⁾ has cautioned that oxidation rates for Nb based alloys do not necessarily increase with temperature. This has been shown to be the case in this program. For any alloy system, the oxide phases responsible for oxidation protection should be determined, its stability with respect to temperature should be investigated, and temperature at which it shows rapid formation rate kinetics should be determined. It appears that in many instances, a protective oxide, formed quickly at an elevated temperature, which is stable at a lower temperature, will afford the oxidation protection required for specific applications of these alloys.

Attempts to fabricate 1 kg samples of several Nb-Fe-Al and Nb-Co-Al alloys proved unsuccessful. Recommendations for other alloy additions, which would provide the desired protective scales while increasing the fabricability of the alloys, are difficult because of no suitable phase relationship information. However, based on its ability to form the rutile structure in the oxide phase for the Solar and B-1 alloys (Tables 3 and 6) and the ductility of these alloys containing Ti, some possible combination of Nb-Ti-(Fe, Co)-Al might be advantageous. Alloys containing chromium are susceptible to internal oxidation^(3, 4). The studies during this program have shown that Fe and Co containing alloys do not exhibit a large degree of metal contamination during oxidation exposure, most likely due to the increased Fe and Co concentration at the metal-oxide interface resulting from the formation of the NbAlO₂ rutile oxides. This effect, due to the accumulation of more noble metals at the metal oxide interface, has been tentatively suggested by Rapp and Goldberg⁽¹¹⁾ from their work on the Nb-Zr-Rh system, when the Rh concentration at the oxide-metal interface was increased during oxidation.

The phases present in the protective oxides of some of the most oxidation resistant Nb alloy and intermetallics have been identified. It is unfortunate that these particular alloys are extremely brittle and very difficult to fabricate. However, the investigation of oxide structures and phases has provided new and useful information that will help to answer some of the questions posed by those interested in this field.

6.0 CONCLUSIONS

1. The oxide phases NbMO_4 (rutile) and spinel types MAI_2O_4 , and/or gamma- M_2O_3 where $M = \text{Al, Fe, Cr, and/or Co}$ are responsible for the oxidation behavior of the alloy systems, Nb-Fe-Al, Nb-Co-Al, Nb-Cr, Nb-Cr-Al-Co, and Nb-Al.
2. Pre-oxidation at elevated temperatures (1275°C) greatly improves the oxidation behavior when oxidation is continued at lower temperatures for Nb-Fe-Al and Nb-Co-Al.
3. Niobium alloys 73.4Nb-15Fe-11.6Al and 60Nb-15Fe-15Al are extremely difficult to fabricate using powder metallurgy techniques either from the alloys elements, intermetallic compounds of the elements, or from pre-alloyed powders.

Based on oxidation data from References 3 and 4 for button melted alloys, scales such as the NbMO_4 rutiles can limit oxidation rates at 1200°C to less than 1.6 mils/100 hours. At these elevated temperatures, thermodynamic equilibrium relationships, rather than kinetic limitations will ultimately control the effectiveness of scales as protective oxides.

Additional phase relationship data is required to determine the alloy composition limits which will support an equilibrium protective oxide. An understanding of oxide phase relationship through a given scale is also required. With more basic data in hand, some of the more protective oxides may be able to be grown on substrates having desirable mechanical properties.

7.0 REFERENCES

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APPENDIX A

CORRECTED "D" SPACINGS AND RELATIVE INTENSITIES

Note: $D(\text{Å}) = \text{"d" spacings (Å)}$
RI = Relative Intensities

Sample No. B-18-A

U(A)	U(B)	U(C)
2.14	2.10	2
2.11	4.7	2
4.27	3.8	2
4.25	3.7	2
4.10	3.6	2
3.75	3.51	2
3.52	3.40	2
3.42	3.31	2
3.32	3.12	2
2.92	2.96	2
2.85	2.92	2
2.74	2.86	2
2.66	2.82	2
2.74	2.76	2
2.44	2.66	2
2.34	2.50	2
2.31	2.46	2
2.27	2.44	2
2.22	2.36	2
2.15	2.29	2
2.10	2.19	2
2.10	2.14	2
2.10	2.06	2
2.05	2.21	2
2.02	2.17	2
1.94	2.15	2
1.90	2.10	2
1.74	2.04	2
1.71	2.00	2
1.67	1.97	2
1.57	1.89	2
1.55	1.85	2
1.54	1.80	2
1.52	1.770	2
1.49	1.750	2
1.47	1.710	2
1.47	1.700	2
1.44	1.670	2
1.41	1.650	2
1.39	1.590	2
1.34	1.570	2
1.32	1.558	2
1.30	1.520	2
1.24	1.482	2
1.23	1.445	2
1.20	1.402	2
1.19	1.393	2
1.14	1.375	2
1.13	1.365	2
1.12	1.349	2
1.10	1.325	2
1.10	1.300	2
1.04	1.272	2
1.04	1.255	2
1.04	1.210	2
1.04	1.112	2

Sample No. B-19-A

U(A)	U(B)	U(C)
2.10	2.10	10
4.7	1.142	2
3.8	1.160	2
3.7	1.150	2
3.6	1.130	2
3.51	1.130	2
3.40	1.120	2
3.31	1.110	2
3.12		2
3.06		2
2.96		10
2.92		10
2.86		2
2.82		2
2.76		2
2.66		20
2.50		10
2.46		2
2.44		2
2.36		10
2.29		10
2.19		10
2.14		2
2.06		2
2.02		2
2.17		2
2.15		20
2.10		10
2.04		2
2.00		2
1.97		2
1.89		20
1.85		20
1.80		2
1.770		20
1.750		20
1.710		20
1.700		20
1.670		20
1.650		20
1.590		20
1.570		2
1.558		2
1.520		2
1.482		2
1.445		2
1.402		2
1.393		10
1.375		10
1.365		10
1.349		10
1.325		2
1.300		2
1.272		2
1.255		2
1.210		2
1.112		2

Sample No. B-19-A (Cont'd.)

