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2nd Quarterly Report: Contract N00019-67-C-0243

June 1967

DEVELOPMENT OF COMPOSITE STRUCTURAL MATERIALS FOR HIGH TEMPERATURE APPLICATIONS

J. Chorné, C. A. Bruch, W. H. Sutton

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February 25 — May 24 1967

DEVELOPMENT OF COMPOSITE STRUCTURAL MATERIALS FOR HIGH TEMPERATURE APPLICATIONS

J. Chorné, C. A. Bruch, W. H. Sutton

NAVAL AIR SYSTEMS COMMAND
DEPARTMENT OF THE NAVY
WASHINGTON, D. C. 20360

SUMMARY

The purpose of this program has been the development of new structural composite materials having high strength-to-weight ratios at elevated temperatures. The current effort is being directed towards the use of heat resistant metals and alloys as the matrix for ultra-high strength Al_2O_3 single crystal whiskers. The major effort during this reporting period (25 February to 25 May 1967) was placed on evaluating factors important to two potential methods for making high strength composites; namely, electroplating and subsequent pressure bonding at high temperatures (EP/PB), and liquid metal infiltration. In support of these studies, some effort was devoted to whisker growth, whisker metallizing, and whisker handling (beneficiation, classification, and orientation) studies. The important results obtained during this reporting period are summarized as follows:

(1) Substantial progress was made in the whisker technology area including: (a) an increase in the whisker coating capability by the completion of an additional cathodic sputtering system, (b) calibration of the sputtering systems, making possible a more accurate estimate of the thickness of the metal coatings on the whiskers, an important consideration in the fabrication of whisker composites, along with a better understanding of the dependence of coating thickness on whisker diameter, and on the number and density of the whiskers in a given run, (c) evaluation of the stability of the whisker coatings at elevated temperatures. Tungsten coatings presently being used for composite fabrication studies were found to be well bonded and structurally stable at temperatures as high as 1500°C, (d) construction of three single stage elutiatiors used extensively in the current composite studies, and (e) modifications in the automatic alignment device for producing semi-oriented whisker tapes on a continuous basis, which resulted in both improved alignment and improved tape strength.

(2) Composites prepared by the EP/PB process using a modified lower temperature, shorter time heat treatment to prevent embrittlement of the electroformed nickel matrix exhibited room temperature tensile strengths similar to those achieved earlier, however, at 1800°F, the composites were weaker than previous ones, with strengths below 4000 psi. Post-test analyses indicated that the most likely cause of low strength at

elevated temperatures was a low whisker/coating/matrix bond. Evidence for this included: (a) failure of the composites at elevated temperature by extensive pull-out of bare whiskers from their matrix, and (b) the observation that considerable diffusion of the W coating into the nickel matrix had occured during fabrication which might be the responsible factor for the degradation of the whisker/coating bond.

(3) Experiments involving the infiltration of molten nichrome into bundles of coated sapphire whiskers resulted in partially penetrated composite specimens. Contamination of the molten nichrome and/or the coated whiskers surfaces prior to infiltration was the probable cause of non-wetting. In related experiments, it was observed that molten nichrome will wet and bond to sapphire whiskers without causing structural degradation of the whiskers.

(4) The feasibility of preparing copper matrix composites by simple capillary action infiltration was demonstrated with a tungsten coating/pure copper matrix system. The results further indicated that this is a stable coating/matrix system and that the whiskers are not deleteriously affected by the infiltration process. Similar experiments with a Cu-Ni matrix clearly indicated that the tungsten coating/ Cu-Ni alloy matrix system is not a stable one due to the high solubility of tungsten in nickel; however, it was possible to achieve some wetting and infiltration and it may be possible to make sound compsites by adjusting parameters to minimize coating dissolution.

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I. INTRODUCTION

The purpose of this program is the development of whisker reinforced composites having high strength-to-weight ratios at elevated temperatures. The program has two major goals. The ultimate goal, as initially established, is the achievement of a specific strength of 600,000* inches at 2000°F in a conventional tensile test. A secondary goal is the developemnt of a technique for preparing whisker reinforced high temperature metals, such as nickel or nickel alloys, which reproducibly exhibit specific strengths greater than 200,000 inches at 1800°F. Composite specimens meeting the second goal will then be used to evaluate a wide variety of properties such as creep, stress rupture, impact, fatique, and long time stability. The feasibility of reinforcing metals with high strength whiskers was demonstrated previously in this program using what may be considered a model system of Al_2O_3 whiskers in a silver matrix[1]. Composites prepared by infiltrating the Al_2O_3 whiskers with molten silver exhibited strength-to-density values as high as 725,000 inches at room temperature with 24 volume percent whiskers, and 320,000 inches at 1600°F with 45 volume percent whiskers.

After this successful demonstration, it was necessary to select a higher temperature matrix metal in order to meet the program's first goal. The matrix selected was nickel, since it is a base for many of the high temperature, oxidation resistant alloys. Many potential ways for fabricating composites have been tried and some which have met with moderate success are being pursued. Presently, two techniques are receiving major attention, a process combining electroplating and subsequent pressure bonding (EP/PB), and liquid metal infiltration.

Prior to the evaluation of the EP/PB process, small composites were prepared by electroforming and exhibited specific strength values as high as 320,000 inches at 1850°F[2]. However, these high strength values were not achieved in larger electroformed specimens due to incomplete penetration of the whisker bundles by the electroplated nickel. Hence, voids

* Specific strengths = strength - to - density ratio

and other matrix irregularities were present which greatly reduced the effective cohesive strength of the matrix and limited the transfer of stresses to the fibers at elevated temperatures. Therefore, an additional step, pressure bonding, was introduced to the process for the purpose of healing the various matrix defects which were incurred during the electroplating.

In the course of a series of EP/PB experiments it was discovered that the electroplated nickel became drastically embrittled during exposures to the high temperatures used in the EP/PB process[3]. The nickel embrittlement was considered to be a major cause of observed low composite tensile strengths, and several studies were undertaken to learn how to solve this problem.

Elimination of matrix embrittlement was finally achieved both by modifying the electroplating conditions and by heat treating the electroformed prepregs in vacuum. Specimens prepared by this modified EP/PB process exhibited room temperature strength-to-density values of 340,000 inches with only 12 volume percent whiskers which was about a five-fold increase over the unreinforced matrix. At elevated temperatures, however, all of the specimens had low strengths. Post tests analyses of the specimens indicated that two factors were the most likely causes of low strength: (a) excessive fiber breakage occuring when the whiskers were not near perfectly aligned resulting in low fiber ℓ / d ratios, and (b) low whisker/coating/matrix bond strength.

This report covers the work performed during 25 February to 25 May 1967 under Contract No. N00019-67-c-0243 sponsored by the Naval Air Systems Command.

Three types of whisker composites were prepared and evaluated during this quarter: (a) Ni-Al_2O_3 prepared by the EP/PB process (b) Nichrome-Al_2O_3 prepared by a pressurized infiltration process and (c) Cu-Ni-Al_2O_3 and Cu-Al_2O_3 prepared by liquid metal infiltration. The results of these studies are presented and discussed.

Another program under Air Force Sponsorship (Contract No. F 33615-67-c-1308 utilizes Al_2O_3 whiskers in aluminum matrix and thus requires a

supply of coated, beneficiated, and oriented α- Al_2O_3 whiskers. Rather than conduct two separate programs on whisker growth, coating, beneficiation and orientation, the efforts of the two contracts were pooled in this area in order to make the most efficient use of the manpower. For completness in reporting the progress, all the results of the joint effort are reported here.

II. WHISKER GROWTH

Alumina 'long wool' whiskers continue to be produced by a batch process previously described[3]. Each of the five furnaces involved has four tubes. These furnaces are usually run on a 24-hour cycle, yielding a total of 100 reaction chamber growth runs per 5-day week. Because of an increasing demand for alumina whiskers due to increasing emphasis on preparing larger-size composite specimens in a normal week will yield 160 reaction chamber growth runs.

A new furnace, purchased on company funds, for continuously producing alumina whiskers is scheduled for delivery in July of this year. The development and fabrication of reaction chambers for testing in the new furnace is underway.

III. WHISKER METALLIZING

Four cathodic sputtering systems have been available for metallizing whiskers. In the past quarter, three of these systems were operational, and modifications were being made to the fourth. These modifications have essentially been completed and after a brief check-out, the fourth system will also be operational.

An important consideration in the fabrication of whisker composites is the coating thicknesses on the whiskers. In the calibration of the sputtering systems described in the previous quarterly report, glass slides were sputtered and coating thicknesses on these were measured using an interferometer. The thickness of the metal coatings on the whiskers has been estimated on the basis of the glass slide calibration data. It is important to know if there is any difference between the coating thickness on a flat plate and that on a whisker and also to know if the coating thickness is related to whisker diameter.

Some simple calculations were made which indicate that the coating thickness is independent of whisker diameter and that the whisker coating thickness may be either equal to that of a flat plate or less than that of a flat plate by a factor of $2/\pi$. These calculations are as follows:

First Plate

The total number of atoms, n, received by a flat plate facing the source of atoms is:

$$n = \varphi t w \ell \qquad (1)$$

where φ = atom flux, atoms/cm^2 sec.

t = exposure time

w = plate width, cm

ℓ = plate length, cm

The thickness of the coating, d, is:

$$d = \frac{\varphi t A}{N \rho} \qquad (2)$$

where A = atomic weight, gram/gm atom

N = Avagadro's number, 6×10^{23} atoms/gm atom

ρ = density/, grams/cc

Rod - Case 1 -

In this case the flux of sputtered atoms is assumed to be anisotropic and therefore the number of atoms received by the rod is dependent on the projected area of the rod. The following equation gives the number of atoms, n, received by the half of a rod (axis normal to the atom flux) facing the sputtered atom source:

$$n = \varphi t D \ell \qquad (3)$$

where D = rod diameter, cm
ℓ = rod length, cm

The thickness of the coating is:

$$d = \frac{2}{\pi} \frac{\varphi t A}{N \rho} \qquad (4)$$

The coating thickness is less than that received by a flat plate, equation (2), by the factor $2/\pi$ and is independent of rod diameter.

Rod Case 2 -

In this case the flux of sputtered atoms is assumed to be isotropic and therefore the number of atoms received by the rod is dependent on the surface area of the rod as follows:

$$n = \varphi t \pi / 2 D \ell \qquad (5)$$

In this case only the half of the rod facing the source of sputtered atoms has been assumed to receive atoms.

The thickness of the coating is:

$$d = \frac{\varphi t A}{N \rho} \qquad (6)$$

This coating thickness equals that of a flat plate, equation (2), and is also independent of rod diameter.

To explore this problem further, an experiment was conducted in which three different diameter tungsten wires (0.5, 1, and 5 mil) and a piece of tungsten sheet were all simultaneously sputtered with tungsten for four (4) hours. Sputtering was done from two cathodes simultaneously, using the two-sided

sputtering system described in the last quarterly report. Long lengths of the two smaller diameter wires were used and these were crumpled to a mat form resembling a 'long wool' alumina growth-mass. All items were weighed before and after coating. Calculation of the coating thicknesses on the wires were done using the following equation:

$$d = \frac{D_o}{2}\left(\sqrt{\frac{W_f}{W_o}} - 1\right) \qquad (7)$$

where D = wire diameter before coating

W_o = wire weight before coating

W_f = wire weight after coating

Equation (7) applies when substrate and coating are of the same material. If the two materials differ, then the following equation applies:

$$d = \frac{D_o}{2}\left(\sqrt{\frac{\rho_1 W_f}{\rho_2 W_o} - \frac{\rho_1}{\rho_2} + 1} - 1\right)$$

where ρ_1 = substrate density

ρ_2 = coating density

The calculation of coating thickness for the plate was done by measuring the total surface area, S, and applying the following equation:

$$d = \frac{W_f - W_o}{S\rho}$$

where ρ = 19.3 g/cc for tungsten (9)

Samples of all types were electroplated with nickel for edge preservation and then metallographically polished. Coating thicknesses were determined by the following methods:

1) Sample of all types were viewed at about 1000X and thicknesses were measured using a calibrated filar eye piece.
2) Photomicrographs were taken of all types of samples at high magnification for measurements and coating thickness determinations.

3) The 5-mil wire sample was viewed under the electron microprobe and measurements were made directly.

A summary of the thickness measurements is given in Table I which also shows the initial and final weights of the samples. It can be seen that the coating thicknesses measured on the metallographically polished samples are greater than those obtained by the weight gain method. However, all methods show that the wires received a thicker coating than the plate. Furthermore, all methods show that the 0.5 and 5 mil wires received coatings of equal thickness, and that the 0.1 mil wire received a slightly thinner coating.

The results based on the weight gain method are considered to be the most reliable for the following reasons:

(1) The results average the coating thickness over each entire sample, whereas in the metallographic samples only one plane of polish was examined.

