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Battelle
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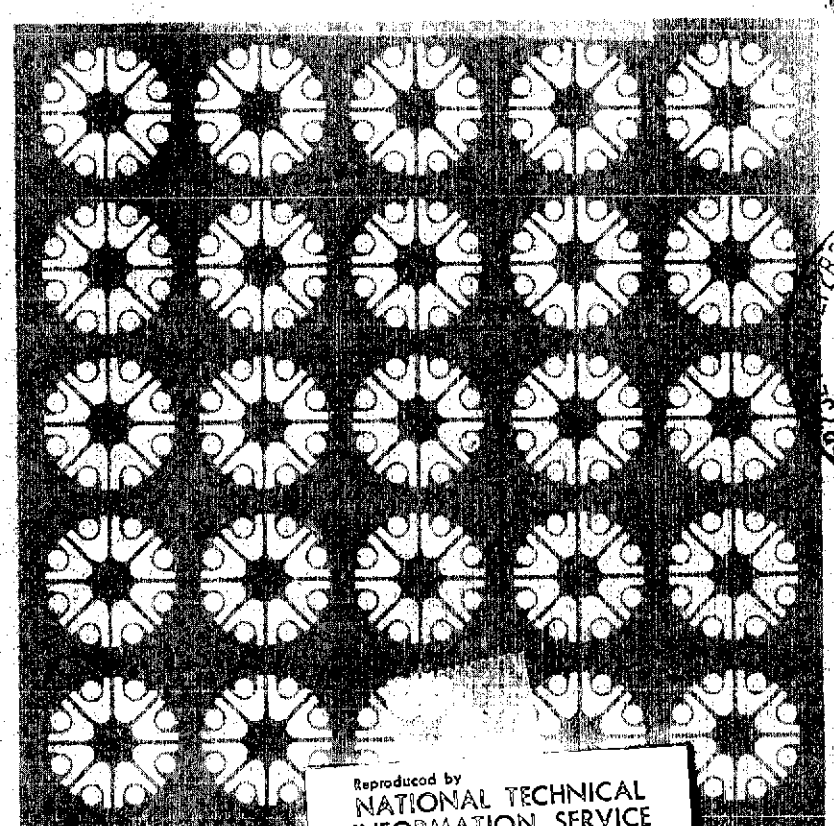
Research Report

PROPERTY INVESTIGATION AND SPUTTER DEPOSITION OF DISPERSION-HARDENED COPPER FOR FATIGUE SPECIMEN FABRICATION

by

ED McClanahan, R Busch, and RW Moss



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NASA CR-134542

FINAL REPORT

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PACIFIC NORTHWEST LABORATORIES
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prepared for

NATIONAL AERONAUTICS AND SPACE ADMINISTRATION

November 12, 1973

CONTRACT NAS3-17491

NASA Lewis Research Center
Cleveland, Ohio
JM Kazaroff, Project Manager

TABLE OF CONTENTS

LIST OF FIGURES

LIST OF FIGURES (continued)

ABSTRACT

Sputter-deposited alloys of dispersion-hardenable Cu-0.25 vol% SiC and Cu-0.50 vol% SiC and precipitation-hardenable Cu-0.15 wt% Zr and Cu-0.05 wt% Mg-0.15 wt% Zr-0.40 wt% Cr were investigated for selection to evaluate fatigue specimen performance with potential application in fabricating regeneratively cooled rocket thrust chambers. Yield strengths in the 700 to 1000-MN/m^2 range were observed with uniform elongation ranging from 0.5 to 1.5% and necking indicative of greater ductility. Electrical conductivity measured as an analog to thermal conductivity gave values > 90% IACS for Cu-0.15 wt% Zr and Cu-0.05 wt% Mg-0.15 wt% Zr-0.40 wt% Cr. A 5500-g sputtered deposit of Cu-0.15 wt% Zr alloy, 12.29 mm (0.484 in.) average thickness in the fatigue specimen gage length, was provided to NASA on one of their substrates.

SUMMARY

The objective of this work was to establish tensile properties in a sputter-deposited dispersion-hardened Cu alloy suitable for a demonstration of acceptable fatigue performance. This was to be accomplished through a program of material development followed by deposition of two selected alloys on four NASA-furnished substrates, i.e. two substrates per alloy.

The tensile properties and microstructure of four copper-based materials produced by sputter deposition were investigated. The experimental variables included composition, substrate temperature, and the temperature of postdeposition heat treatment. Two types of dispersion-hardenable CuSiC (0.25 and 0.50 vol% SiC) and two commercially available precipitation-hardenable copper alloys (0.15 wt% Zr and 0.05 wt% Mg-0.15 wt% Zr-0.40 wt% Cr) were sputter deposited on copper substrates held at ≈ 30°C and 175°C. The thickness deposited was about 0.6 mm and the deposition rate was about 0.1 mm/hour. After separation from their substrates, the sputtered deposits were heat treated at temperatures up to 600°C and tested in tension at room temperature. Yield strengths up to ≈ 1000 MN/m^2 were observed with many combinations of material and conditions exceeding 700 MN/mm^2. Ductility as measured by uniform elongation was in the 0.5-1.5% range but these samples exhibited necking indicative of greater ductility.

The electrical conductivity was measured as an analog to the thermal conductivity, which was not experimentally accessible. Values were commonly as low as 40% IACS in the as-deposited condition increasing to > 90% for the heat-treated precipitation-hardened alloys and to 65% for similarly treated dispersion-hardened materials.

This study resulted in the selection of the Cu-0.15 wt% Zr and the Cu-0.05 wt% Mg-0.15 wt% Zr-0.40 wt% Cr alloys for the preparation of the required fatigue specimens.