1.200	2
1.142	2
1.160	2
1.150	2
1.130	2
1.130	2
1.120	2
1.110	2

Sample No. B-16-A

U(A)	U(B)	U(C)
5.1	5.1	2
3.75	3.75	2
3.57	3.57	2
3.57	3.57	2
3.11	3.11	2
2.91	2.91	2
2.76	2.76	2
2.64	2.64	2
2.52	2.52	2
2.45	2.45	10
2.40	2.40	10
2.35	2.35	100
2.27	2.27	10
2.22	2.22	20
2.14	2.14	20
2.16	2.16	2
2.12	2.12	10
2.04	2.04	2
2.03	2.03	2
1.97	1.97	10
1.91	1.91	10
1.74	1.74	2
1.64	1.64	2
1.600	1.600	2
1.590	1.590	2
1.580	1.580	2
1.541	1.541	2
1.541	1.541	2
1.525	1.525	2
1.515	1.515	2
1.482	1.482	10
1.462	1.462	10
1.170	1.170	10
1.160	1.160	2
1.149	1.149	2
1.137	1.137	2
1.124	1.124	2
1.116	1.116	2

Sample No. B-12

U(A)	U(B)	U(C)
3.51	3.51	10
3.25	3.25	100
3.41	3.41	20
3.31	3.31	20
3.19	3.19	10
3.04	3.04	20
2.99	2.99	10
2.92	2.92	20
2.84	2.84	20
2.82	2.82	10
2.76	2.76	20
2.67	2.67	2
2.52	2.52	10
2.45	2.45	10
2.37	2.37	2
2.29	2.29	20
2.24	2.24	2
2.16	2.16	2
2.07	2.07	10
2.05	2.05	20
1.90	1.90	20
1.87	1.87	20
1.74	1.74	20
1.73	1.73	10
1.64	1.64	2
1.675	1.675	2
1.635	1.635	2
1.540	1.540	20
1.535	1.535	2
1.515	1.515	2
1.446	1.446	2
1.425	1.425	20
1.345	1.345	20
1.320	1.320	10
1.275	1.275	10
1.245	1.245	10
1.215	1.215	10
1.145	1.145	2
1.167	1.167	10
1.153	1.153	10
1.135	1.135	10

Sample No. B-11-A

U(A)	U(B)	U(C)
6.4	6.4	10
6.1	6.1	10
5.7	5.7	2
5.6	5.6	10
5.0	5.0	10
4.75	4.75	10
4.10	4.10	2
3.71	3.71	10
3.70	3.70	20
3.65	3.65	20
3.25	3.25	20
3.41	3.41	100
3.31	3.31	20
3.19	3.19	20
3.04	3.04	10
2.99	2.99	10
2.92	2.92	2
2.84	2.84	20
2.82	2.82	10
2.76	2.76	20
2.67	2.67	20
2.52	2.52	10
2.45	2.45	10
2.37	2.37	2
2.29	2.29	20
2.24	2.24	2
2.16	2.16	2
2.07	2.07	10
2.05	2.05	20
1.90	1.90	20
1.87	1.87	20
1.74	1.74	20
1.73	1.73	10
1.64	1.64	2
1.675	1.675	2
1.635	1.635	2
1.540	1.540	20
1.535	1.535	2
1.515	1.515	2
1.446	1.446	2
1.425	1.425	20
1.345	1.345	20
1.320	1.320	10
1.275	1.275	10
1.245	1.245	10
1.215	1.215	10
1.145	1.145	2
1.167	1.167	10
1.153	1.153	10
1.135	1.135	10

Sample No. 5714

U(A)	U(B)	U(C)
2.1	2.1	2.1
3.04	3.04	3.04
3.40	3.40	3.40
3.23	3.23	3.23
2.05	2.05	2.05
2.74	2.74	2.74
2.06	2.06	2.06
2.50	2.50	2.50
2.44	2.44	2.44
2.24	2.24	2.24
2.20	2.20	2.20
2.14	2.14	2.14
2.10	2.10	2.10
2.07	2.07	2.07
2.03	2.03	2.03
1.04	1.04	1.04
1.71	1.71	1.71
1.045	1.045	1.045
1.060	1.060	1.060
1.070	1.070	1.070
1.742	1.742	1.742
1.515	1.515	1.515
1.462	1.462	1.462
1.451	1.451	1.451
1.420	1.420	1.420
1.360	1.360	1.360
1.340	1.340	1.340
1.315	1.315	1.315
1.285	1.285	1.285
1.265	1.265	1.265
1.250	1.250	1.250
1.244	1.244	1.244
1.244	1.244	1.244