(2) The boundaries in the polished samples were broad and difficult to locate precisely.

The reason for a thicker coating on wires than on the sheet is not understood. A possible explanation is that sputtered atoms diffusing out from a cathode behave as a Brownian motion gas and deposit on the back of an object as well as on the front; however, in the case of a plate the longer diffusion distances may significantly reduce the number of atoms striking the back surface as compared to a small-diameter wire.

The results obtained in this experiment are compared with glass slide calibration data in Figure 1. In all cases sputtering conditions were essentially constant. The glass slide data was obtained from 45-minute sputtering runs. An extrapolation to 4 hours yields a coating thickness which is in good agreement with that obtained for the plate in the present 4-hour sputtering experiment. As shown in Figure 1, the wires received a coating about 25 percent thicker than the plates. Since the wire data are more representative of whiskers, henceforth, whisker coating thickness will be estimated on the basis of the wire data.

TABLE I

SUMMARY OF COATING THICKNESS DETERMINATIONS

SUBSTRATE			
Type	Dimensions	W_o Grams	W_f Grams
Wire	.00050" D	.0365	.0575
"	.00102" D	.0921	.1114
"	.00510" D	.2397	.2520
Sheet	18.1 cm^2 (surface Area)	2.4035	2.4471

Coating Thickness, microns by various methods

Substrate	Weight Increase	Filar Eyepiece	Photo-Micrographs	Electron Microprobe
.5 mil wire	1.63	2.2	1.9	-
1 mil wire	1.29	2.0	1.7	-
5 mil wire	1.63	2.2	1.9	1.8
Sheet	1.25 to 134*	1.8	1.4	-

* Part of sample was masked sometime during run. An estimation indicates 7 percent of sample surface area was involved. The correction yields the thicker coating.

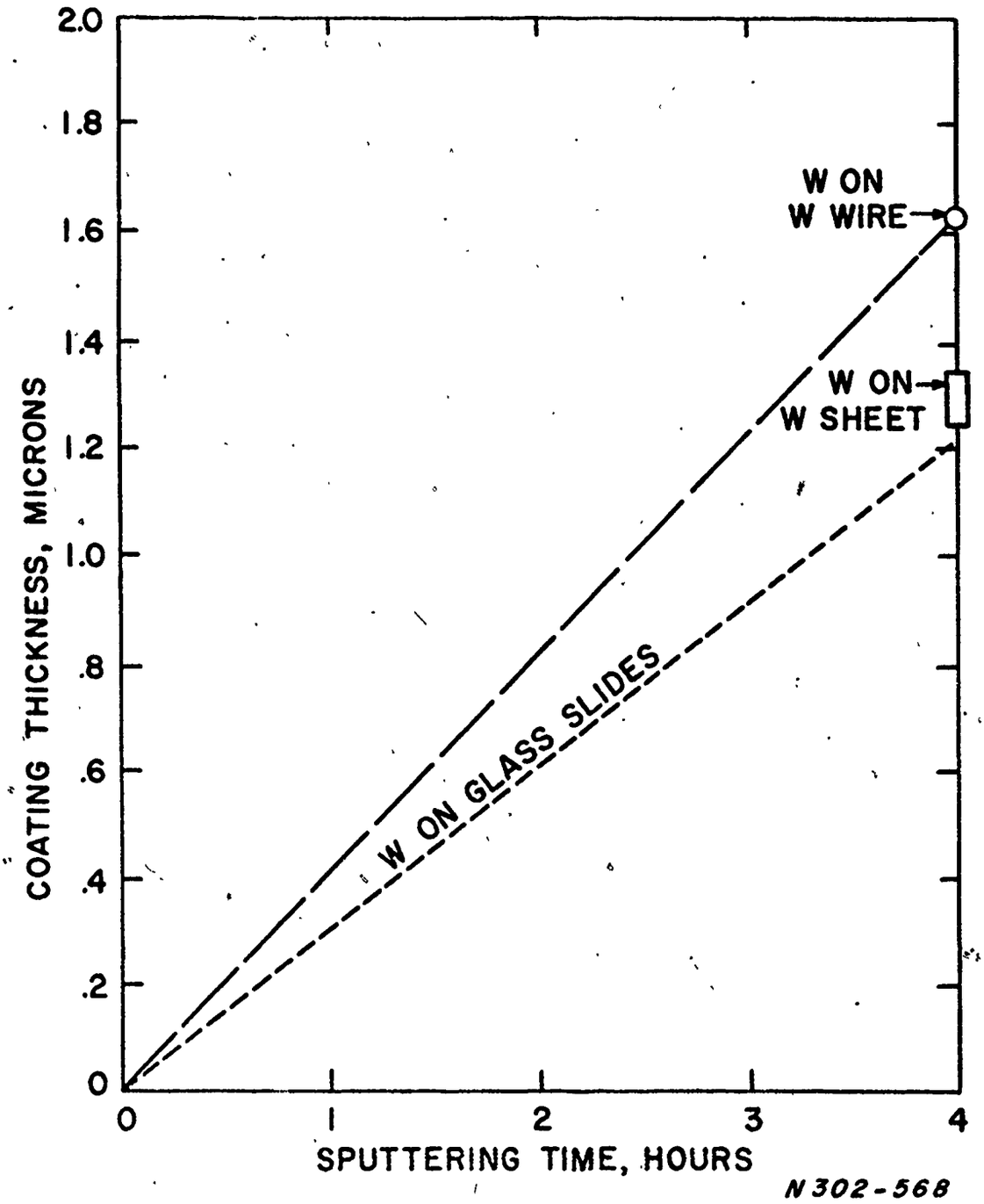


Figure 1. Coating thickness determination as a function of sputtering time.

As a final consideration, the actual coating thickness on whiskers can be expected to be dependent on the number and density of whiskers in a given coating run. Thus the data in Figure 1 represents an upper limit to coating thickness for the same sputtering conditions. This fact is recognized and the geometry and amout of whiskers in each coating run is kept within narrow limits.

IV. BENEFICIATION, CLASSIFICATION AND ORIENTATION OF COATED SAPPHIRE WHISKERS

In the previous quarter, substantial progress was made in the development and improvement of an air elutriation device[4] capable of accomplishing: (1) benefication, by smashing and eliminating weaker whiskers and debris, (2) classification, by eliminating the very fine and the very coarse materials and (3) partial fiber alignment, by collecting the elutriated fibers with special alignment devices.

During this period, the major effort in this area was in the beneficiation and classification of coated sapphire whiskers by elutriation as an essential step of the composite fabrication processes being evaluated.

To facilitate this activity, three new elutriator units were constructed and assembled as shown in Figure 2. These units which are equipped with: (1) a device for automatic removal of separated and classified mats from the collection area, (2) provisions for continuous loading of the separatory chamber, and (3) improved methods for removal of accumulated debris are now capable of processing about 10 grams of coated whiskers per day.

In addition, some effort was devoted to the production of continuous strands of oriented whiskers in the form of tape. The whisker tape-making apparatus (shown in Fig. 2) consists of a rectangular tapered cone with various vents to control the air flow patterns, collection and removal belts, take-up rollers, compaction rollers and a vacuum assisted air intake.

Installation of multiple slots in the tapered cone section and refined adjustments in the clearance of the collection and removal belt resulted in a considerable improvement in the fiber alignment and the strength quality of the tapes. These tapes can now be easily handled and further aligned by hand thus simplifying the manufacture of composite test specimens and saving a considerable amount of time.

Efforts are continuing for better and more effective means for separating, and classifying whiskers using a cascading elutriator shown also in Figure 2. The results of these investigations will be reported at a later date.

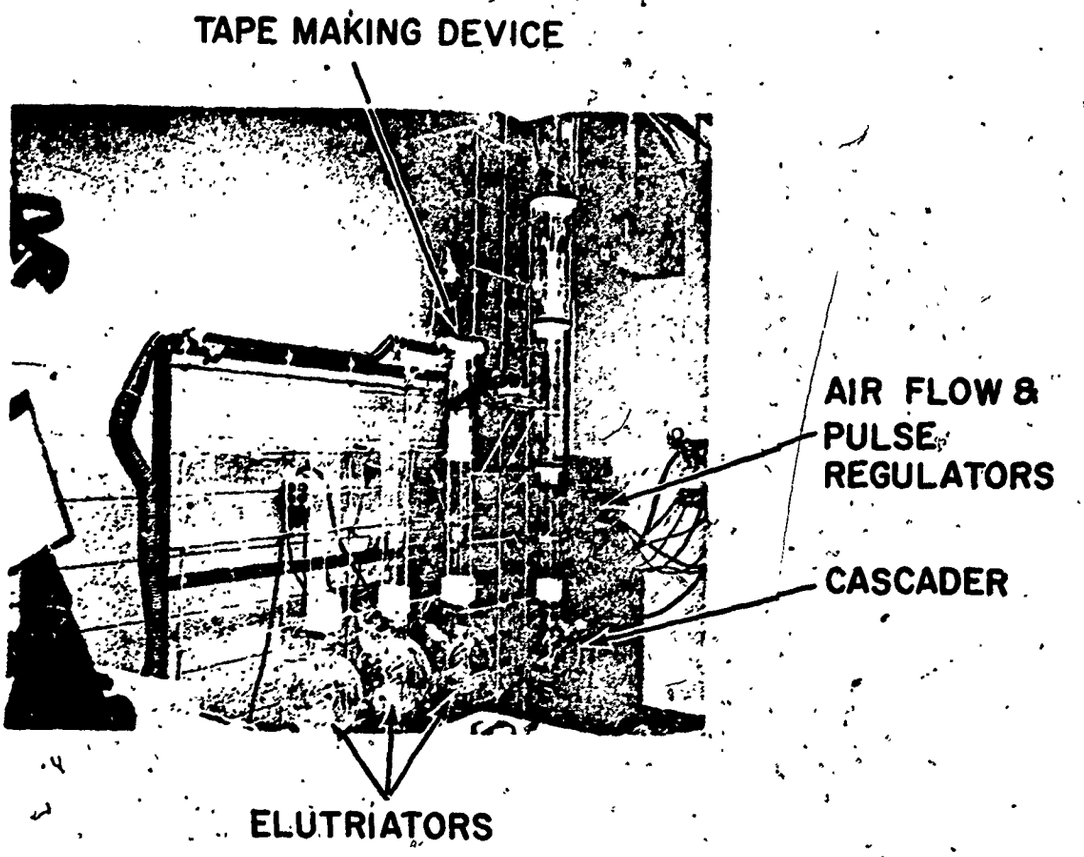


Figure 2. Photograph of whisker beneficiation, classification, and orientation equipment.

V. EVALUATION OF Ni-Al_2O_3 WHISKER COMPOSITES FABRICATED BY ELECTROPLATING/PRESSURE BONDING (EP/PB) TECHNIQUES

During the previous contract period[3] many test specimens were prepared for the purpose of optimizing the EP/PB process and of evaluating the elevated temperature properties of Ni-Al_2O_3 whisker composites fabricated by this technique. Unfortunately, the results of most of these studies were completely masked by the embrittlement of the electroplated nickel matrix during exposures to the high temperatures used in the EP/PB process. A suitable method for eliminating matrix embrittlement, prolonged vacuum heat treatment at 1200°C, was finally uncovered and specimens prepared by this modified process (Set No. 1, Table II) exhibited significant reinforcement at room temperatue.

The work performed to date on the present contract has been primarily directed toward evaluating the elevated temperature strength properties of Ni-Al_2O_3 whisker composites prepared by the modified EP/PB process. During the first quarter of the present contract, two sets (No. 2, 3) of EP/PB experiments were conducted toward this end. During this reporting period the fourth sequential set of experiments was completed. The purpose of each set of EP/PB experiments in the series was to help solve the problems defined in the previous experimental set. However, despite continued improvements in the process and elimination of all the composite weakening factors, the elevated temperature tensile strengths of successive EP/PB composites decreased. Diffusion between the whisker coatings and the nickel matrix during processing is considered to be the most serious problem with this process; it is suspected that this leads to degradation of the whisker/matrix bond, and constitutes the major cause of observed low composite tensile strengths at elevated temperatures.