Concurrently with the materials development work, sputtering hardware was fabricated and satisfactorily tested for use in the deposition of the alloys on the NASA-furnished substrates. Within the funding available it was possible to provide a thick, 12.29 mm (0.484 in.), sputtered deposit of 5500 g of Cu-0.15 wt% Zr alloy on only one substrate.

INTRODUCTION

The demand for increased performance from rocket engines has required continued improvement in the performance of regeneratively cooled thrust chambers. High-performance thrust chamber operation requires a combination of high thermal conductivity and high strength over the temperature range -200 to 1000°F for the inner liner material plus adequate bonding to the load-carrying outer structure. The latitude available in high-rate triode sputter deposition for producing new materials and also for obtaining a high bond strength between a sputtered layer and its substrate or between sputtered layers indicates that this process has a high potential for providing a technology that permits greater freedom in the design and fabrication of thrust chambers.

The objective of this work was to provide a quantity of sputter-deposited copper alloy for use by NASA-Lewis in evaluation of fatigue performance; pending a successful outcome, this could lead to additional development of sputtered materials for thrust chamber application. There were three phases to the contract effort. In Phase I, selection of the sputter-deposition conditions and heat treatment if required were made based on ≃ 0.6 mm (≃ 25 mil) deposits sputtered in planar hardware. In Phase II, cylindrical sputtering hardware and targets were designed, fabricated and tested. Adjustment of deposition conditions was made to obtain the metallurgical conditions selected in Phase I. In Phase III tubular substrates supplied by NASA-Lewis were to each receive ≃ 10 mm (400 mils) of sputtered copper alloy deposit on their interior contoured surfaces. Two of the substrates were to receive a deposit of one alloy composition, the others were to be deposited with a second alloy composition. All deposited substrates were to be shipped to NASA-Lewis.

PHASE I

Procedure

The objective of Phase I was to determine the tensile properties of several copper-base materials as a function of sputtering parameters and postdeposition heat treatment. This data would then be used to select the material and parameters for the deposition of fatigue specimen material in Phase III.

The materials investigated were of two types -- copper, dispersion-hardened with small amounts of silicon carbide, and precipitation-hardenable copper alloys. The materials are listed below with their sources and nominal compositions. The abbreviated nomenclatures will be used in the rest of this report.

Target Materials	Abbreviation	Source of Supply
Copper-0.25 vol% silicon carbide	0.25 SiC	OFHC copper powder plus silicon carbide powder.
Copper-0.50 vol% silicon carbide	0.5 SiC	
Copper-0.15 wt% zirconium	AMZIRC*	American Metal Climax, Inc.
Copper-0.05 wt% magnesium 0.15 wt% zirconium 0.40 wt% chromium	MZC	" " " "
OFHC copper	OFHC	Alaska Brass & Copper

*Trademark of American Metal Climax, Inc.

For the dispersion-hardened materials, sputtering targets were fabricated at 500°C by a high energy rate forming technique. Appropriate powder mixtures were compacted and simultaneously bonded to OFHC backup discs, which were then electron beam welded to water jackets for cooling. The precipitation-hardened alloys were purchased as bar stock, machined to size, and brazed to OFHC backup discs which were handled as above. In both cases the sputtering targets were ≈ 9 cm (3.5 in.) diameter and ≈ 1 cm (0.5 in.) thick.

The targets were mounted opposite 7.6 cm (3 in.) diameter OFHC substrates in a triode sputtering apparatus, as illustrated in Figure 1. The apparatus was evacuated to a pressure of 1×10^{-8} torr and backfilled to 3×10^{-3} torr with research grade krypton. The substrate was ion etched at -100 volts for five minutes at a current density of 5 mA/cm^2. Deposition was then begun and continued for 10 to 12 hours at a rate of 0.089 to 0.102 mm/hr (3.5 - 4.0 mils/hr). The substrate temperature was controlled at the desired level by either water cooling or gas cooling. Previous experience indicated that a substrate temperature of ≤ 35°C was attained with water cooling. When using gas cooling the actual temperature was measured with a thermocouple. The substrate was allowed to assume its floating potential (≈ -20 volts) in all depositions.

After completion of sputtering, the deposit was machined to uniform thickness and the substrate was machined off. The deposit, then about 0.6 mm (0.025 in.) thick, was sheared into tensile specimen blanks and metallographic specimens. The tensile specimens used are illustrated in Figure 2. Specimens were cut on a Tensilkut Model 20-66 machine and tested on a floor model Instron. Elongation was measured with resistance strain gages, cemented to the specimen. A strain rate of 8×10^{-4}/sec was used for all tests.

Specimens were tested in both the as-deposited condition and after one-hour heat treatment in dynamic vacuum at temperatures of 175, 325, and 450°C; selected specimens were also tested after heat treatment at 600°C.

All fracture surfaces were examined optically at ≈ 50X. Several specimens were selected for electron fractography by either replication or scanning microscope methods.