Sample No. 5908

U(A)	U(B)	U(C)
4.0	4.0	4.0
7.15	7.15	7.15
7.17	7.17	7.17
4.75	4.75	4.75
4.100	4.100	4.100
3.730	3.730	3.730
3.000	3.000	3.000
3.440	3.440	3.440
3.350	3.350	3.350
2.950	2.950	2.950
2.790	2.790	2.790
2.090	2.090	2.090
2.640	2.640	2.640
2.501	2.501	2.501
2.470	2.470	2.470
2.340	2.340	2.340
2.315	2.315	2.315
2.240	2.240	2.240
2.160	2.160	2.160
2.085	2.085	2.085
2.060	2.060	2.060
2.010	2.010	2.010
1.910	1.910	1.910
1.840	1.840	1.840
1.802	1.802	1.802
1.775	1.775	1.775
1.701	1.701	1.701
1.682	1.682	1.682
1.657	1.657	1.657
1.577	1.577	1.577
1.542	1.542	1.542
1.512	1.512	1.512
1.475	1.475	1.475
1.447	1.447	1.447
1.405	1.405	1.405
1.392	1.392	1.392
1.304	1.304	1.304
1.283	1.283	1.283
1.242	1.242	1.242
1.233	1.233	1.233
1.202	1.202	1.202
1.192	1.192	1.192
1.172	1.172	1.172
1.154	1.154	1.154
1.138	1.138	1.138
1.115	1.115	1.115

Sample No. 5703

U(A)	U(B)	U(C)
7.0	7.0	7.0
7.0	7.0	7.0
3.64	3.64	3.64
3.35	3.35	3.35
3.01	3.01	3.01
2.91	2.91	2.91
2.72	2.72	2.72
2.57	2.57	2.57
2.22	2.22	2.22
2.13	2.13	2.13
2.07	2.07	2.07
1.75	1.75	1.75
1.67	1.67	1.67
1.495	1.495	1.495
1.348	1.348	1.348
1.367	1.367	1.367
1.267	1.267	1.267
1.204	1.204	1.204
1.165	1.165	1.165
1.118	1.118	1.118
1.074	1.074	1.074
1.060	1.060	1.060

Sample No. 5919

U(A)	U(B)	U(C)
7.0	7.0	7.0
5.75	5.75	5.75
3.57	3.57	3.57
3.29	3.29	3.29
2.54	2.54	2.54
2.71	2.71	2.71
2.33	2.33	2.33
2.22	2.22	2.22
2.04	2.04	2.04
1.848	1.848	1.848
1.715	1.715	1.715
1.655	1.655	1.655
1.448	1.448	1.448
1.422	1.422	1.422
1.346	1.346	1.346
1.325	1.325	1.325
1.315	1.315	1.315
1.282	1.282	1.282
1.275	1.275	1.275
1.255	1.255	1.255
1.250	1.250	1.250
1.242	1.242	1.242
1.232	1.232	1.232
1.13	1.13	1.13

Sample No. 8-24

U(A)	U(B)	U(C)
5.1	5.1	5.1
4.75	4.75	4.75
3.81	3.81	3.81
3.70	3.70	3.70
3.62	3.62	3.62
3.53	3.53	3.53
3.40	3.40	3.40
3.30	3.30	3.30
3.13	3.13	3.13
3.07	3.07	3.07
2.94	2.94	2.94
2.82	2.82	2.82
2.84	2.84	2.84
2.87	2.87	2.87
2.72	2.72	2.72
2.67	2.67	2.67
2.51	2.51	2.51
2.42	2.42	2.42
2.24	2.24	2.24
2.21	2.21	2.21
2.13	2.13	2.13
2.07	2.07	2.07
2.04	2.04	2.04
2.01	2.01	2.01
1.95	1.95	1.95
1.89	1.89	1.89
1.85	1.85	1.85
1.81	1.81	1.81
1.77	1.77	1.77
1.70	1.70	1.70
1.67	1.67	1.67
1.60	1.60	1.60
1.57	1.57	1.57
1.542	1.542	1.542
1.520	1.520	1.520
1.485	1.485	1.485
1.445	1.445	1.445
1.415	1.415	1.415
1.345	1.345	1.345
1.340	1.340	1.340
1.305	1.305	1.305
1.295	1.295	1.295
1.275	1.275	1.275
1.265	1.265	1.265
1.255	1.255	1.255
1.250	1.250	1.250
1.203	1.203	1.203
1.180	1.180	1.180
1.165	1.165	1.165
1.142	1.142	1.142
1.120	1.120	1.120

Sample No. 8-22

U(A)	U(B)	U(C)
5.1	5.1	5.1
4.75	4.75	4.75
3.81	3.81	3.81
3.70	3.70	3.70
3.62	3.62	3.62
3.53	3.53	3.53
3.40	3.40	3.40
3.30	3.30	3.30
3.13	3.13	3.13
3.07	3.07	3.07
2.94	2.94	2.94
2.82	2.82	2.82
2.84	2.84	2.84
2.87	2.87	2.87
2.72	2.72	2.72
2.67	2.67	2.67
2.51	2.51	2.51
2.42	2.42	2.42
2.24	2.24	2.24
2.21	2.21	2.21
2.13	2.13	2.13
2.07	2.07	2.07
2.04	2.04	2.04
2.01	2.01	2.01
1.95	1.95	1.95
1.89	1.89	1.89
1.85	1.85	1.85
1.81	1.81	1.81
1.77	1.77	1.77
1.70	1.70	1.70
1.67	1.67	1.67
1.60	1.60	1.60
1.57	1.57	1.57
1.542	1.542	1.542
1.520	1.520	1.520
1.485	1.485	1.485
1.445	1.445	1.445
1.415	1.415	1.415
1.345	1.345	1.345
1.340	1.340	1.340
1.305	1.305	1.305
1.295	1.295	1.295
1.275	1.275	1.275
1.265	1.265	1.265
1.255	1.255	1.255
1.250	1.250	1.250
1.203	1.203	1.203
1.180	1.180	1.180
1.165	1.165	1.165
1.142	1.142	1.142
1.120	1.120	1.120