Other contributing factors are as follows: (a) There is always some degree of fiber breakage associated with this process. Even though this can be minimized by optimizing the pressing temperature and pressure, breakage of whiskers is unavoidable when any of the whiskers are aligned cross-wise

TABLE II. SUMMARY OF PREVIOUS ELECTRO PLATING/PRESSURE BONDING EXPERIMENTS

Set No.	No. of Specimens	Coating	Thickness (Microns)	V_f	Fiber Alignment Techniques	Treatment to Eliminate Matrix Embrittlement	Test	Test Temp.	Highest Strength Values (K_{si})	Reasons for Conducting Next Set of EP/PB Experiments
1	4	W	~0.5 μ	0.1-0.25	Manual	Vac 1175° C. 22 Hrs.	Tensile	R.T.	100	To gain knowledge of elevated temperature composite behavior
2	7	W, Ti/W	~0.6 μ	0.2-0.3	Manual	Vac 1175° C. 22 Hrs.	Tensile	R.T.	66	To isolate the effects of temperature, Testing Technique, Whisker Volume Fraction and Fabrication Variations
								1800° F	14	
3	8	W, Ti/W	~0.6 μ	0.1-0.15	Semi-Automatic	Vac 1175° C 22 Hrs.	Tensile	1800° F	6.4	1. To minimize fiber breadage due to fiber misorientations 2. To improve whisker/coating/matrix bond.
							3-Point Bond	R.T.	44 20*	

* After 1000°C exposure in tensile testing furnace

to one another. The presence of only a few highly misaligned whiskers, especially if they are relatively large in diameter, can lead to built-in weak sections in the composite particularly when the composite cross-sectional areas are small, (b) embrittlement of the electroplated nickel matrix is an additional prossibility which has to be considered although on the basis of previous extensive studies, it is felt that this is not a responsible factor.

An important observation of the EP/PB experimental studies is that the whiskers were not degraded by the entire process. This evidence is indeed encouraging and further attests to the stability of the Al_2O_3 whiskers.

In view of the low elevated temperature tensile strengths of the EP/PB composites, the problems associated with the process, and the excessive amount of time and effort required to prepare composite test specimens by this technique, it was decided to abandon the EP/PB approach at this time in order to concentrate the effort on infiltration schemes for specimen preparation. The details of the EP/PB studies which led to this conclusion will now be summarized.

A. PRIOR EXPERIMENTS AND RESULTS (EP/PB Sets 1-3)

The essential steps of the basic EP/PB process, described in previous reports[3,4], are summarized by the diagram shown in Figure 3. Table II summarizes the pertinent fabrication details of the first three sequential sets of EP/PB experiments conducted prior to this reporting period. The first set of experiments (set No. 1) represents the work conducted during the previous contract period in which significant reinforcement at room temperature was first achieved. This was accomplished with low whisker volume fractions, manual whisker alignment techniques, and a heat treatment to eliminate matrix embrittlement during processing. The second set of EP/PB experiments was intended to evaluate the elevated temperature tensile strengths of the Ni-Al_2O_3 EP/PB composites. The fabrication procedures of the first set were duplicated in set No. 2, with the exception than an additional coating composition was evaluated and the composite whisker volume fractions were about doubled in order to maximize

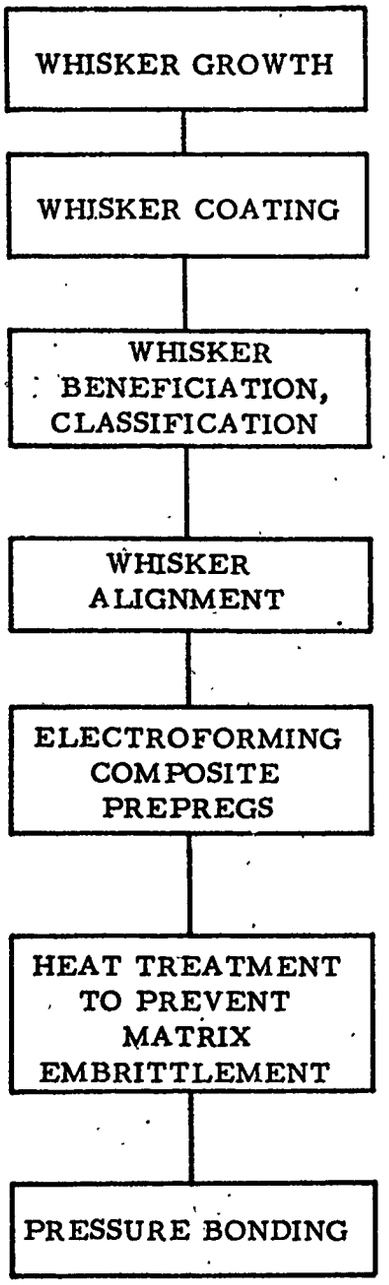


Figure 3. Process steps in the preparation of Ni-Al_2O_3 whisker composites by EP/PB technique

the high temperature strength. The room temperature tensile strengths of set No. 2 composites were not as high as those of the previous set containing much lower whisker volume fraction. No difference in strength properties could be assigned to the two coatings used. A third set of experiments was therefore conducted in order to evaluate some of the factors which could possibly account for the observed low tensile strengths at 1800°F. Specifically, the experiments of set No. 3 were designed to evaluate the following:

(1) Influence of the testing procedure on composite strength such as premature failures due to stress concentrations and bending stresses during tension testing, or to deleterious effects of test temperature and atmosphere, such as grain boundary oxidation.

(2) Influence of whisker volume fraction on composite strength other than the rule of mixtures relationship. For example, the possibility of increased fiber breakage with increased whisker volume fractions or to premature matrix failure with higher volume fraction composites arising from a higher state of stress in the matrix.

(3) Effect of large variations from specimen to specimen leading to erroneous conclusions regarding the elevated temperature properties of the previous specimens.

(4) The independent effect of temperature on the strength of the whiskers and the integrity of the whisker/coating/matrix bond.

Accordingly, the third set of specimens was fabricated with lower whisker volume fractions (similar to set No. 1) and the whisker alignment was accomplished by a semi-automatic technique in order to improve specimen uniformity. In addition to tensile tests at 1800°F, room temperature bend test were conducted on "as fabricated" specimens and specimens exposed in the tensile testing chamber during an actual 1800°F tensile test. Extensive post test specimen analysis involving fractography, and extraction of the whiskers from their matrix for assessment of whisker breakage, whisker strength degradation and coating stability was conducted on specimens from sets 2 and 3. As a result of this study, the factors responsible for low strength at elevated temperatures were reduced to the following:

(1) Whisker breakage in pressure bonding, particularly severe in set no. 3 made from whisker bundles aligned by a semiautomatic method.

(2) Low coating/whisker bond strength as evidenced by a significant number of whiskers protruding from the fracture surfaces which were not coated with metal, and also the unusual dissolution characteristics of finished composite specimens.

A final conclusion of importance was that there was no evidence of whisker strength degradation.

B. CURRENT STUDIES

The indicated weakness of the whisker/coating bond in the previous EP/PB composites was considered to be the most important problem to be solved. Coating stability was also a serious problem in previous infiltration studies. Thus, the development of suitable coatings is considered to be a key problem which must be solved before the present elevated temperature strength barrier can be overcome.

Preliminary experiments of two types were conducted during this reporting period in an effort to determine whether the observed low whisker/coating bond is related to the coating (sputtering) process or to composite fabrication and testing. On the basis of these studies further EP/PB experiments were then conducted.

1. Coating Stability Study

An effective method which has been used in past studies[5] to test the stability of the whisker coatings and the integrity of the whisker/coating bond involves heating the coated whiskers to anticipated composite fabrication or service temperatures in vacuum. Poorly bonded coatings will blister or peel at moderate temperatures. Coatings which are unstable will undergo solid-state or liquid phase agglomeration or balling-up at temperatures which are below the melting temperature of the coating composition.

In previous work,[5] sputtered W-coatings were found to be the most stable sputtered coatings at temperatures of 1500°C. For this reason W-coatings have been used extensively in the fabrication of nickel or nickel alloy matrix composites.

In order to determine whether the present sputtering technique is producing coatings which are as well bonded and as thermally stable as those produced previously,[5] a series of coating stability studies were conducted. Sapphire whiskers sputtered with W, and Ti/W and combinations of Ni over the W and Ti/W were subjected to one hour heat treatments at 1200°, 1500° and 1700°C in vacuum (10^{-4}Torr). Table III summarizes the results of examining the heat-treated coated whisker surfaces at high magnifications. It can be seen that under combined transmitted and reflected light and magnifications of 625X all of the as-coated whisker surfaces appeared opaque and smooth as shown in Figure 4A. After a 1200°C heat treatment, only the W coated whisker surfaces remained opaque and smooth. The Ti/W coated whisker surfaces though still opaque underwent a slight change in the surface texture of the coating as did the W/Ni. The Ti/W/Ni coated whiskers were clearly agglomerated at this temperature as shown in Figure 4B. At 1500°C all of the whisker coatings were affected although in the case of the W coatings only slight changes in the surface texture were observed. At 1700°C none of the whisker coatings survived. Figures 4C and D illustrate the types of ratings assigned to the specimens heat treated at 1500 and 1700°C.

It was concluded from this study that the W sputtered coatings deposited by the current technique are as well bonded and as thermally stable as those produced previously and that they will resist peeling, blistering or agglomeration at temperatures below 1500°C. At the present time there is not interpretation relative to the whisker/coating bond or to coating structural stability, which can be assigned to the slight changes in coating surface textures that occurs in the W coatings heated to 1500°C or which similarly occurs in other coating compositions at lower heat treatment temperatures. However, it is felt that the low, whisker/matrix bonds observed in composites prepared by

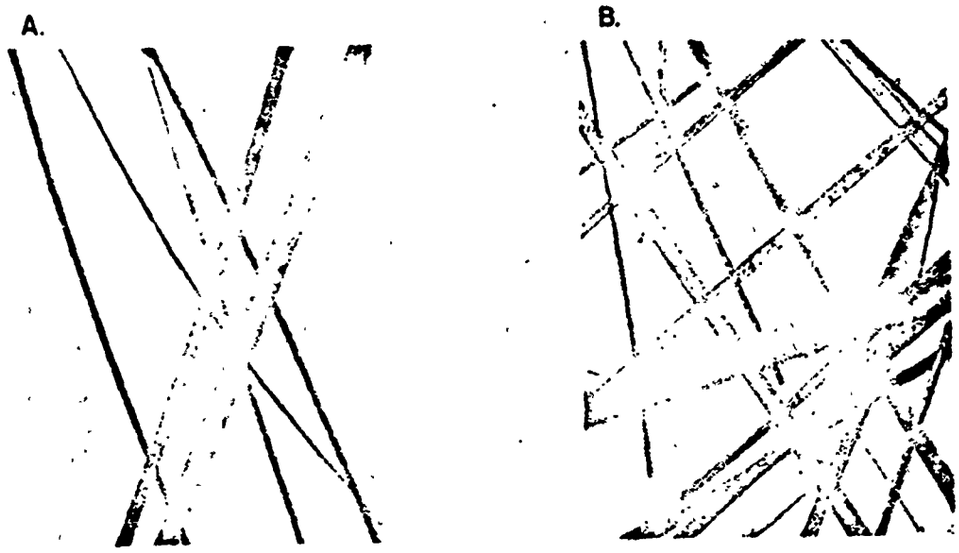
TABLE III. COATING STABILITY STUDIES

Coating	Appearance of Coated Whiskers Under Combined Transmitted and Reflected Light. @ 625x			
		Vacuum Heat Treated - 1 Hr.		
	As Coated	1210°C	1500°C	1700°C
W	A) Opaque B) Smooth	A) Opaque B) Smooth	A) Opaque B) Rough	A) Transparent - Opaqe Patches B) Agglomerated
W/Ni	A) Opaque B) Smooth	A) Opaque B) Rough	A) Opaque-Transparent Patches B) Slightly Agglomerated	A) Transparent-Opaque Patches B) Grossly Agglomerated
Ti/N	A) Opaque B) Smooth	A) Opaque B) Rough	A) Opaque-Transparent Patches B) Slightly Agglomerated	A) Transparent-Opaque Patches B) Grossly Agglomerated
Ti/W/Ni	A) Opaque B) Smooth	A) Opaque Transparent Patches B) Agglomerated	A) Transparent B) Droplets	A) Transparent B) Droplets

Ratings

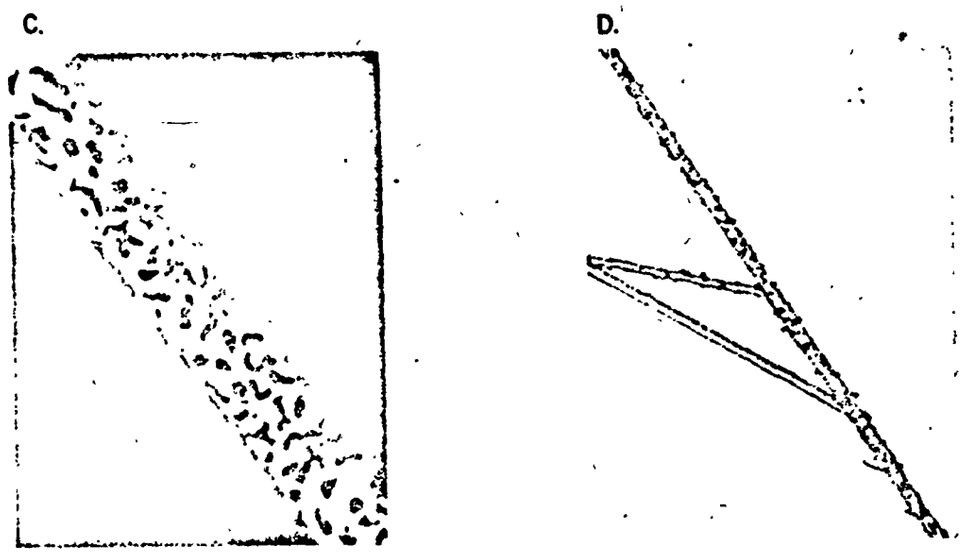
A. Light Transmission - Opaque, Transparent

B. Coating Texture & Topography - Smooth, Rough, Agglomerated, Droplets



COATING: W
TREATMENT: NONE
RATING: OPAQUE, SMOOTH

COATING: Ti/W/Ni
TREATMENT: 1200°C - 1 HR - 10^{-4} TORR.
RATING: OPAQUE - TRANSPARENT PATCHES, AGGLOMERATED



COATING: W/Ni
TREATMENT: 1700°C - 1 HR - 10^{-4} TORR.
RATING: TRANSPARENT - OPAQUE PATCHES, AGGLOMERATED

COATING: Ti/W/Ni
TREATMENT: 1500°C - 1 HR - 10^{-4} TORR
RATING: TRANSPARENT, DROPLETS

Figure 4. Photographs illustrating different types of whisker coating appearances after heat treatment.