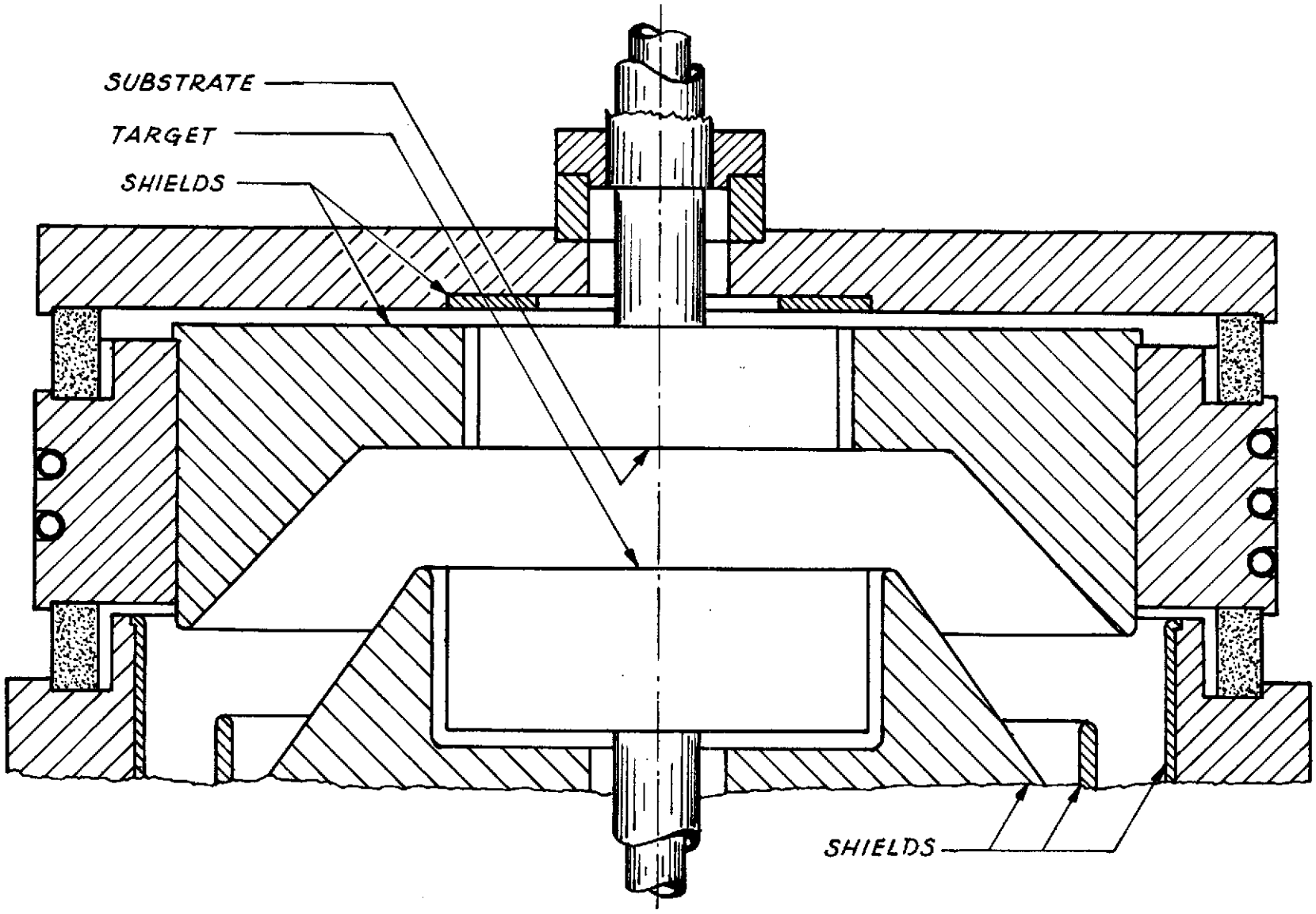


FIGURE 1. Target-substrate arrangement for deposition of tensile specimen material.

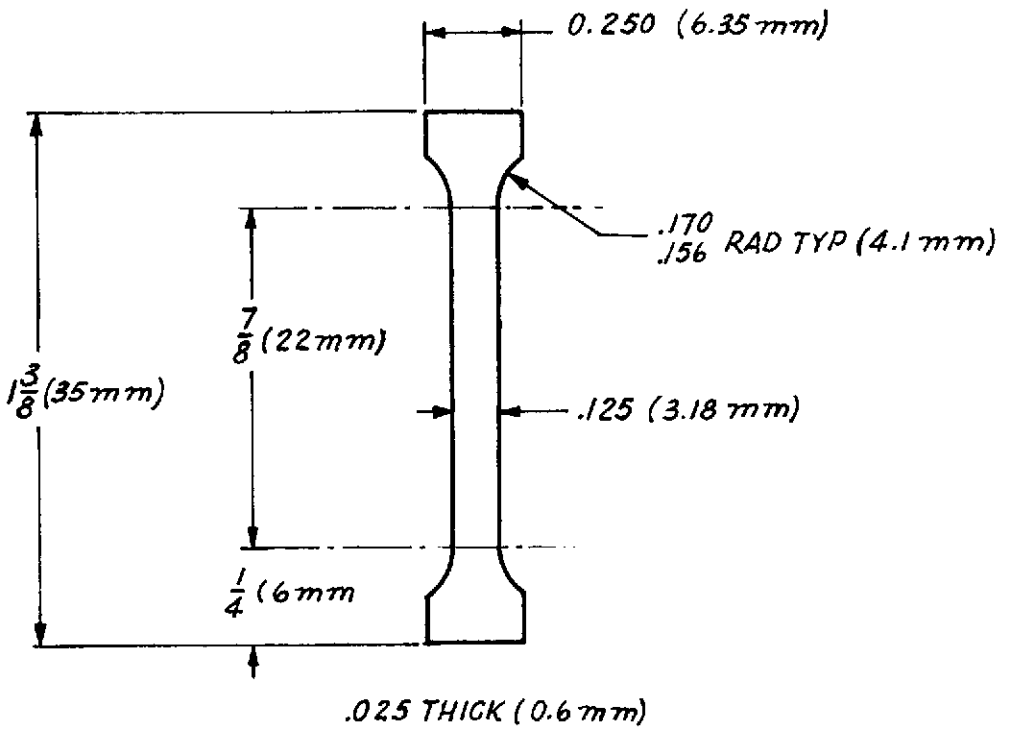


FIGURE 2. Sheet-type specimen used for tensile measurements on sputter-deposited material. Nominal 0.6 mm thickness. Dimensions in inches and millimeters.

Optical metallography utilized standard polishing techniques and an etchant consisting of 5 gm $FeCl_3$, 2 ml HCL, and 99 ml ethyl alcohol.