Sample No. B-16

U (A)	U (B)	U (C)
7.10	1.0	1.0
6.1	2.0	1.0
5.7	1.0	2.0
5.05	2.0	2.0
4.75	1.0	2.0
3.70	2.0	2.0
3.60	2.0	2.0
3.55	1.0	2.0
3.40	1.0	2.0
3.35	1.0	2.0
3.18	2.0	2.0
2.84	2.0	2.0
2.84	2.0	2.0
2.77	2.0	2.0
2.70	2.0	2.0
2.67	2.0	2.0
2.54	2.0	2.0
2.49	1.0	2.0
2.45	1.0	2.0
2.37	1.0	2.0
2.37	2.0	2.0
2.30	1.0	2.0
2.20	1.0	2.0
2.19	2.0	2.0
2.14	1.0	2.0
2.14	2.0	2.0
2.07	1.0	2.0
2.04	2.0	2.0
1.94	1.0	2.0
1.90	1.0	2.0
1.87	2.0	2.0
1.85	1.0	2.0
1.74	1.0	2.0
1.73	2.0	2.0
1.69	1.0	2.0
1.64	2.0	2.0
1.61	1.0	2.0
1.582	2.0	2.0
1.507	1.0	2.0
1.477	1.0	2.0
1.447	1.0	2.0
1.427	2.0	2.0
1.395	1.0	2.0
1.385	1.0	2.0
1.375	1.0	2.0
1.350	1.0	2.0
1.337	2.0	2.0
1.325	1.0	2.0
1.218	1.0	2.0
1.215	1.0	2.0
1.188	1.0	2.0
1.180	1.0	2.0
1.180	1.0	2.0
1.175	2.0	2.0
1.155	1.0	2.0
1.150	1.0	2.0
1.147	1.0	2.0
1.145	2.0	2.0

Sample No. B-16-C

U (A)	U (B)	U (C)
7.1	2.0	2.0
6.1	1.0	2.0
5.7	2.0	2.0
5.05	2.0	2.0
4.75	1.0	2.0
3.70	2.0	2.0
3.60	2.0	2.0
3.55	1.0	2.0
3.40	1.0	2.0
3.35	1.0	2.0
3.18	2.0	2.0
2.84	2.0	2.0
2.84	2.0	2.0
2.77	1.0	2.0
2.70	2.0	2.0
2.67	2.0	2.0
2.54	2.0	2.0
2.49	1.0	2.0
2.45	2.0	2.0
2.37	2.0	2.0
2.37	2.0	2.0
2.30	2.0	2.0
2.20	2.0	2.0
2.19	1.0	2.0
2.14	1.0	2.0
2.14	1.0	2.0
2.07	1.0	2.0
2.04	2.0	2.0
1.94	1.0	2.0
1.90	1.0	2.0
1.87	2.0	2.0
1.85	2.0	2.0
1.74	1.0	2.0
1.73	2.0	2.0
1.69	2.0	2.0
1.64	2.0	2.0
1.61	2.0	2.0
1.582	2.0	2.0
1.507	1.0	2.0
1.477	1.0	2.0
1.447	1.0	2.0
1.427	2.0	2.0
1.395	1.0	2.0
1.385	2.0	2.0
1.375	2.0	2.0
1.350	2.0	2.0
1.337	2.0	2.0
1.325	2.0	2.0
1.218	1.0	2.0
1.215	1.0	2.0
1.188	1.0	2.0
1.180	1.0	2.0
1.180	1.0	2.0
1.175	2.0	2.0
1.155	2.0	2.0
1.150	2.0	2.0
1.147	2.0	2.0
1.145	2.0	2.0

Sample No. 5718

U (A)	U (B)	U (C)
7.1	1.0	2.0
6.1	1.0	2.0
5.7	2.0	2.0
5.05	1.0	2.0
4.75	1.0	2.0
3.70	2.0	2.0
3.60	2.0	2.0
3.55	1.0	2.0
3.40	2.0	2.0
3.35	2.0	2.0
3.18	1.0	2.0
2.84	2.0	2.0
2.84	2.0	2.0
2.77	1.0	2.0
2.70	2.0	2.0
2.67	2.0	2.0
2.54	2.0	2.0
2.49	2.0	2.0
2.45	2.0	2.0
2.37	2.0	2.0
2.37	2.0	2.0
2.30	2.0	2.0
2.20	2.0	2.0
2.19	1.0	2.0
2.14	1.0	2.0
2.14	1.0	2.0
2.07	1.0	2.0
2.04	2.0	2.0
1.94	1.0	2.0
1.90	1.0	2.0
1.87	2.0	2.0
1.85	2.0	2.0
1.74	1.0	2.0
1.73	2.0	2.0
1.69	2.0	2.0
1.64	2.0	2.0
1.61	2.0	2.0
1.582	2.0	2.0
1.507	1.0	2.0
1.477	1.0	2.0
1.447	1.0	2.0
1.427	2.0	2.0
1.395	1.0	2.0
1.385	2.0	2.0
1.375	2.0	2.0
1.350	2.0	2.0
1.337	2.0	2.0
1.325	2.0	2.0
1.218	1.0	2.0
1.215	1.0	2.0
1.188	1.0	2.0
1.180	1.0	2.0
1.180	1.0	2.0
1.175	2.0	2.0
1.155	2.0	2.0
1.150	2.0	2.0
1.147	2.0	2.0
1.145	2.0	2.0