EP/PB and liquid infiltration are probably not directly attributable to the whisker coating process.

2. Coating/Matrix Diffusion Study

The purpose of this study was to assess the degree of solid-state diffusion which occurs between the coating and the matrix during the EP/PB process. For use in this study, thin plates of electrodeposited nickel were sputtered with about 0.6μthick coating of W. The resulting W-Ni diffusion couple specimens were then heated to about 1250°C in vacuum ($\sim 10^{-5}$ torr) for 16 hours in order to roughly simulate the most severe thermal treatment of the EP/PB process, i.e. the heat treatment to eliminate matrix embrittlement. After this treatment the specimens were sectioned and examined in the electron probe microscope. The results of this study are summarized in Figures 5 and 6. Figure 5 shows the scanning electron probe photographs of the sectioned W-Ni specimens before and after heat treatments. It can be observed that before heating, tungsten was concentrated only in the coating section.

After heat-treatment, the tungsten from the coating diffused markedly into the nickel section. Figure 6 graphically illustrates the depth to which W diffused into Ni as a result of this treatment. It was concluded from this investigation that the heat treatment being used for the purpose of eliminating embrittlement of the electroplated nickel matrix can cause considerable diffusion between W coatings and the nickel matrix. This might well account for the observed low whisker/coating bonds in previous EP/PB composites.

3. Heat Treatment Studies of Electroformed Nickel

A brief study was made to eliminate embrittlement in the electroplated nickel matrix by using a less severe treatment (i.e. lower temperatures and times) than the prolonged vacuum heat treatment (1200°C, 22 hours) used previously. Unreinforced nickel specimens were heated to lower temperatures and times in a flowing hydrogen atmosphere and subsequently tested in tension at room temperatue in order to evaluate strength and ductility. The results

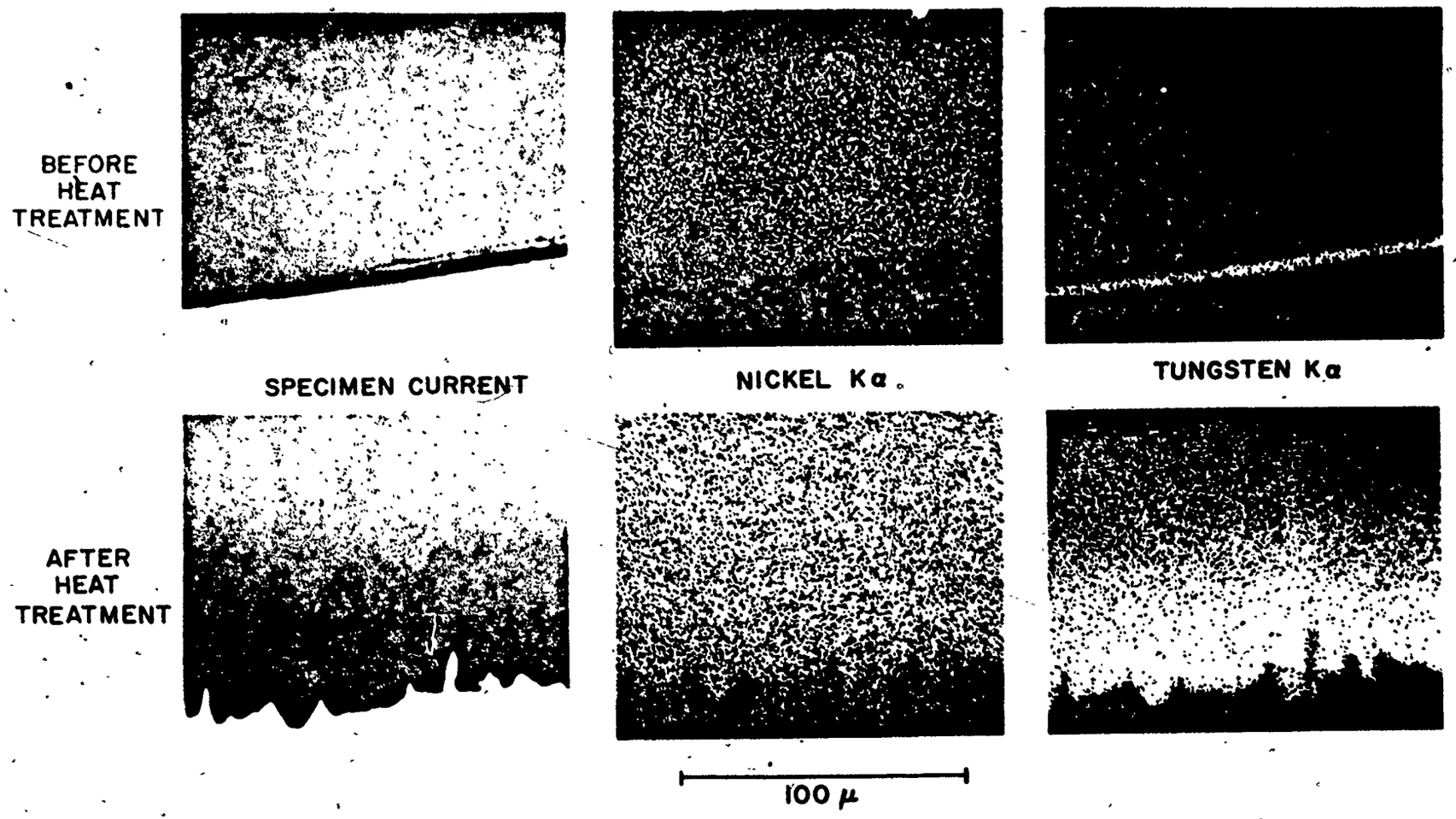


Figure 5. Scanning electron probe photographs of sectioned specimens of electrodeposited nickel sputtered with tungsten. Before and after heat treatment (16 hrs., 1250°C, 10^{-5} Torr). Magnification = 575X

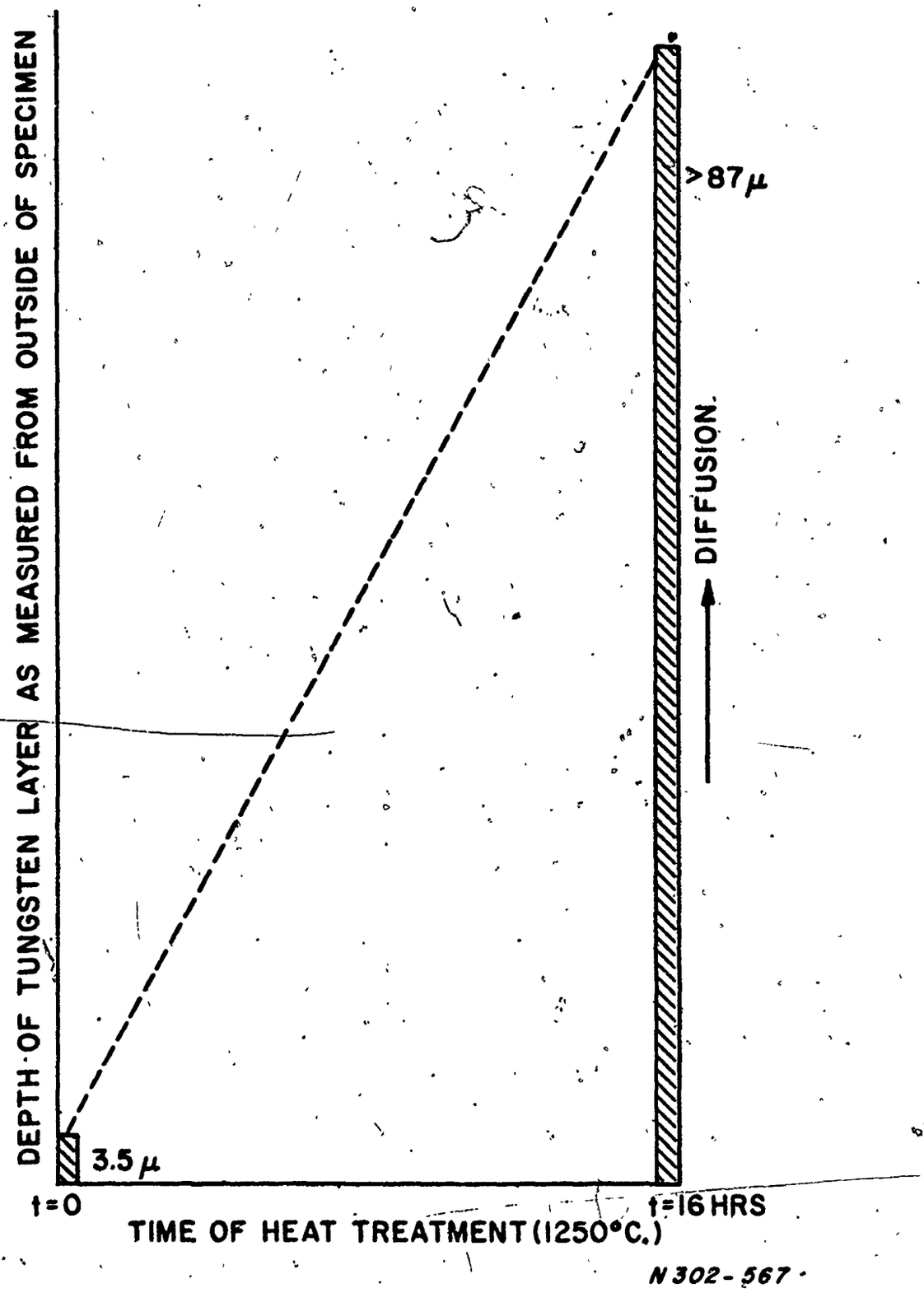


Figure 6. Graphical reprosentation of depth of penetration (by diffusion) of tungsten into nickel resulting from heat treatment at 1250°C.

were very encouraging and are summarized in Table IV. It can be seen that at 940°C, embrittlement is eliminated in periods as short as 1 hour as evidenced by total elongation values as high as 49%. It is interesting to note that this effective heat treatment in hydrogen is in the temperature range which gave maximum embrittlement in vacuum studies conducted previously[3]. At a lower temperature (895°C) the effectiveness of the heat treatment (in completely eliminating embrittlement) is questionable. As a result of this study it was concluded that a shorter time, lower temperature treatment (940°C for at least one hour) in a flowing hydrogen atmosphere can be used in the EP/PB process for the purpose of eliminating grain boundary embrittlement of the electrodeposited nickel matrix. This lower temperature treatment may in turn reduce the diffusion between the coating and the matrix and help to preserve the whisker/coating bond.

4. EP/PB Experiments (Set. No. 4)

In view of the results obtained in the coating stability studies, the coating/matrix diffusion studies, and the electroformed nickel heat treatment studies, a last set of EP/PB composites was prepared by the standard procedure described previously[3,4] with the following refinement:

(1) The sapphire whiskers were sputtered with W-coatings of varying thickness from 0.6 μ to 1.2 μ.

(2) Beneficiation and classification of the coated whiskers was accomplished by repeated elutriation treatments; whisker alignment was accomplished by meticulous manual techniques.

(3) Electroformed composite prepregs were heat treated in a flowing H_2 atmosphere at 935°C for about 2 hours.