Electrical resistivity measurements were made at room temperature on selected tensile blanks before cutting the reduced sections. Each value is the average of ten measurements; the precision is estimated at ± 0.04 μΩcm.

Results and Discussion (Phase I) --

Experimental Variables --

The experimental variables investigated were material composition, substrate temperature during deposition, and temperature of heat treatment after deposition. Both deposition rate and substrate electrical potential which are known or expected to affect deposit structure and properties were held constant. The rationale for this decision is presented below.

The effect of the deposition rate on deposit structure has a strong resemblance to the effect of substrate temperature. For example, a high deposition rate results in a deviation from the equilibrium structure similar to that produced by a low substrate temperature. To a first approximation, the structure will vary linearly with deposition rate and exponentially with temperature. This dependence, together with the inconvenience of producing thick deposits at low deposition rates, led to the selection of substrate temperature as the primary means of varying deposit structure.

The effect of substrate electrical potential is complex. A grounded (0 volt) substrate is bombarded by a high density of electrons with ≃ 20 eV energy, resulting in surface heating. A floating substrate is bombarded with equal intensities of ions and electrons. A negatively biased substrate draws an ion current on the order of 10 - 20 mA/cm^2, with e.g. 30 eV energy, resulting in back sputtering from the substrate.

Varying substrate electrical potential therefore can produce changes in the deposit microstructure and crystallographic orientation in pure metals and may also produce alterations in deposit composition in alloys with constituents which have differing sputtering yields. Finally, these effects would be expected to differ in magnitude depending on the substrate temperature. For these reasons, it was not considered feasible to include substrate potential as a variable within the scale of the present program.

Tensile Properties --

The tensile properties of the sputtered materials are presented in Table I. The yield strength data are illustrated in Figures 3 and 4 as a function of heat treatment temperature. The probable significance level is ± 3%.

Considering the dispersion-hardened material, the following observations can be made:

TABLE I. - Sputter-Deposited Copper Alloy Tensile Properties
(measured at room temperature after 1-hr heat treatment at indicated temperatures)

	Yield Strength (0.2%)		Ultimate Strength		Elongation
	MN/m^2	(KSI)	MN/m^2	(KSI)	%
I. Copper - 0.25 vol% silicon carbide					
A. Cold Substrate					
As-deposited	909.5	(131.9)	909.5	(131.9)	--
175°C	425.8	(64.3)	425.8	(64.3)	--
325°C	475.1	(68.9)	475.1	(68.9)	--
450°C	220.0	(31.9)	284.1	(41.2)	25.5
B. 170°C Substrate					
As-deposited	722.6	(104.8)	722.6	(104.8)	--
175°C	740.2	(107.4)	740.2	(107.4)	0.2
325°C	753.6	(109.3)	753.6	(109.3)	--
450°C	114.5	(16.6)	220.0	(31.9)	38.0
II. Copper - 0.50 vol% silicon carbide					
A. Cold Substrate					
As-deposited	750.9	(108.9)	888.1	(128.8)	0.5
175°C	702.6	(101.9)	702.6	(101.9)	0.2
325°C	321.3	(46.6)	321.3	(46.6)	--
450°C	244.1	(35.4)	244.1	(35.4)	--
600°C	253.0	(36.7)	261.3	(37.9)	11.0
B. 175°C Substrate					
As-deposited	691.6	(100.3)	691.6	(100.3)	--
175°C	773.7	(112.2)	782.6	(113.5)	0.2
325°C	800.2	(116.1)	828.5	(120.2)	0.3
450°C	120.0	(17.4)	237.9	(34.5)	22.7
III. Copper - 0.15 wt% zirconium (AMZIRC)					
A. Cold Substrate					
As-deposited	791.5	(114.8)	939.8	(136.3)	1.0
175°C	786.7	(114.1)	908.8	(131.8)	0.7
325°C	1019.1	(147.8)	1019.1	(147.8)	--
450°C	779.8	(113.1)	779.8	(113.1)	--
B. 175°C Substrate					
As-deposited	697.1	(101.1)	776.4	(112.6)	0.7
175°C	715.0	(103.7)	787.4	(114.2)	0.8
325°C	824.0	(119.5)	824.0	(119.5)	--
450°C	765.4	(111.0)	806.0	(116.9)	1.6
600°C	84.1	(12.2)	237.9	(34.5)	30.0
300°C Substrate					
As-deposited	635.7	(92.2)	681.9	(98.9)	4.0
450°C	521.9	(75.7)	595.8	(86.4)	5.0
600°C	169.6	(24.6)	271.7	(39.4)	32.0
IV. Copper - 0.05 wt% magnesium - 0.15 wt% zirconium - 0.4 wt% chromium					
A. Cold Substrate					
As-deposited	803.3	(116.5)	1032.9	(149.8)	0.8
175°C	857.1	(124.3)	1004.6	(145.7)	0.6
325°C	935.4	(135.7)	935.4	(135.7)	--
450°C	951.5	(138.0)	951.5	(138.0)	--
600°C	187.5	(27.2)	293.0	(42.5)	18.0
B. 175°C Substrate					
As-deposited	870.1	(127.5)	897.7	(130.2)	--
175°C	751.6	(109.0)	783.3	(113.6)	0.4
325°C	856.4	(124.2)	856.4	(124.2)	--
450°C	950.1	(137.8)	992.2	(143.9)	1.0
600°C	459.2	(66.6)	499.9	(72.5)	4.0
V. Copper (OFHC)					
A. Cold Substrate					
As-deposited	690.2	(100.1)	690.2	(100.1)	2.0
175°C	166.9	(24.2)	203.4	(29.5)	12.0
325°C	112.4	(16.3)	172.4	(25.0)	19.0
450°C	101.4	(14.7)	189.6	(27.5)	30.0
600°C	90.3	(13.1)	157.9	(22.9)	24.0