Sample No. B-17-C

U (A)	U (B)	U (C)
2.1	2.0	2.0
4.75	2.0	2.0
3.70	2.0	2.0
3.60	1.0	2.0
3.55	2.0	2.0
3.40	2.0	2.0
3.35	2.0	2.0
3.18	2.0	2.0
2.84	2.0	2.0
2.84	2.0	2.0
2.77	2.0	2.0
2.70	2.0	2.0
2.67	2.0	2.0
2.54	2.0	2.0
2.49	2.0	2.0
2.45	2.0	2.0
2.37	2.0	2.0
2.37	2.0	2.0
2.30	2.0	2.0
2.20	2.0	2.0
2.19	2.0	2.0
2.14	2.0	2.0
2.14	2.0	2.0
2.07	2.0	2.0
2.04	2.0	2.0
1.94	2.0	2.0
1.90	2.0	2.0
1.87	2.0	2.0
1.85	2.0	2.0
1.74	2.0	2.0
1.73	2.0	2.0
1.69	2.0	2.0
1.64	2.0	2.0
1.61	2.0	2.0
1.582	2.0	2.0
1.507	1.0	2.0
1.477	1.0	2.0
1.447	1.0	2.0
1.427	2.0	2.0
1.395	1.0	2.0
1.385	2.0	2.0
1.375	2.0	2.0
1.350	2.0	2.0
1.337	2.0	2.0
1.325	2.0	2.0
1.218	1.0	2.0
1.215	1.0	2.0
1.188	1.0	2.0
1.180	1.0	2.0
1.180	1.0	2.0
1.175	2.0	2.0
1.155	2.0	2.0
1.150	2.0	2.0
1.147	2.0	2.0
1.145	2.0	2.0

Sample No. B-9

U (A)	U (B)	U (C)
4.5	2.0	2.0
3.67	2.0	2.0
3.57	2.0	2.0
3.54	1.0	2.0
2.97	2.0	2.0
2.93	1.0	2.0
2.84	2.0	2.0
2.75	2.0	2.0
2.56	1.0	2.0
2.51	1.0	2.0
2.47	2.0	2.0
2.35	1.0	2.0
2.25	1.0	2.0
2.15	1.0	2.0
2.07	1.0	2.0
1.87	2.0	2.0
1.81	1.0	2.0
1.76	1.0	2.0
1.74	1.0	2.0
1.72	2.0	2.0
1.70	2.0	2.0
1.67	2.0	2.0
1.572	2.0	2.0
1.495	2.0	2.0
1.470	2.0	2.0
1.447	2.0	2.0
1.427	1.0	2.0
1.390	1.0	2.0
1.370	1.0	2.0
1.345	2.0	2.0
1.290	2.0	2.0
1.285	2.0	2.0
1.280	2.0	2.0
1.250	2.0	2.0
1.210	2.0	2.0
1.185	2.0	2.0
1.140	2.0	2.0
1.130	2.0	2.0
1.115	2.0	2.0
1.105	2.0	2.0