The fabrication details and the tensile test results are summarized in Table V. Two specimens were pressed at 940°C in an attempt to minimize coating/matrix solid state interaction. These specimens were poorly bonded, not completely densified and extremely weak. The specimens pressure-bonded at normal temperatures (1175°C) were about as strong at room temperature as those produced in the previous sets, however, at 1800°F they were weaker than those prepared previously.

TABLE IV. HEAT TREATMENT STUDIES OF ELECTROFORMED NICKEL IN A FLOWING HYDROGEN ATMOSPHERE.

Heat Treatment Temperature(°C)	Time (Hrs.)	Maximum UTS (psi)	Maximum % Total Elong.
940	1	45,700	49.1
940	$7\frac{3}{4}$	42,300	34.9
940	24	38,500	42.4
895	1	47,500	718

TABLE V. SUMMARY OF EP/PB EXPERIMENTS (SET #4)

Specimen No.	Coating	Coating Thickness (microns)	Bonding Temperature °C	Bonding Pressure (psi)	Bonding Time (min)	Volume Fraction	Density lb/in^3	Test Temperature °F	UTS (psi)	Fracture Characteristics
28	W	~1.2	940°C Repressed 1120°C	2000 3000	45 30	0.40	n.d.(1)	n.d.	n.d.	Specimen delaminated
24	W	0.9	1175	3000	20	0.23	0.274	1800°F	3000	Gross whisker pull-out
30	W	1.2	1175	3000	40	0.20	0.302	1800°F	2000	Gross whisker pull-out
31	W	0.6	1175	3000	20	0.19	0.284	R.T.(4)	52,000	Brittle type Fracture
32	W	0.6	940	3000	20	0.19	0.274	Broke in Mounting	—	—

(1) n.d. - not determined

(2) R.T. - room temperature

C. POST TEST ANALYSES

After specimens from the last EP/PB series were broken in tension tests, additional studies were conducted to identify, if possible, reasons for the low composite strength values at elevated temperatures.

1. Fractography

The first study involved examination of the fracture surfaces using a stereo microscope at magnifications less than 100X. The findings of this study are summarized in Figure 7. Specimens which were fractured at 1800°F revealed a significant number of whiskers protruding from the fracutre surfaces as shown in the top photograph of Figure 7. The protruding whiskers were not coated with metal, indicating low coating/whisker bond strength. The fracture surfaces of the composite specimens broken at room temperature were quite different as shown in the bottom photograph in Figure 7. Very few whisker "pull-outs" at the fracture surfaces were observed and, furthermore, the protruding lengths of bare whiskers were much shorter than those of the 1800°F fractures. These observations indicated that the whisker/coating bond strengths were probably much stronger at room temperature than at 1800°F, and thus the critical fiber transfer lengths* at room temperature were much shorter, making it possible to utilize a greater degree of the reinforcing potential of the fibers. The composite strength properties at room temperature and at 1800°F corroborate this hypothesis.

2. Microstructural Evaluation

The second type of evaluation involved an examination of the composite microstructures for assessment of fiber concentration and distribution, degree of fiber alignment, matrix irregularities, and integrity of

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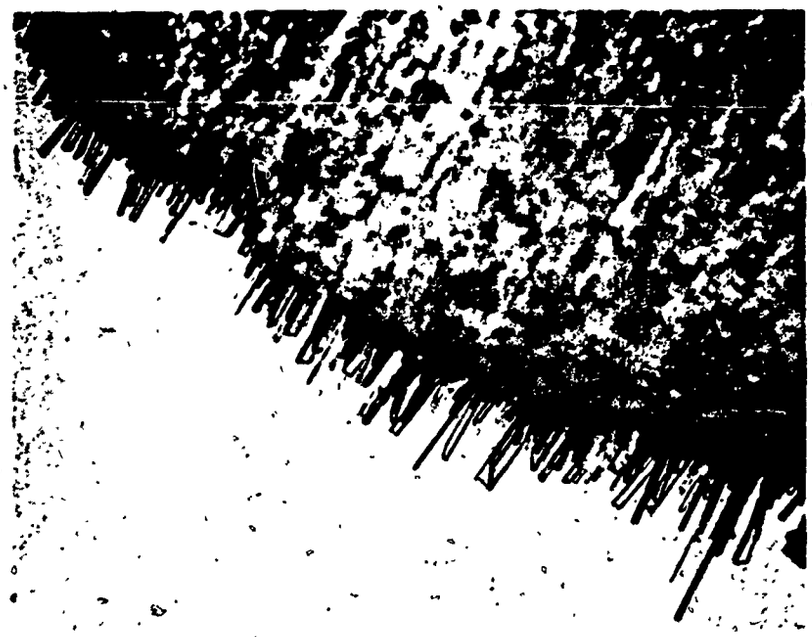
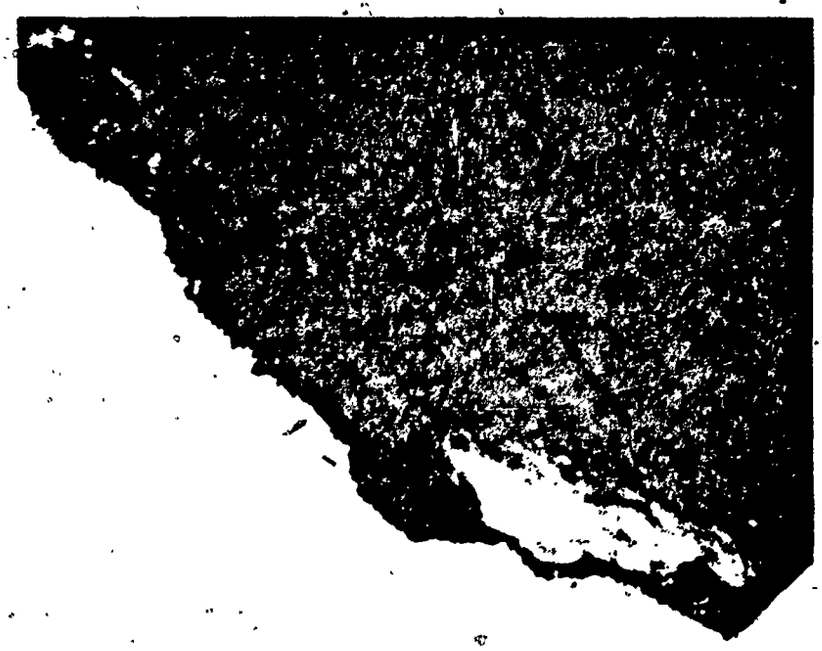
* The critical fiber transfer length is the minimum length of fiber required to allow transfer of stresses from the matrix.



1800° F FRACTURE MAG 76X



ROOM TEMPERATURE FRACTURE MAG 76 X

Figure 7. Fractured details of Ni-Al_2O_3 whisker composites fabricated EP/PB and tested in tension at 1800°F (Spec. #29) and at room temperature (Spec. #31)

whisker/coating/matrix bond. The microstructure of the transverse cross-section of a representative specimen is shown in Figure 8. It can be observed that the composite microstructure is ideal. The uniformity of fiber distribution is perfect, and the degree of fiber alignment appears good. In addition, the matrix is free of microstructural imperfections, such as porosity, and the whisker/coating/matrix bond appears sound from a microstructural point of view.

3. Electron Probe Study

The next type of evaluation involved scanning electron probe analysis of the elevated temperature composite fracture surface for an assessment of coating/matrix diffusion. The results of this examination are summarized in Figure 9, which shows scanning electron probe photographs of the undisturbed fracture cross-section of EP/PB composite specimen #29 which had been tensile tested at 1800°F. Figure 9A shows the specimen current image which reveals rough outlines of the whiskers appearing either as black or white polygonal shapes. Figure 9B shows the Ni K α_1 x-ray image revealing the distribution of nickel (light phase) in the composite fracture cross-section. By referring to the specimen current image photograph (Figure 9A) it can be seen that the areas depleted in nickel are whisker sites. Figure 9C shows the W K α_1 x-ray image which reveals the concentration of tungsten in the composite fracture cross section. It can be seen that the 'W' coatings on the whiskers were diffused throughout the nickel matrix during composite fabrication and elevated temperature tensile testing.

4. Sonic Modulus and Damping

As a final analysis, the sonic modulus and the damping characteristics of the composite specimens were measured. In previous studies[4] the sonic modulus of the EP/PB composites were between 80 to 90% of the rule of mixture values, and some very general correlations of

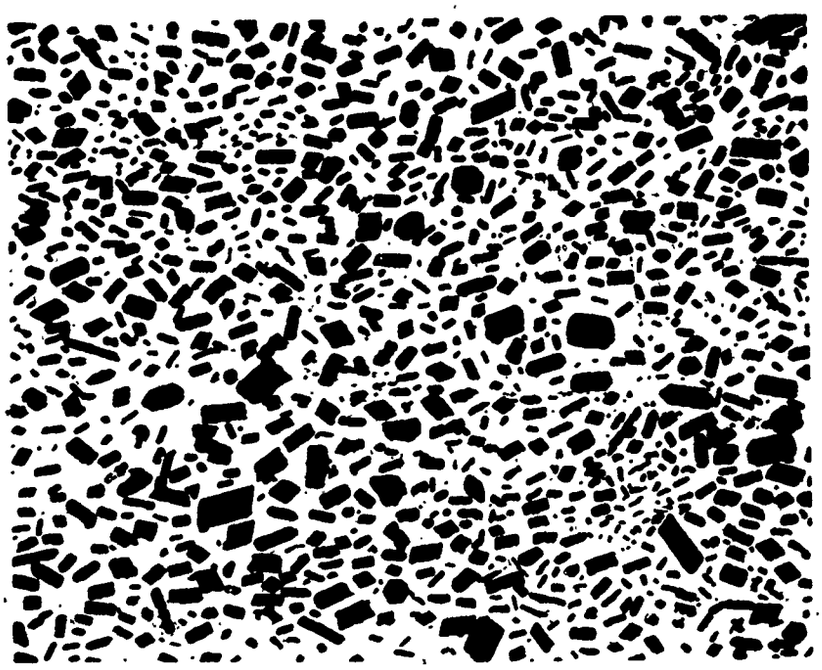
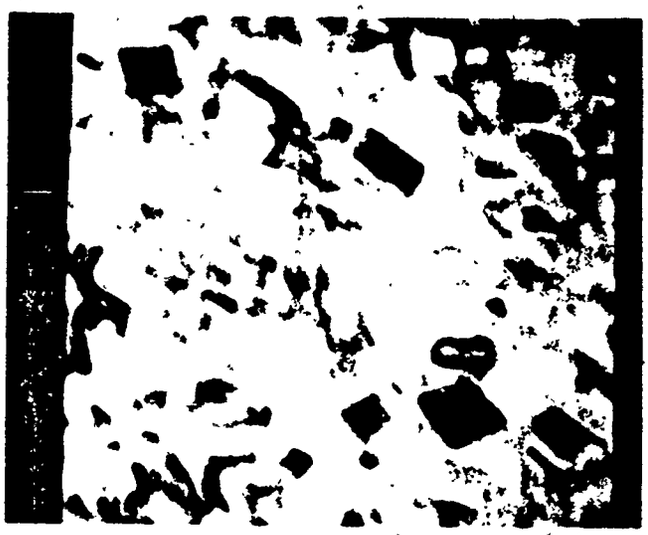
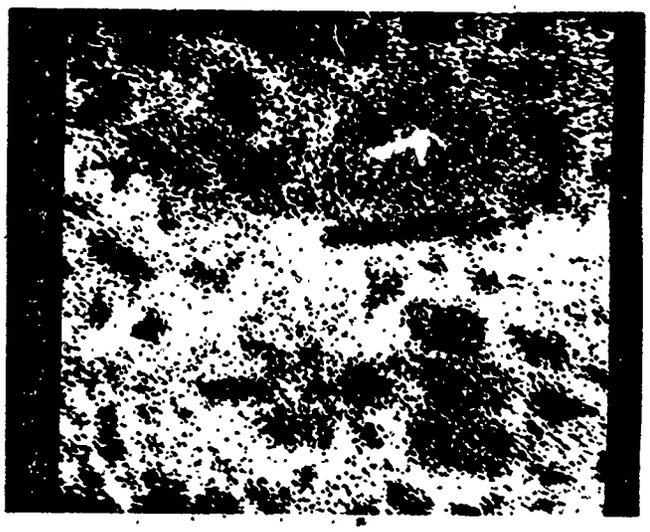


Figure 8. Microstructure of transverse cross-section of Ni - 23 v/o% Al_2O_3 whisker composite (#29) prepared by the EP/PB process.