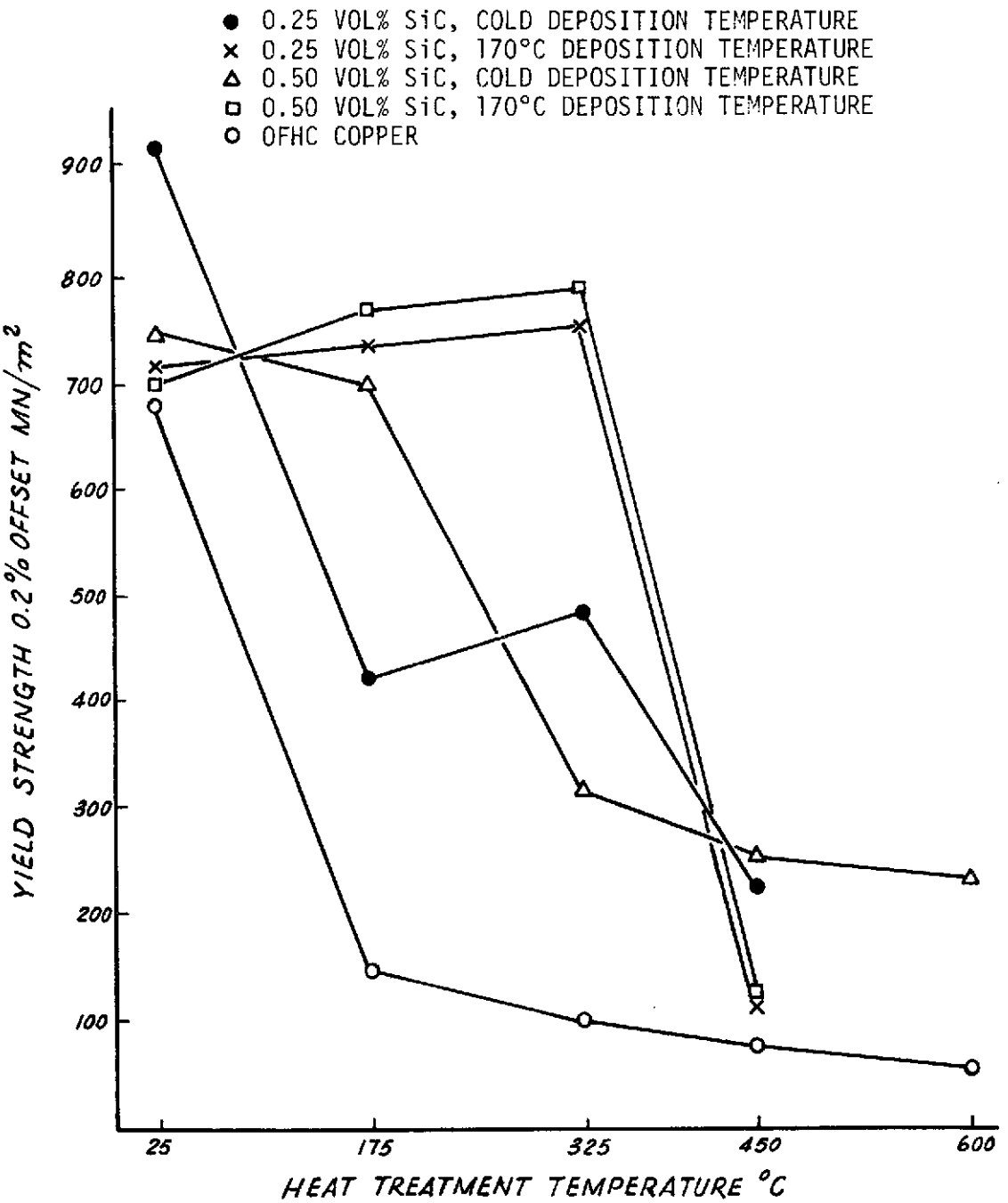


FIGURE 3. Influence of heat treatment on room temperature yield strength of sputtered dispersion-hardened copper and OFHC copper.