Sample No. 5530

Sample No. 5524

Sample No. B-13-A

Sample No. B-25-A

Sample No. B-27-A

U(A)	U(A)	U(A)	U(A)	U(A)	U(A)	U(A)	U(A)	U(A)
2.2	10.0	6.5	7.1	7.1	7.1	7.1	7.1	7.1
2.0	7.80	6.1	6.7	6.7	6.7	6.7	6.7	6.7
4.7	7.20	7.2	7.2	7.2	7.2	7.2	7.2	7.2
4.6	2.0	2.0	4.7	4.7	4.7	4.7	4.7	4.7
3.7	4.7	4.7	3.7	3.7	3.7	3.7	3.7	3.7
3.7	4.04	4.2	4.2	4.2	4.2	4.2	4.2	4.2
3.7	3.7	3.7	3.7	3.7	3.7	3.7	3.7	3.7
3.5	3.54	3.6	3.6	3.6	3.6	3.6	3.6	3.6
3.5	3.54	3.5	3.5	3.5	3.5	3.5	3.5	3.5
3.5	3.50	3.40	3.40	3.40	3.40	3.40	3.40	3.40
2.8	3.25	3.30	3.30	3.30	3.30	3.30	3.30	3.30
2.7	2.87	3.11	3.11	3.11	3.11	3.11	3.11	3.11
2.7	2.7	3.04	3.04	3.04	3.04	3.04	3.04	3.04
2.7	2.67	2.96	2.96	2.96	2.96	2.96	2.96	2.96
2.7	2.44	2.92	2.92	2.92	2.92	2.92	2.92	2.92
2.5	2.50	2.84	2.84	2.84	2.84	2.84	2.84	2.84
2.5	2.50	2.62	2.62	2.62	2.62	2.62	2.62	2.62
2.5	2.14	2.74	2.74	2.74	2.74	2.74	2.74	2.74
2.5	2.05	2.64	2.64	2.64	2.64	2.64	2.64	2.64
2.5	2.04	2.66	2.66	2.66	2.66	2.66	2.66	2.66
2.5	1.84	2.55	2.55	2.55	2.55	2.55	2.55	2.55
2.5	1.77	2.51	2.51	2.51	2.51	2.51	2.51	2.51
2.5	1.72	2.47	2.47	2.47	2.47	2.47	2.47	2.47
2.5	1.64	2.33	2.33	2.33	2.33	2.33	2.33	2.33
2.5	1.60	2.28	2.28	2.28	2.28	2.28	2.28	2.28
2.5	1.52	2.25	2.25	2.25	2.25	2.25	2.25	2.25
2.5	1.50	2.19	2.19	2.19	2.19	2.19	2.19	2.19
2.5	1.47	2.05	2.05	2.05	2.05	2.05	2.05	2.05
2.5	1.43	1.97	1.97	1.97	1.97	1.97	1.97	1.97
2.5	1.39	1.90	1.90	1.90	1.90	1.90	1.90	1.90
2.5	1.35	1.85	1.85	1.85	1.85	1.85	1.85	1.85
2.5	1.29	1.74	1.74	1.74	1.74	1.74	1.74	1.74
2.5	1.21	1.70	1.70	1.70	1.70	1.70	1.70	1.70
2.5	1.17	1.60	1.60	1.60	1.60	1.60	1.60	1.60
2.5	1.10	1.50	1.50	1.50	1.50	1.50	1.50	1.50
2.5	1.04	1.43	1.43	1.43	1.43	1.43	1.43	1.43
2.5	1.00	1.39	1.39	1.39	1.39	1.39	1.39	1.39
2.5	0.97	1.35	1.35	1.35	1.35	1.35	1.35	1.35
2.5	0.93	1.30	1.30	1.30	1.30	1.30	1.30	1.30
2.5	0.89	1.26	1.26	1.26	1.26	1.26	1.26	1.26
2.5	0.85	1.21	1.21	1.21	1.21	1.21	1.21	1.21
2.5	0.81	1.17	1.17	1.17	1.17	1.17	1.17	1.17
2.5	0.77	1.13	1.13	1.13	1.13	1.13	1.13	1.13
2.5	0.73	1.09	1.09	1.09	1.09	1.09	1.09	1.09
2.5	0.69	1.05	1.05	1.05	1.05	1.05	1.05	1.05
2.5	0.65	1.01	1.01	1.01	1.01	1.01	1.01	1.01
2.5	0.61	0.97	0.97	0.97	0.97	0.97	0.97	0.97
2.5	0.57	0.93	0.93	0.93	0.93	0.93	0.93	0.93
2.5	0.53	0.89	0.89	0.89	0.89	0.89	0.89	0.89
2.5	0.49	0.85	0.85	0.85	0.85	0.85	0.85	0.85
2.5	0.45	0.81	0.81	0.81	0.81	0.81	0.81	0.81
2.5	0.41	0.77	0.77	0.77	0.77	0.77	0.77	0.77
2.5	0.37	0.73	0.73	0.73	0.73	0.73	0.73	0.73
2.5	0.33	0.69	0.69	0.69	0.69	0.69	0.69	0.69
2.5	0.29	0.65	0.65	0.65	0.65	0.65	0.65	0.65
2.5	0.25	0.61	0.61	0.61	0.61	0.61	0.61	0.61
2.5	0.21	0.57	0.57	0.57	0.57	0.57	0.57	0.57
2.5	0.17	0.53	0.53	0.53	0.53	0.53	0.53	0.53
2.5	0.13	0.49	0.49	0.49	0.49	0.49	0.49	0.49
2.5	0.09	0.45	0.45	0.45	0.45	0.45	0.45	0.45
2.5	0.05	0.41	0.41	0.41	0.41	0.41	0.41	0.41
2.5	0.01	0.37	0.37	0.37	0.37	0.37	0.37	0.37
2.5	0.00	0.33	0.33	0.33	0.33	0.33	0.33	0.33
2.5	0.00	0.29	0.29	0.29	0.29	0.29	0.29	0.29
2.5	0.00	0.25	0.25	0.25	0.25	0.25	0.25	0.25
2.5	0.00	0.21	0.21	0.21	0.21	0.21	0.21	0.21
2.5	0.00	0.17	0.17	0.17	0.17	0.17	0.17	0.17
2.5	0.00	0.13	0.13	0.13	0.13	0.13	0.13	0.13
2.5	0.00	0.09	0.09	0.09	0.09	0.09	0.09	0.09
2.5	0.00	0.05	0.05	0.05	0.05	0.05	0.05	0.05
2.5	0.00	0.01	0.01	0.01	0.01	0.01	0.01	0.01
2.5	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00

Sample No. B-26-A

U(A)	U(B)	U(C)
7.15	7.15	7
5.26	5.26	10
2.50	2.50	75
2.45	2.45	5
3.05	2.54	2
2.91	2.52	10
2.74	2.26	75
2.66	2.20	70
2.52	2.12	30
2.44	2.11	2
2.30	1.70	20
2.25	1.64	5
2.20	1.60	10
2.12	1.60	10
2.02	1.495	10
1.94	1.375	2
1.84	1.360	10
1.74	1.312	10
1.64	1.135	2
1.54	1.105	2
1.44	1.058	2
1.34	1.045	2
1.24	1.016	2
1.14		
1.04		
0.94		
0.84		
0.74		
0.64		
0.54		
0.44		
0.34		
0.24		
0.14		
0.04		

Sample No. 5716

U(A)	U(B)	U(C)
7.15	7.15	7
5.26	5.26	100
2.50	2.50	75
2.45	2.45	5
3.05	2.54	2
2.91	2.52	10
2.74	2.26	75
2.66	2.20	70
2.52	2.12	30
2.44	2.11	2
2.30	1.70	20
2.25	1.64	5
2.20	1.60	10
2.12	1.60	10
2.02	1.495	10
1.94	1.375	2
1.84	1.360	10
1.74	1.312	10
1.64	1.135	2
1.54	1.105	2
1.44	1.058	2
1.34	1.045	2
1.24	1.016	2