A. SPECIMEN CURRENT IMAGE
570 X



B. Ni Kα X-RAY IMAGE
570 X



C. W Kα X-RAY IMAGE
570 X

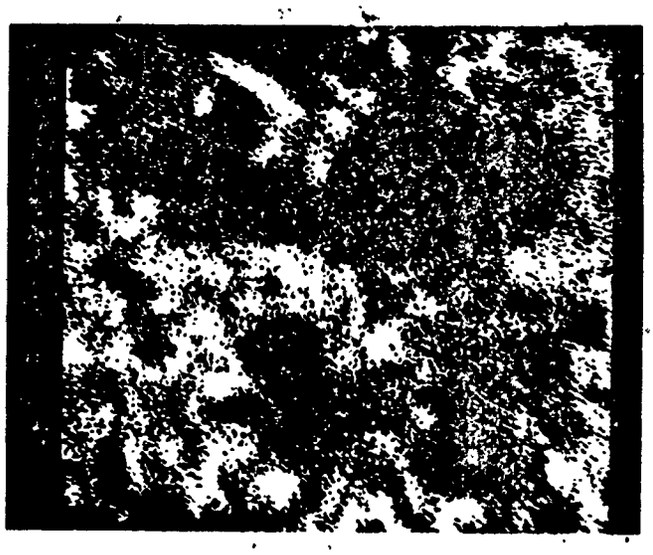


Figure 9. Scanning electron probe photographs of fracture cross-section of Ni-Al_2O_3 whisker composite (#29) fabricated by the EP/PB process.

composite properties with damping characteristics were obtained, namely, that the higher strength composites had the lower damping characteristics.

The values of elastic modulus as a function of whisker volume fraction for the last series of composites are shown in Figure 10 together with the results of previous EP/PB composites reported last period[4]. The small numbers beside the new data points represent the speciemn identification from the last series of composites (Set No. 4). Because the "rule of mixtures" value is a lower bound for composite modulus[6] values lower than this can be due either to misorientation of the fibers with respect to the tensile axis or to structural imperfections in the composite. It is interesting to note, for example, that the lowest modulus value was obtained with Specimen #32 which was a poorly bonded, weak composite.

Figure 11 shows the relative damping values of composties from the different EP/PB Experimental composites as a function of whisker concentration. Recent data points are identified by small numbers adjacent to the data ponts which correspond to the specimen identification. A meaningful damping curve could not be obtained for specimen #32. It is observed that a general trend of incrasing damping values with increasing whisker volume fraction exists, and that composites containing Ti/W coated whiskers exhibited higher damping values than composites of similar volume fractions containing W-coated whiskers. The reasons for this are not understood.

Since the values of sonic modulus and damping for composites of the last series were in general about the same as those of composites prepared previously, no new clues on the reasons for low composite strengths could be derived.

As a result of these post test analyses, it was concluded that the major cause for low EP/PB composite strengths at elevated temperatures is low whisker/coating/matrix bond strenths and that diffusion of

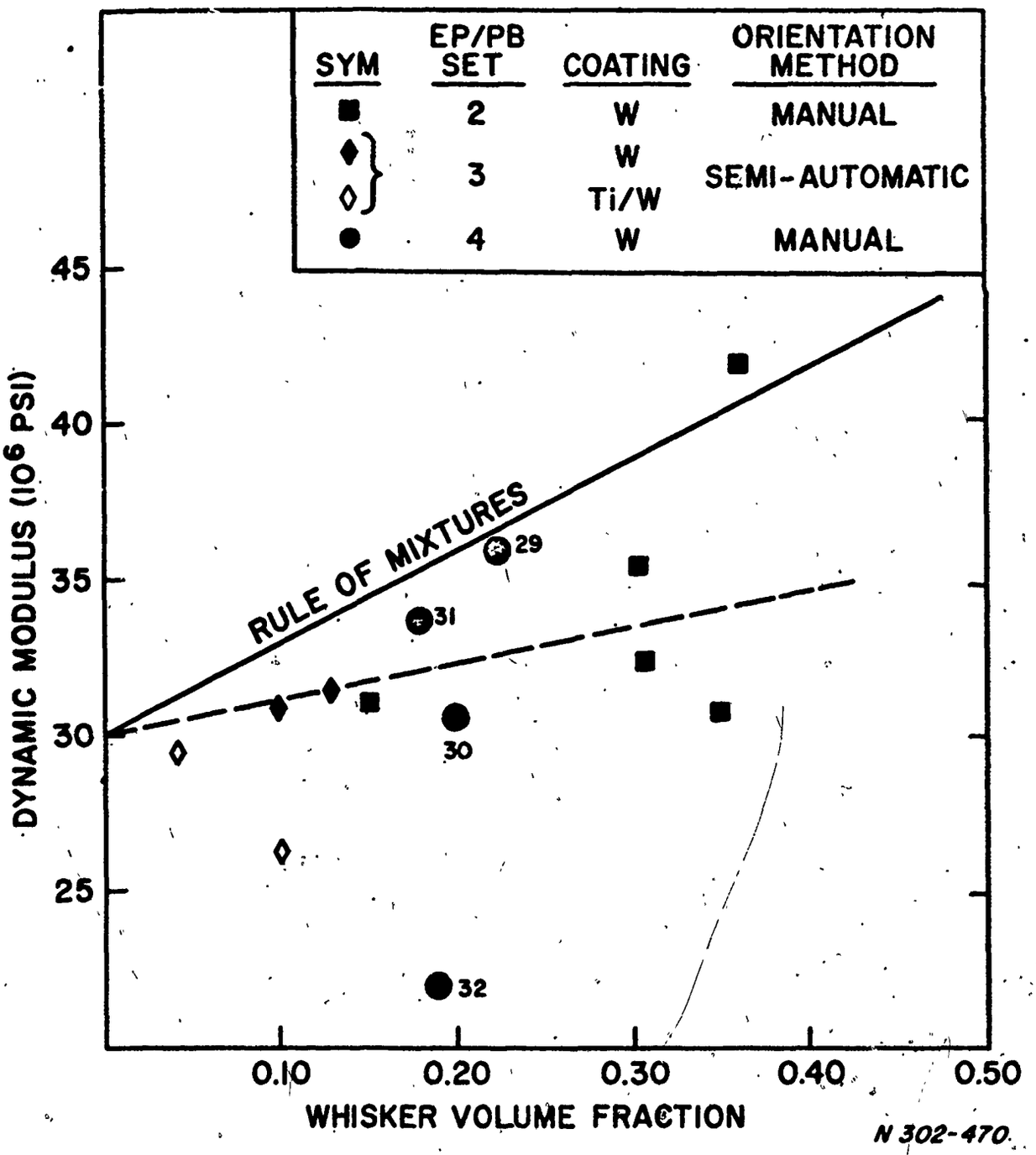


Figure 10. Relation between dynamic modulus and fiber volume fraction

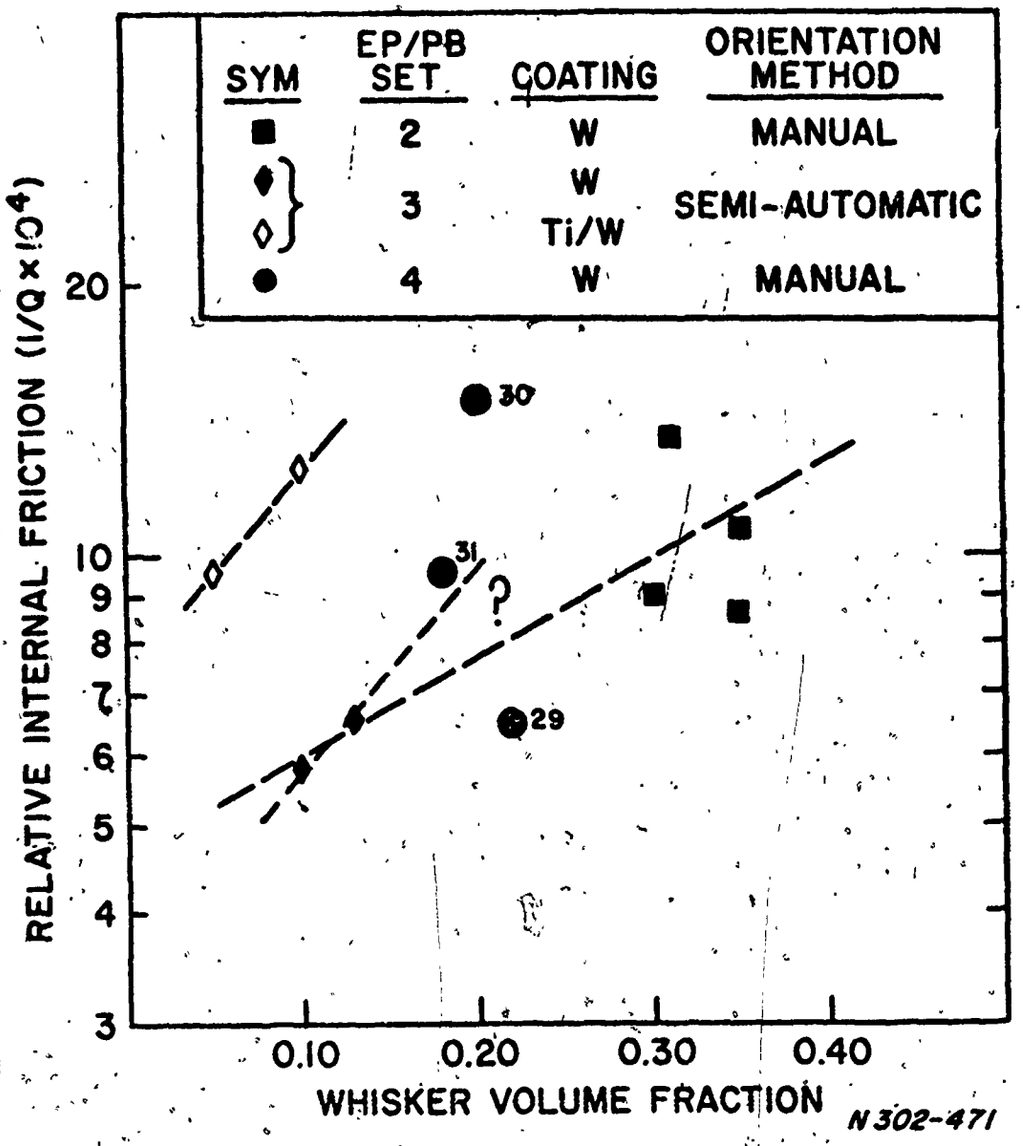


Figure 11. Relation between relative internal friction and whisker volume fraction

the coating and the matrix during processing and elevated temperature testing may be the responsible factor for the degradation of these bonds.

VI. INFILTRATION EXPERIMENTS

A. NICHROME MATRIX

During the previous contact period, studies on the wetting between nichrome and metal coated sapphire plaques were conducted and revealed that liquid nichrome wetted sapphire coated with either tungsten or with a duplex of tungsten over titanium, and formed strong bonds between the sapphire and the solidified nichrome. On the basis of microscopic examinations, it appeared that only the Ti/W coated whiskers were found to survive exposures to molten nichrome without structural degradation[3]. Hence, all of the infiltration experiments conducted in previous studies involved Ti/W coated whiskers. A summary of these experiments is presented in Table VI (Specimens 1 to 6), in which two methods of applying pressure to the liquid matrix for infiltration were tried: (1) dead weight loading of a moveable punch which produced no penetration of the whisker bundle by the molten nichrome and (2) a pneumatically pressurized system which encouragingly, produced partial penetration of the whiskers by the molten nichrome. Failure to achieve complete penetration with the second system was attributed in large to inadequate control over the temperature with the susceptor system used to inductively melt the nichrome.

During this reporting period, additional infiltration experiments were conducted with an improved mold system.