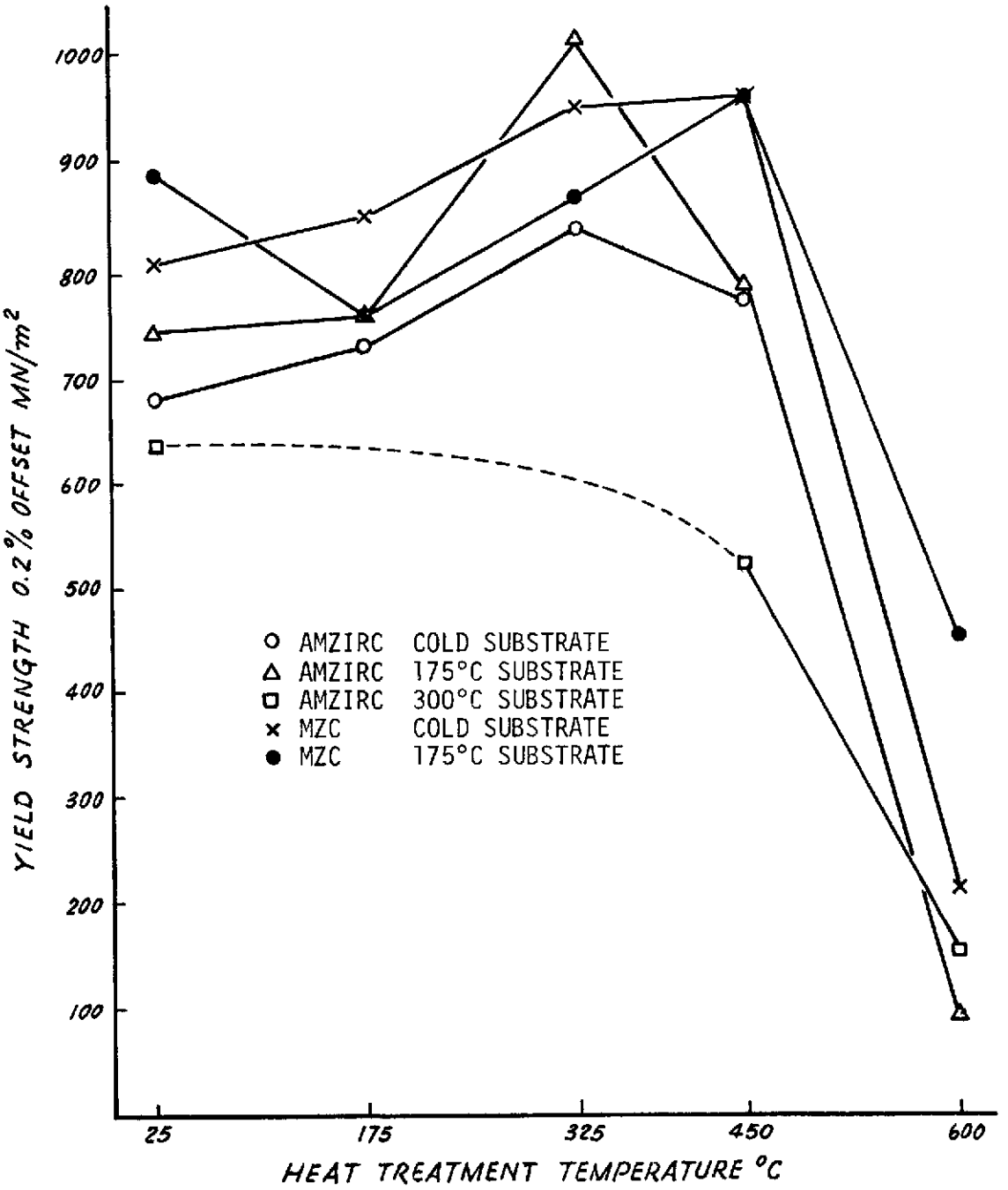


FIGURE 4. Influence of heat treatment on room temperature yield strength of sputtered AMZIRC and MZC alloys.

1. The dependence of yield strength on composition was much smaller than expected. Although significant differences did exist at particular treatments, in general the 0.50 SiC material was not significantly stronger than the 0.25 SiC material.

2. The substrate temperature had a major influence on the tensile properties. In the as-deposited condition, the cold substrate deposits had higher strength than their 170°C counterparts. However, the cold substrate samples showed loss of strength upon heat treatments at 175 and 325°C. The 170°C substrate temperature deposits maintained their strength through these treatments and showed a severe softening after the 450°C heat treatment. This behavior suggests a rapid recrystallization. The behavior of the cold substrate deposits, in contrast, suggests a more or less continuous recovery process which removes sufficient stored energy so that these samples do not recrystallize during the 450°C heat treatment. The cold substrate temperature would be preferred for high temperature service.

The data for the OFHC copper samples, which were used as a control in this program, are also shown in Figure 3. The as-deposited yield strength is similar to that of the dispersion-hardened samples but it is lost rapidly upon heat treatment. This suggests that the strength of the dispersion-hardened materials is due primarily to their very fine microstructure rather than dispersion hardening per se. The role of the dispersoid is, then, to stabilize this microstructure against recrystallization and growth during annealing. Sputter-deposited OFHC copper has been observed by Patten[11] to recrystallize at room temperature.

The effect of substrate temperature was less uniform on the precipitation-hardened alloys, AMZIRC and MZC. The AMZIRC alloy exhibited the highest strength in the cold substrate condition and maintained this strength advantage through the heat treatment schedule up to and including 450°C. This temperature corresponded to the beginning of the overaged condition.

In contrast, the 175°C substrate temperature resulted in higher strength than the cold substrate in the MZC alloy. The differential was not consistently maintained during heat treatment; in fact the two conditions became equal in strength after the 450°C heat treatment, which resulted in peak strength in this alloy. However, the 175°C substrate sample was much more resistant to softening upon exposure to 600°C, retaining a yield strength of 450 MN/m^2 vs. 188 MN/m^2 for the cold substrate sample similarly heat treated.

The general trend of increasing strength with moderate temperature heat treatment in these alloys provides evidence for the formation of solid solutions of the alloying elements during deposition. The precipitation hardening is less pronounced in the sputtered deposits than in conventionally formed materials due to the higher initial strength level

(due to fine microstructure) in the former material. The fact that the strength of the AMZIRC deposited on the 300°C substrate was less than that of the lower temperature deposits together with the fact that the 350°C heat treatment temperature resulted in the peak strength in this alloy can be taken as an indication that the microstructural strengthening in these deposits was of greater magnitude than the precipitation-hardening.

For purposes of comparison with conventionally fabricated materials, the yield strengths of OFHC copper and the precipitation-hardened alloys are as follows:[2]

OFHC copper	"(full) hard"	307 MN/m^2
OFHC copper	"annealed"	38 "
AMZIRC	"half hard"	336 "
MZC	"cold worked and aged"	536 "

These data indicate that the strength obtained through the microstructure developed by sputter deposition is on the order of double that which can be developed by conventional processing.