Sample No. B-5-B

U(A)	U(B)	U(C)
6.15	6.15	7
5.11	5.11	20
4.77	4.77	25
3.35	3.35	5
3.75	3.75	70
3.57	3.57	75
3.45	3.45	70
3.25	3.25	100
3.11	3.11	2
3.01	3.01	5
2.90	2.90	5
2.77	2.77	20
2.69	2.69	25
2.52	2.52	70
2.46	2.46	5
2.37	2.37	10
2.34	2.34	20
2.22	2.22	25
2.085	2.085	70
2.045	2.045	70
1.907	1.907	70
1.780	1.780	25
1.740	1.740	25
1.707	1.707	75
1.677	1.677	70
1.635	1.635	25
1.597	1.597	20
1.572	1.572	20
1.503	1.503	5
1.467	1.467	10
1.450	1.450	5
1.400	1.400	70
1.372	1.372	75
1.335	1.335	5
1.275	1.275	5
1.242	1.242	5
1.233	1.233	5
1.217	1.217	5
1.144	1.144	10
1.139	1.139	5
1.126	1.126	5
1.104	1.104	5
1.075	1.075	10

Sample No. 5713

U(A)	U(B)	U(C)
7.15	7.15	7
7.11	7.11	2
5.77	5.77	5
5.4	5.4	5
5.22	5.22	100
5.15	5.15	5
5.04	5.04	100
4.92	4.92	2
4.85	4.85	100
4.77	4.77	25
4.69	4.69	5
4.64	4.64	5
4.52	4.52	5
4.44	4.44	5
4.37	4.37	2
4.29	4.29	2
4.21	4.21	10
4.15	4.15	5
4.07	4.07	5
4.04	4.04	5
3.90	3.90	5
3.81	3.81	5
3.70	3.70	5
3.69	3.69	5
3.61	3.61	5
3.53	3.53	5
3.42	3.42	5
3.31	3.31	5
3.25	3.25	5
3.12	3.12	5
3.03	3.03	10
2.90	2.90	10
2.81	2.81	10
2.70	2.70	10
2.55	2.55	10
2.44	2.44	11
2.40	2.40	5
2.32	2.32	5
2.25	2.25	5
2.17	2.17	10
2.05	2.05	10
1.94	1.94	5
1.91	1.91	5
1.855	1.855	5
1.790	1.790	10
1.733	1.733	10
1.690	1.690	10
1.640	1.640	10
1.510	1.510	10
1.430	1.430	10
1.395	1.395	10
1.355	1.355	5
1.300	1.300	5
1.275	1.275	5
1.245	1.245	5
1.210	1.210	5
1.192	1.192	5
1.168	1.168	5
1.155	1.155	5

Sample No. B-11

U(A)	U(B)	U(C)
5.1	5.1	5
4.5	4.5	10
3.7	3.7	5
3.74	3.74	5
3.65	3.65	2
3.54	3.54	100
3.51	3.51	2
3.42	3.42	20
3.33	3.33	10
3.12	3.12	5
3.03	3.03	10
2.90	2.90	10
2.81	2.81	10
2.70	2.70	10
2.55	2.55	10
2.44	2.44	11
2.40	2.40	5
2.32	2.32	5
2.25	2.25	5
2.17	2.17	10
2.05	2.05	10
1.94	1.94	5
1.91	1.91	5
1.855	1.855	5
1.790	1.790	10
1.733	1.733	10
1.690	1.690	10
1.640	1.640	10
1.510	1.510	10
1.430	1.430	10
1.395	1.395	10
1.355	1.355	5
1.300	1.300	5
1.275	1.275	5
1.245	1.245	5
1.210	1.210	5
1.192	1.192	5
1.168	1.168	5
1.155	1.155	5

Sample No. 5712

U(A)	V
1.77	5
2.4	5
3.64	5
3.311	5
3.22	5
2.45	5
2.45	5
2.57	5
2.24	5
2.145	5
2.050	5
1.890	5
1.665	5
1.620	5
1.442	5
1.457	5
1.431	5
1.365	5
1.350	5
1.325	5
1.177	5
1.152	5
1.124	5
1.045	5
1.045	5
1.045	5
1.027	5

Sample No. B-15

U(A)	V
7.2	10
6.1	5
5.62	5
5.07	5
4.60	5
3.71	5
3.62	5
3.56	5
3.53	5
3.08	5
2.95	5
2.90	5
2.80	5
2.67	5
2.55	5
2.44	5
2.37	5
2.32	5
2.14	5
2.16	5
2.06	5
2.03	5
1.98	5
1.86	5
1.83	5
1.74	5
1.765	5
1.730	5
1.715	5
1.695	5
1.640	5
1.600	5
1.570	5
1.525	5
1.505	5
1.480	5
1.460	5
1.455	5
1.430	5
1.415	5
1.340	5
1.352	5
1.315	5
1.245	5
1.240	5
1.220	5
1.210	5
1.196	5
1.170	5
1.160	5
1.146	5
1.139	5
1.131	5
1.115	5
1.100	5