In a preliminary parametric experiment conducted prior to the new infiltration investigations, sapphire whiskers were coated with about a 0.4 μ thick coating of nichrome by sputtering* and heated to 1500°C in vacuum in order to melt the coating and observe its wetting characteristics and its effect on the structural stability of the sapphire whiskers. Subsequent microscopic examination revealed that the whisker surfaces were covered with a number of solidified nichrome droplets, fairly uniform in size and

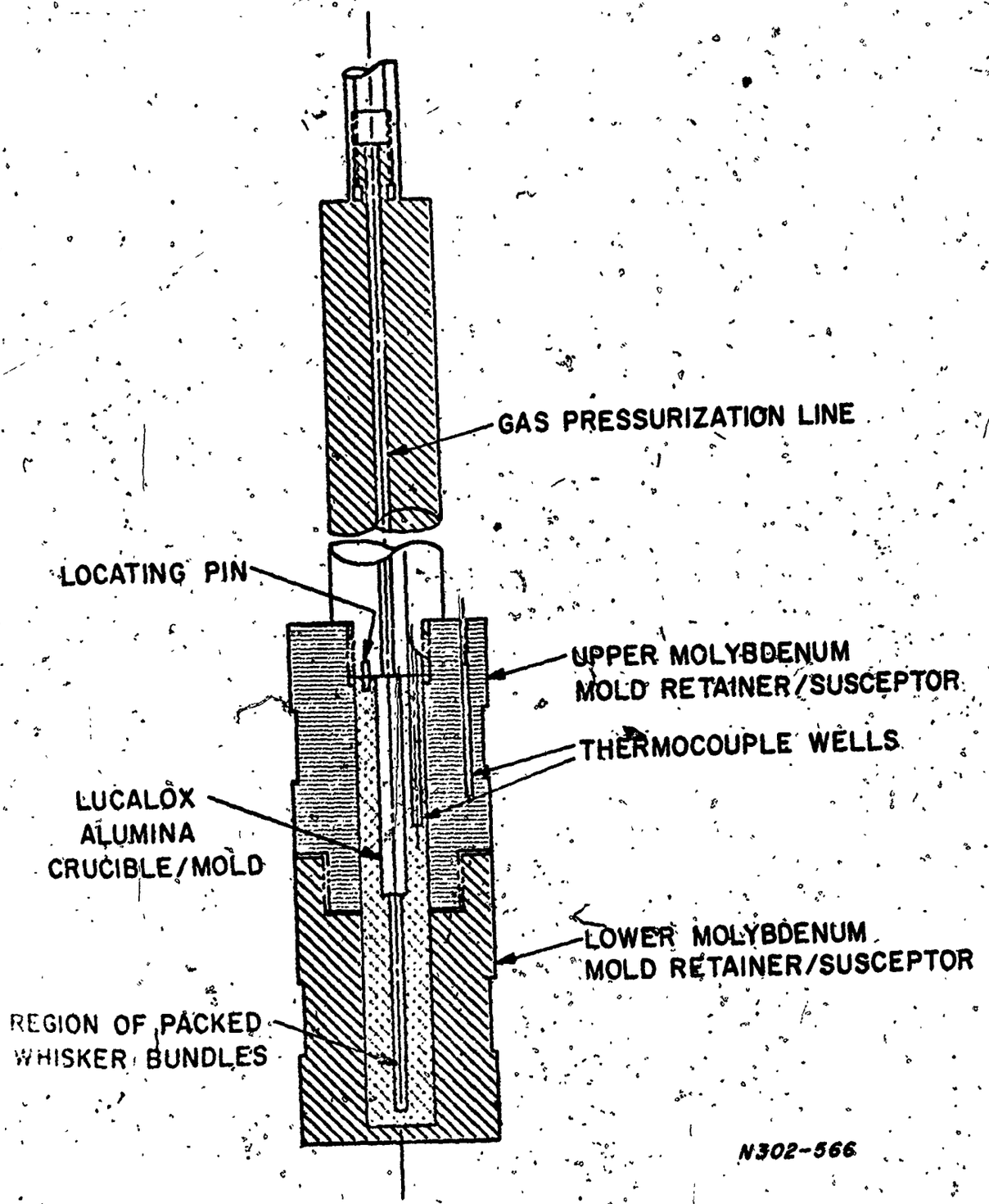
* X-ray analysis indicated that the composition of the sputtered coatings was identical to that of the nichrome cathode material (60 Ni-24 Fe-16 Cr) used for sputtering.

evenly distributed throughout the whisker surfaces. By examining the profile of individual sessile droplets at high magnifications it was learned that a wetting contact angle ($\theta \sim 80^{\circ}$) existed between the solidfied drops and the sapphire whisker surfaces. The solidified droplets could not be separated from the whisker surfaces by prying with needles and tweezers indicating that a strong bond had been formed between the solidified nichrome and the sapphire whiskers. On the basis of the angles of bend attainable in the whiskers with the droplets, it was concluded that the sapphire whiskers remained strong and were therefore not degraded by contact with molten nichrome.

The fact that molten nichrome wets the alumina whiskers and forms a strong bond without structurally degrading the whiskers is a significant finding and certainly adds encouragement to the infiltration approach. The pressurized infiltration experiments were conducted utilizing an improved infiltration mold assembly. The new mold assembly (shown schematically in Figure 12) is basically the same as the one used previously, with added modifications to provide improved control over the infiltration temperatures and the solidification rate of the infiltrating metal. The modifications consist of provisions for thermocouples in the alumina mold proper and in the mold/retainer/susceptor sections as shown in Figure 12, and of enlargement of the mold retainer dimensions to allow direct coupling with the induction generator instead of being heated radiantly via a separate susceptor, as accomplished previously.

Experimental difficulties hampered the progress of nichrome infiltration experiments. At the infiltration temperatures and pressures being used, sufficient vaporization of the nichrome occured to cause appreciable amounts to condense on the molybdenum hardware forming an excellent brazing alloy which wet the molybdenum spontaneously and caused all of the threaded joints in the mold assembly to be sealed together. In order to retrieve the composite specimens after each run, time consuming machining and grinding operations were necessary due to the extreme hardness of the alloy formed.

The results of three infiltration runs which were completed are summarized in Table VI (specimens 7, 8, 9). In all of the attempts, the molten



ure 12. Improved infiltration mold assembly used for infiltration of coated sapphire whisker bundles by liquid nichrome.

TABLE VI. SUMMARY OF LIQUID NICHROME INFILTRATION EXPERIMENTS

	SPECIMEN	MATRIX	WHISKER COATING	WHISKER VOLUME FRACTION	INFILTRATION PARAMETERS				RESULTS
					TEMP. (°C)	TIME (min.)	ATMOS.	PRESSURE APPLIED BY	
PRIOR WORK	1	Nichrome	Ti/W	~0.15	1450	5	Vac 10^{-5} Torr.	Dead Weight	No Penetration
	2	"	"	"	"	"	"	"	"
	3	"	"	"	"	"	"	"	"
	4	"	"	"	1500	"	H_2	H_2	~60% Penetration
	5	"	"	0.30	"	"	"	"	~75% Penetration
	6	"	"	0.30	"	"	"	"	No Penetration of Whisker Bundle. Metal Shell formed by Prefered Channeling
RECENT RESULTS	7	Nichrome V	Ti/W	0.20	1580	~5	H_2	H_2	"
	8	"	Thick W ~1.5 μ	~0.20	1582	60	H_2	H_2	"
	9	Nichrome	Ti/W	0.20	1582	60	H_2	H_2	"

Nichrome-60 Ni - 24 Fe - 16 Cr
Nichrome V-80 Ni - 20 Cr

metal channeled preferentially around the outer surface of the whisker bundle and formed a metal shell around the whisker bundle as shown in Figure 13. The molten nichrome failed to penetrate the whisker bundle even when the infiltration time was increased to periods of one hour. In every case, the metal coating on the whiskers which had been in contact with the molten nichrome was dissolved. By bending the uninfiltrated whiskers with tweezers under the microscope it was learned that even the uncoated whiskers which had been in contact with the molten nichrome had retained their strength. This was also true of the W-coated whiskers which in previous microscopic studies appeared to be structurally degraded by molten nichrome. The fact that both the W and Ti/W coatings on the whiskers were dissolved by the liquid nichrome was not surprising since this had been observed in previous wetting studies[3]. However, it was disappointing that the nichrome did not wet and penetrate the whisker bundle uniformly.

On the basis of the previous wetting studies[3], it was hoped that these coatings would be effective "fugitive types", which would promote spontaneous wetting of the whisker surfaces by the molten nichrome before being completely dissolved and which would in turn cause the nichrome to wet and bond to the alumina whiskers.

It is suspected that contamination of the molten nichrome and/or the coated whisker surfaces led to the non-wetting conditions experienced in the last series of experiments. Different infiltration schemes will be investigated in future studies in order to improve the wetting and bonding between nichrome and alumina whiskers.

B. COPPER MATRIX

Exploratory experiments were conducted to examine the feasibility of preparing composites by simple capillary action infiltration. These experiments involved a type of coating/matrix system not previously explored in this program, namely; an insoluble coating. For this purpose whiskers were coated with tungsten, which is wetted by, but is essentially insoluble in molten copper which was used as the matrix. The results to be described

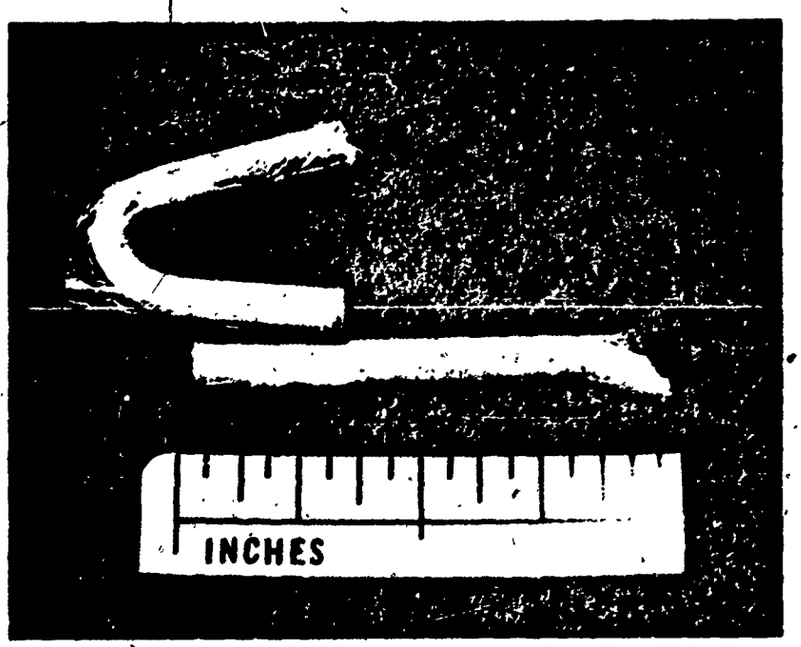


Figure 13. Incompletely penetrated nichrome - Al_2O_3 whisker composite showing the metal shell structure produced by preferred channeling of the molten nichrome.

indicate that it is feasible to prepare composites in the W coated Al_2O_3 whisker/Cu matrix system by simple capillary action.

All of the experiments to be described were done in a Sentry furnace equipped with horizontal 2-1/2 inch I.D. alumina tube, an RTV cap at the rear for introduction of hydrogen, and a refractory plug at the front. For each experiement, metal coated whisker bundles were prepared and loaded into several types of tubes. Fisher Reagent grade copper shot was placed in suitable positions so that on melting, it would contact the whiskers. The assemblies were placed in a suitable molybdenum boat which was slowly withdrawn. The various types of experiments and results obtained will now be discussed by topic.

1. Environment Suitability -

A section of fused silica tubing, about one cm. I.D., was drawn to about one millimeter I.D. Saw cuts were made to yield a container shaped like a golf tee. These were stood on end in the boat and copper was placed in the large section. The molten copper did not flow down into the empty capillary section over the temperature range explored, 1150° to 1270° C for times ranging from 20 to 90 minutes. Subsequently, tungsten wires were cut, bundled and placed in the capillary section of the container. Seven mil wires were completely penetrated by the molten copper after 10 minutes at 1265°C and one mil wires were also completely penetrated after 30 minutes at 1235°C. Since the fused silica is not wetted by the copper, the surface of these wire composites were rough, following the contours of the wires at the periphery of the bundle. These preliminary experiments showed that the environment, hydrogen atmosphere, copper shot, and fused silica containers were suitable for wetting and infiltration of tungsten by copper.

2. Effects of Time and Temperature -

In subsequent experiments involving tungsten coated whiskers, infiltrations were conducted at temperatures ranging from 1150° to 1365°C and times ranging from 5 minutes to 93 minutes. The appearance and degree of penetration

of the composites was better at the higher temperatures, above 1300°C. The shortest time, 5 minutes, was adequate to give good penetration. No de-wetting was observed for long holding periods.

3. Effects of Container Materials -

The initial experiments utilized fused silica containers. The whisker bundles extended from at least one end of the container, for initial contact with the molten copper. In general, the surfaces of the composites were rough, due to the non wetting of the fused silica by the copper. It was also noted that the surfaces extending from the container were much better in appearance than the surfaces within the container.

In an attempt to improve the surface finish, of the composites, fused silica tubes were internally coated with thin layers of tungsten either by cathodic sputtering or by a carbonyl vapor decomposition process. No improvement in surface finish of the composites was noted. The tungsten coating did not adhere well to the fused silica and was generally observed to be bonded to the surface of the composite.

Next, a tungsten tube was used as a container and an infiltration was done at 1225°C for about 35 minutes. The copper did not wet the tungsten tubing well, which is surprising in view of the excellent wetting of tungsten wire by the copper. The tungsten tubing approach is not considered attractive, however, in view of the high cost of $5 to $25 per inch.