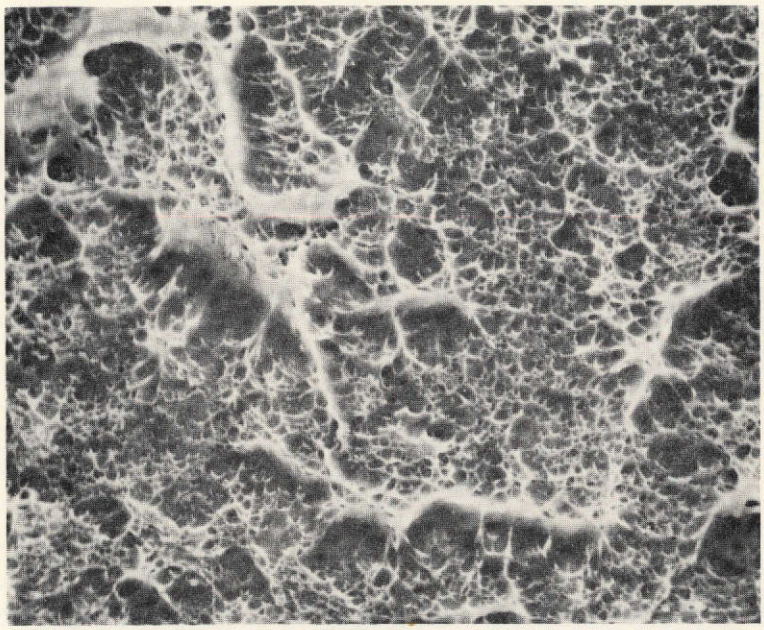
The uniform elongations observed in this program were disappointingly low at yield strengths of 700 MN/m^2 (100 KSI) and above. Only one material and condition (AMZIRC -- 175°C substrate, 450°C heat treatment) produced an elongation greater than 1% for yield strengths above 700 MN/m^2.

For the "cold" substrate samples in the as-deposited condition, the low elongation was indicative of low energy fracture. After the intermediate heat treatment temperature, e.g. 325°C, the samples necked soon after yielding (due to low work hardening rate) and exhibited ductility via extensive reduction in area. With higher temperature heat treatments, the elongation values increased to the several percent level.

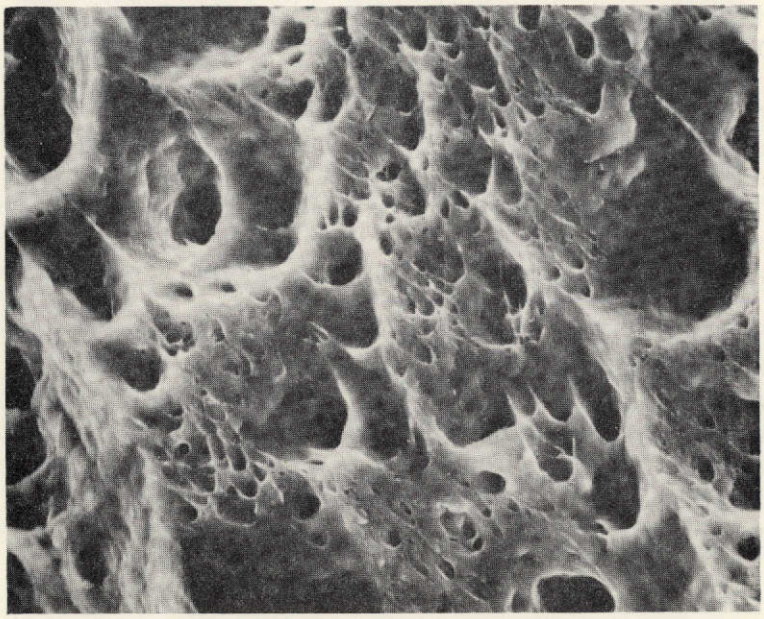
Examination of fracture surfaces from tensile specimens confirmed the above observations. An example is illustrated in Figure 5 for the 0.5 SiC sample deposited on a cold substrate. In the as-deposited condition, the surface morphology indicates low energy fracture, although this case is not as severe as that of cleavage in inherently brittle materials. For the sample tested after heat treatment at 450°C, the failure was completely ductile.

Conductivity --

The thrust chamber application for which these materials were investigated requires high thermal conductivity as well as high tensile strength. To obtain an indication of thermal conductivity, electrical conductivity was measured, since both conductivities were expected to be closely related by the Wiedemann-Franz ratio. The electrical conductivity, being a much simpler measurement for copper-base alloys, could be accommodated within the scope of the present program.



As-Deposited



After 450°C Heat Treatment

FIGURE 5. Room temperature tensile fractures of Cu-0.5 vol% SiC sputter deposited on a cold substrate and tested in the indicated condition. 3000X

The electrical conductivity data is presented in Table II. The trends observed were, in general, as expected. As-deposited samples have low conductivity values due to their high defect densities and also due to partial solution of alloying elements. Higher substrate temperatures and post-deposition heat treatment result in increased conductivity through annealing out of defects and precipitation of alloying elements.

It was observed that although all alloys had similar conductivities in the as-deposited cold substrate condition, the precipitation-hardened alloys (AMZIRC and MZC) developed high (90 - 100% IACS) conductivities upon heat treatment, whereas the dispersion-hardened SiC samples did not improve above the 60 to 65% IACS level. This behavior was attributed to the anomalous composition of these materials, which will be discussed in a later section.

The relationship between yield strength and electrical conductivity is illustrated in Figures 6 and 7 for the dispersion-hardened and precipitation-hardened alloys, respectively. It is readily apparent that the latter alloys offer a superior combination of these properties.

Microstructure --

The optical microstructures of the experimental materials in the as-deposited and heat treated conditions are illustrated in Figures 8 through 14.

The angle at which the columnar structure is aligned indicates the distance of the area photographed from the center of symmetry of the target and substrate; that is, the deposit growth structure is directed towards the maximum flux of sputtered atoms. This feature should not be considered significant in comparing deposits.

For the 0.25 and 0.50 SiC deposits on 170 to 175°C substrates in Figures 8 and 9, there is little significant difference between these samples in the as-deposited condition. In both heat treated conditions the 0.5 SiC deposit has a marginally larger grain size but the difference is not large enough to be expected to influence the properties. Referring to Table I the yield and ultimate tensile strengths of these deposits are in fact similar.