Sample No. B-17-A

U(A)	V
7.5	5
6.1	5
7.1	5
6.1	5
5.9	5
5.1	5
4.75	5
5.74	5
5.62	5
5.55	5
5.42	5
5.33	5
5.04	5
4.84	5
4.78	5
4.67	5
4.52	5
4.47	5
4.44	5
4.35	5
4.23	5
4.19	5
4.16	5
4.06	5
4.02	5
3.97	5
3.91	5
3.88	5
3.86	5
3.84	5
3.81	5
3.78	5
3.76	5
3.74	5
3.72	5
3.70	5
3.68	5
3.66	5
3.64	5
3.62	5
3.60	5
3.58	5
3.56	5
3.54	5
3.52	5
3.50	5
3.48	5
3.46	5
3.44	5
3.42	5
3.40	5
3.38	5
3.36	5
3.34	5
3.32	5
3.30	5
3.28	5
3.26	5
3.24	5
3.22	5
3.20	5
3.18	5
3.16	5
3.14	5
3.12	5
3.10	5
3.08	5
3.06	5
3.04	5
3.02	5
3.00	5
2.98	5
2.96	5
2.94	5
2.92	5
2.90	5
2.88	5
2.86	5
2.84	5
2.82	5
2.80	5
2.78	5
2.76	5
2.74	5
2.72	5
2.70	5
2.68	5
2.66	5
2.64	5
2.62	5
2.60	5
2.58	5
2.56	5
2.54	5
2.52	5
2.50	5
2.48	5
2.46	5
2.44	5
2.42	5
2.40	5
2.38	5
2.36	5
2.34	5
2.32	5
2.30	5
2.28	5
2.26	5
2.24	5
2.22	5
2.20	5
2.18	5
2.16	5
2.14	5
2.12	5
2.10	5
2.08	5
2.06	5
2.04	5
2.02	5
2.00	5
1.98	5
1.96	5
1.94	5
1.92	5
1.90	5
1.88	5
1.86	5
1.84	5
1.82	5
1.80	5
1.78	5
1.76	5
1.74	5
1.72	5
1.70	5
1.68	5
1.66	5
1.64	5
1.62	5
1.60	5
1.58	5
1.56	5
1.54	5
1.52	5
1.50	5
1.48	5
1.46	5
1.44	5
1.42	5
1.40	5
1.38	5
1.36	5
1.34	5
1.32	5
1.30	5
1.28	5
1.26	5
1.24	5
1.22	5
1.20	5
1.18	5
1.16	5
1.14	5
1.12	5
1.10	5
1.08	5
1.06	5
1.04	5
1.02	5
1.00	5

Sample No. 5723

U(A)	V
6.1	5
7.1	5
4.7	5
4.10	5
3.70	5
3.54	5
3.54	5
3.57	5
3.54	5
3.50	5
3.40	5
3.30	5
3.12	5
3.07	5
2.95	5
2.92	5
2.85	5
2.76	5
2.67	5
2.54	5
2.46	5
2.34	5
2.30	5
2.21	5
2.16	5
2.04	5
1.95	5
1.93	5
1.89	5
1.85	5
1.85	5
1.81	5
1.76	5
1.76	5
1.71	5
1.68	5
1.66	5
1.615	5
1.570	5
1.540	5
1.520	5
1.495	5
1.470	5
1.445	5
1.395	5
1.370	5
1.300	5
1.275	5
1.244	5
1.232	5
1.213	5
1.145	5
1.144	5
1.136	5
1.122	5
1.110	5

Sample No. B-21-A

U(A)	V
4.0	5
7.0	5
5.1	5
4.7	5
3.9	5
3.7	5
3.6	5
3.54	5
3.40	5
3.30	5
3.12	5
3.07	5
2.95	5
2.92	5
2.85	5
2.76	5
2.67	5
2.54	5
2.46	5
2.34	5
2.30	5
2.21	5
2.16	5
2.04	5
1.95	5
1.93	5
1.89	5
1.85	5
1.85	5
1.81	5
1.76	5
1.76	5
1.71	5
1.68	5
1.66	5
1.615	5
1.570	5
1.540	5
1.520	5
1.495	5
1.470	5
1.445	5
1.395	5
1.370	5
1.300	5
1.275	5
1.244	5
1.232	5
1.213	5
1.145	5
1.144	5
1.136	5
1.122	5
1.110	5

Sample No. 5742

U(A)	(t)
4.1	10
5.57	10
5.24	100
2.09	20
2.51	100
2.47	100
2.51	5
2.22	10
2.05	10
1.70	100
1.68	2
1.65	10
1.582	20
1.500	20
1.455	100
1.370	20
1.260	10
1.160	5
1.108	5
1.071	10
1.070	5
1.030	5

Sample No. 5720

U(A)	(t)
8.2	2
7.1	2
5.2	2
4.7	2
4.15	2
3.75	2
3.01	75
3.48	10
2.92	100
2.81	10
2.50	10
2.46	10
2.40	10
2.32	5
2.20	2
2.17	2
2.07	10
2.04	2
2.02	2
1.91	2
1.87	10
1.805	2
1.750	10
1.705	20
1.690	20
1.650	5
1.510	20
1.500	2
1.472	5
1.460	5
1.435	75
1.380	2
1.285	2
1.270	2
1.255	5
1.225	2
1.202	2
1.177	2
1.167	2
1.145	2
1.115	2
1.105	5

Sample No. 5529

U(A)	(t)
7.1	2
4.75	25
4.10	5
3.75	25
3.69	100
3.57	2
3.53	25
3.40	100
3.26	10
3.22	10
2.85	2
2.76	75
2.65	10
2.48	25
2.36	2
2.29	20
2.18	2
2.04	100
1.89	75
1.85	2
1.77	5
1.72	2
1.68	5
1.66	20
1.62	2
1.56	25
1.52	5
1.48	5
1.455	2
1.437	5
1.389	25
1.360	2
1.349	2
1.295	2
1.269	25
1.210	5
1.170	2
1.159	2
1.149	2
1.130	2
1.095	2
1.080	2
1.060	2
1.045	2
1.020	2