Finally, alumina tubes were used as the container in a single experiment in which both plain and tungsten coated fused silica tubes were also used. The composites made in alumina and bare fused silica were about equivalent in appearance, and significantly better than those made in tungsten coated fused silica containers. In all cases, the surface appearance of the composite which protruded from the ends of the container was better than the surface within the container.

4. Coating Thickness -

The thickness of the tungsten coating was varied form about 0.41 to about 1.23 microns. No effect of coating thickness was noted with respect to

infiltration time, de-wetting, and surface appearance.

5. Type of Coating -

Attempts were made to prepare composites using whiskers which had duplex coatings of molybdenum over titanium (Ti/Mo) and tungsten over titanium (Ti/W). The Ti/Mo coated whiskers were not wetted by the copper and therefore the copper did not infiltrate. This was surprising because copper wets bulk molybdenum extremely well. The copper did penetrate bundles of Ti/W coated whiskers, but the composite appearances were poor compared to the tungsten coated whiskers.

6. Infiltration Direction -

Initially the copper was placed above the whisker bundles so that gravity aided the capillary infiltration. It was noted that, when some composites were deliberately broken, there were large porous regions, devoid of whiskers. It was considered a possibility that if the infiltration direction were up, there might be a better filling of all void spaces. Hence many infiltrations were done by placing the whisker loaded container vertically in an alumina crucible containing the copper. Some additional infiltrations were done with the container tilted at about 45° because of furnace size limitations. In these the infiltration direction was upwards at a 45° angle. The composites prepared in both types of upward infiltrations also on occasion contained some large porous regions which were also devoid of whiskers.

These results indicate that the uniformity of whisker packing is the most important parameter which essentially governs the presence or absence of these porous regions. No significant effect of infiltration direction has been noted.

There is, however, one potential major advantage of infiltrating in an upward direction: the top end of the specimen is likely to cool and solidify first whereas the bottom end immersed in the copper is likely to solidify last. This situation may provide molten metal to the solidification front thereby reducing or eliminating shrinkage voids and pipes during solidification.

7. Composite strength -

Six of the composites were tested in 3-point bending at room temperature. The samples were in the as-cast condition, were often irregular in cross-section, and were not machined. The modulus of rupture ranged from 42,600 to 80,200 psi. Furthermore, in most samples the load-elongation curve was linear to fracture which is a desirable characteristic. Since the volume fraction of whikers in these composites were not measured, a comparison between actual strength and rule-of-mixtures predicted strength cannot be made.

8. Post Test Analyses -

The fracture surfaces were examined and very few whisker pull-outs were observed; however, there were some and a few of the whiskers were not coated. After examination the copper was dissolved near the fracture surface, and the exposed whiskers were found to be coated and could be bent. These results further indicate that the tungsten coating/copper matrix is a stable system, and that the whiskers are not deleteriously affected by the infiltration process.

These exploratory experiments into the copper matrix/tungsten coating system demonstrate the feasibility of preparing composites by infiltration. To demonstrate this feasibility, a relatively large, 3/16-inch diameter tungsten coated whisker bundle was infiltrated with copper and is shown in Figure 14. still in contact with the solidified copper reservoir.

The major difficulty uncovered with this system involves the uniformity of whisker packing, or the presence of large void spaces in the whisker bundle prior to infiltration. These void spaces are subsequently not filled by the copper during capillary infiltration and are presummed to be undersirable from a mechanical properties standpoint although they do produce a favorable decrease in density. Several potential methods for eliminating these void spaces include:

1. More uniform whisker packing
2. Higher whisker volume fractions so that the largest void spaces are relatively small

Figure 14. Tungsten-coated sapphire whiskers infiltrated with copper by capillary action. Composite still in contact with solidified copper reservoir.

3. Pressurized infiltration either in closed end or open end containers.

Attempts will be continued to solve the problem by either of the first two methods, since the third method would add substantial complexity to the infiltration apparatus and proces.

C. COPPER-NICKEL ALLOY MATRIX

One experiment was done using the capillary action infiltration technique. Three copper-nickel alloys containing 5, 10 and 20 weight percent nickel were prepared, using the same copper shot used previously and commercially pure-nickel wire. The alloys were pre-melted in small alumina crucibles at 1300°C and held for 20 minutes. Subsequently bundles of W coated/alumina whiskers were packed in straight fused silica tubes, which were then held upright in the alumina crucibles. A coated sample involving pure copper was included.

The boat was then pushed into the furnace and held for 5 minutes at 1355°C. The following observations concerning the four samples are considered important:

(1) Pure copper - the matrix infiltrated and rose to the top of the whisker bundle as in previous experiments discussed in section B.

(2) 95 Cu - 5 Ni - the matrix infiltrated some whiskers and rose to the top; however, many sections of the bundle were not infiltrated.

(3) 90 Cu - 10 Ni - the matrix infiltrated some whiskers and rose three-fourths of the distance to the top. Most whiskers were not infiltrated.

(4) 80 Cu - 20 Ni - The matrix partially infiltrated the whiskers, and a thin column of the alloy rose to the top of the whisker bundle. This column remained during solidification. The whiskers at the base of the container, closest to the molten alloy pool had no coating, were white in appearance, and there were only a few isolated globules of metal entrapped. A microscopic examination of the whiskers in close proximity to the metal column at the top,

revealed that the whiskers were either completely stripped of coating or the remaining coating was melted and broke into globules as described earlier in section V A-1.

This experiment clearly shows that the tungsten coating/Cu-Ni alloy matrix system is not a stable one, due to the high solubility of tungsten in nickel. However, it does show that some wetting and infiltration does occur. This partial infiltration probably occurred because the alloy matrix wets the tungsten coating well, and because the capillary rise preceded dissolution of the coating. Further enhancement of the penetration may have occurred because the matrix, dissolved coating as it advanced, and had reduced tendency to dissolve additional coating. Hence, it may be possible to make a sound composite by adjusting parameters to minimize the amount of dissolution such as: increase coating thickness, apply pressure to the molten matrix for more complete infiltration, and reduce the contact time between the molten matrix and the coated whisker bundle. This general procedure is being used successfully for aluminum matrix composites on another project of this laboratory sponsored by AFML.

D. TUNGSTEN SATURATED COPPER-NICKEL ALLOY MATRIX

A general method which may prevent coating dissolution by the matrix, discussed in previous reports, is that of pre-saturating the matrix with the coating material. To test the possibility of this method, two preliminary experiments were done in which a tungsten saturated, 80 Cu - 20 Ni alloy was pre-melted in an alumina crucible. The weight percent of tungsten required to saturate the 80 Cu-20 Ni is not known; hence, on the basis of Ni-W equilibrium phase diagram, a weight of tungsten slightly greater than the weight of nickel was used. To prepare the alloy, copper shot, nickel wire and both tungsten wire and tungsten sheet were weighed out in the desired proportions. These were heated in an alumina crucible for 3 hours at 1375°C, and then cooled to room temperature. There was evidence of undissolved tungsten wire in the ingot, indicating an excess of tungsten was present. This of course, does not prove that saturation was achieved.

Following this, a tungsten coated whisker bundle was placed in a bare fused silica tube and the container in turn was placed horizontally in a Vee-grooved molybdenum tray, the container being held higher than the alumina crucible. This assembly was pushed into the hot zone and held at 1375°C for one hour. After this holding period, a molybdenum rod was used to push the container down the Vee-groove until it fell end first into the molten alloy puddle, and was inclined at about a 45 degree angle with the horizontal. After a contact time of 10 minutes, the boat was withdrawn from the furnace. There was absolutely no wetting or penetration of the whisker bundle by the molten alloy. Several problems with the experiment were: first, the molten alloy does not wet the alumina crucible and therefore forms a convex surface at the top; second, the whisker bundle protruding from the fused silica tube may not have contacted the melt. The end of the container from which the whiskers protruded and floated on the melt due to the density differences. One edge of the silica tube end was bonded to the melt.

In the second experiment additional alloy was prepared to fill the crucible more completely. A two holed alumina insulator was used as the container. One hole was filled with a bundle of 7-mil diameter tungsten wires and the other was filled with tungsten coated whiskers. In both cases the fibers protruded from the tubing. In this experiment the entire assembly of crucible containing the old melt as well as the new charge, and the Vee-groove with container in place were pushed into the furnace and held for 3 hours at 1450°C. After this the container was tipped into the melt and held there for 11 minutes prior to removal from the furnace. Once again the container was tipped at about a 45-degree angle with the horizontal. In this case, the container fell into the melt in such a way that only the tungsten wires contacted the melt, and these were completely infiltrated throughout the full 2-inch length. At best, only a few whiskers made contact with the melt, and there was no observed melting or infiltration. This experiment however, is considered partially successful in that it demonstrated the fact that the tungsten saturated 80 Cu - 20 Ni alloy wets tungsten well.

VII. DISCUSSION AND FUTURE WORK

Work during this quarter was involved with: (1) whisker technology, (2) electroplating/pressure bonding composite fabrication technology and (3) liquid metal infiltration composite fabrication technology.

Important progress in the whisker technology area includes:

(1) A better understanding of the factors which directly affect the thickness of the sputtered coatings on the whiskers, and a more accurate basis for estimating the coating thickness produced under prescribed sputtering conditions.

(2) An increase in the whisker coating capability.

(3) An increased number of single stage elutriators which achieve beneficiation and classification of the coated whiskers used in the composite fabrication studies.

(4) Improvements in the degree of whisker alignment and in the strength of "as formed" whisker tape produced with an automatic whisker alignment device.

In the future, additional work will be done in the whisker technology area to improve whisker alignment by an automatic process.

Ni - Al_2O_3 whisker composites prepared by the EP/PB process this quarter were manually aligned in order to minimize fiber breakage. In addition, thicker coatings and a lower temperature, shorter time, heat treatment for eliminating embrittlement of the electroformed nickel was utilized in order to eliminate or minimize solid-state diffusion between the whisker coatings and the matrix. Despite these precautions, the composite strengths at 1800°F were dissappointingly low. Post test analyses of the specimens indicated that low whisker/coating/matrix bonds were the major cause of low strength. It was also learned that the W-coating/nickel matrix system is not stable under the EP/PB fabrication conditions. Appreciable solid-state diffusion between the W-coating and the nickel matrix occurs which might in turn destroy the whisker/coating bond.

In view of the associated problems with the EP/PB process no further work will be conducted in this area.

Infiltration experiments involving W and Ti/W coated sapphire whiskers and a molten nichrome matrix met with considerable experimental difficulty. Preliminary experiments resulted in only partially penetrated composite specimens due to non-wetting between the molten nichrome and the coated whisker surfaces. Further optimization of the process is needed before fully dense composite test specimens can be prepared by this technique. An important observation of this study was that nichrome will wet and bond to sapphire whiskers without structurally degrading them. Although nichrome cannot be made to infiltrate uncoated whiskers, this evidence adds encouragement to the approach of using fugitive-type coatings to promote wetting and infiltration of the sapphire whisker bundle before being completely dissolved by the molten nichrome.

Infiltration studies with a nichrome matrix will be continued with the major emphasis on optimizing the infiltration process in order that sound composites with an oxidation resistant matrix can be prepared and evaluated.

The second type of infiltration studies involved pure copper and Cu - Ni alloys as the matrix and a simple capillary action technique for accomplishing infiltration. Sapphire whiskers coated with tungsten were wet and completely infiltrated with molten copper by capillary action. The tungsten coatings remained stable and wettable by liquid copper under the most severe conditions of temperature and time which were investigated, and the whiskers were not structurally degraded by the infiltration process. When Cu - Ni alloys were used as the matrix, the tungsten coating/ Cu - Ni alloy matrix system was found to be unstable due to the high solubility of tungsten in nickel. Nevertheless, some infiltration was achieved with this system.

The infiltration studies with Cu and Cu - Ni matrices will continue. Experiments will be aimed at further optimizing the capillary rise infiltration process in order to improve the surface appearance of the Cu - Al_2O_3 whisker composites. Efforts will also be devoted to developing techniques for achieving

higher whisker volume fractions in these infiltrated composites. Following this, Cu - Al_2O_3 whisker composites will be fabricated and tested in order to evaluate a stable type of whisker coating/matrix system not previously explored.

The infiltration studies with Cu - Ni alloy matrices will be concerned with investigating the feasibility of preparing sound composites with W-coated sapphire whiskers by adjusting the infiltration parameters to minimize coating dissolution. A study of the nickel content limitation of the alloys due to coating instability by dissolution will be conducted as an attempt to achieve successful infiltration with monel, an alloy which has high corrosion resistance. Infiltration techniques involving a presaturated matrix will be further explored in view of encouraging results of the prelimnary experiments. Initially, a W-coating/W-saturated Cu - Ni alloy matrix system will be explored in order to demonstrate the principle. However, a search will also be made for a system involving a less dense coating. It can be expected that once these infiltration processes are optimized, rapid progress can be made in view of the facilities and technology which have been built up.

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