Since the extremely fine grain structure in the as-deposited condition appeared to be at or below the resolution of the optical microscope, a 0.50 SiC sample was thinned by electropolishing and examined by electron transmission. The grain structure is illustrated in Figure 10, which is a section in the plane of the deposit rather than normal to that plane, as for the optical micrograph. The columnar grains appear equiaxed and have diameters ranging from 20 - 50 nm, which is about an order of magnitude less than the optical resolution limit.

TABLE II. - Sputter-Deposited Copper Alloy Electrical Conductivity (measured at room temperature after 1-hour heat treatment at indicated temperatures)

	% IACS
Copper - 0.25 vol% Silicon Carbide	
Cold substrate - as-deposited	48
170°C substrate - as-deposited	63
Copper - 0.50 vol% Silicon Carbide	
Cold substrate - as-deposited	51
Cold substrate - 600°C	60
175°C substrate - as-deposited	64
Copper - 0.15 wt% Zirconium	
Cold substrate - as-deposited	45
175°C substrate - as-deposited	66
175°C substrate - 450°C	81
175°C substrate - 600°C	100
300°C substrate - as-deposited	75
300°C substrate - 450°C	75
300°C substrate - 600°C	92
Copper - 0.05 wt% Magnesium-0.15 wt% Zirconium-0.40 wt% Chromium	
Cold substrate - as-deposited	29
Cold substrate - 600°C	96
170°C substrate - as-deposited	36
170°C substrate - 600°C	92
Copper (OFHC)	
Cold substrate - as-deposited	84
Cold substrate - 175°C	92
Cold substrate - 325°C	96
Cold substrate - 450°C	96
Cold substrate - 600°C	98

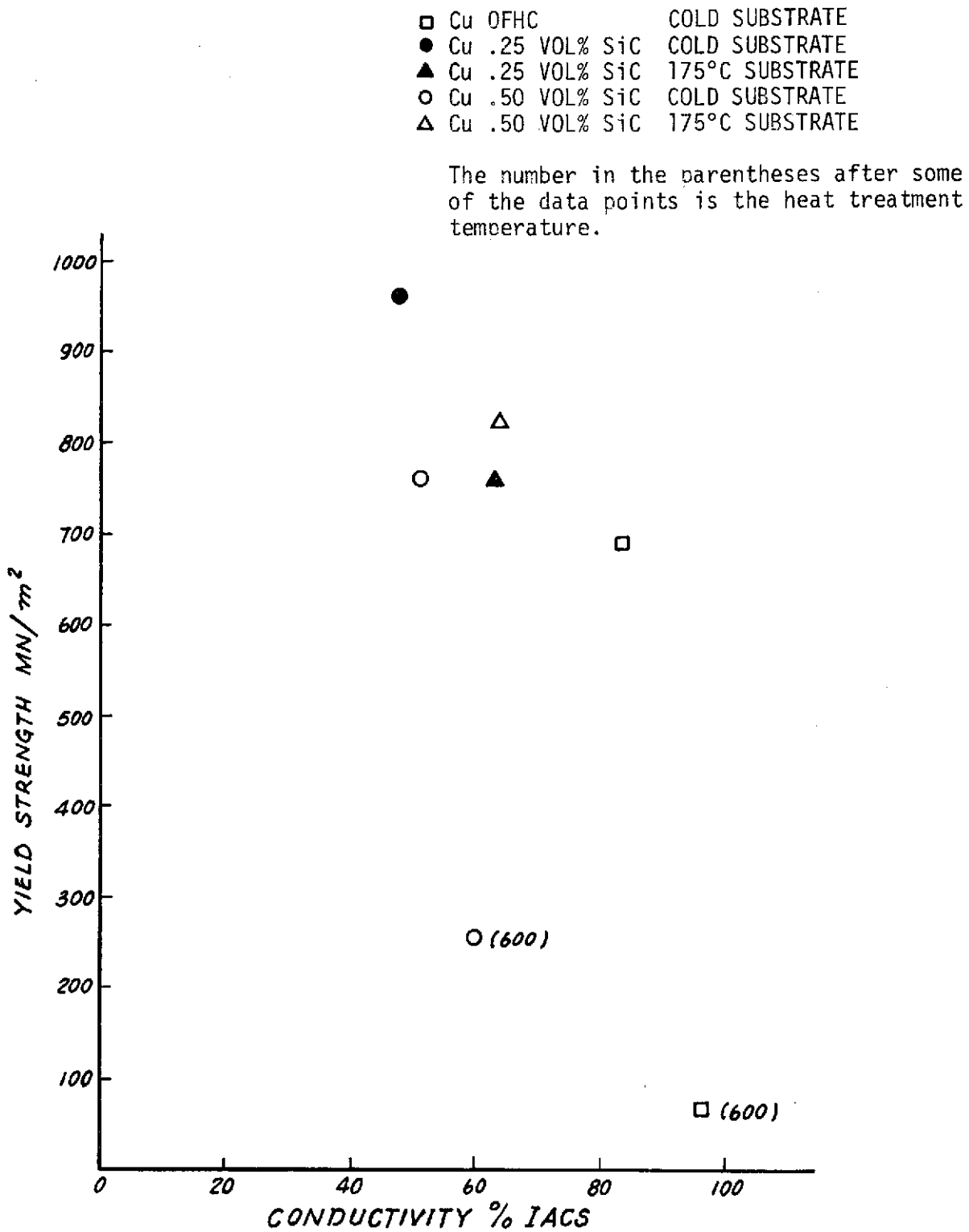


FIGURE 6. Relationship between yield strength and conductivity for sputtered dispersion-hardened copper and OFHC copper.

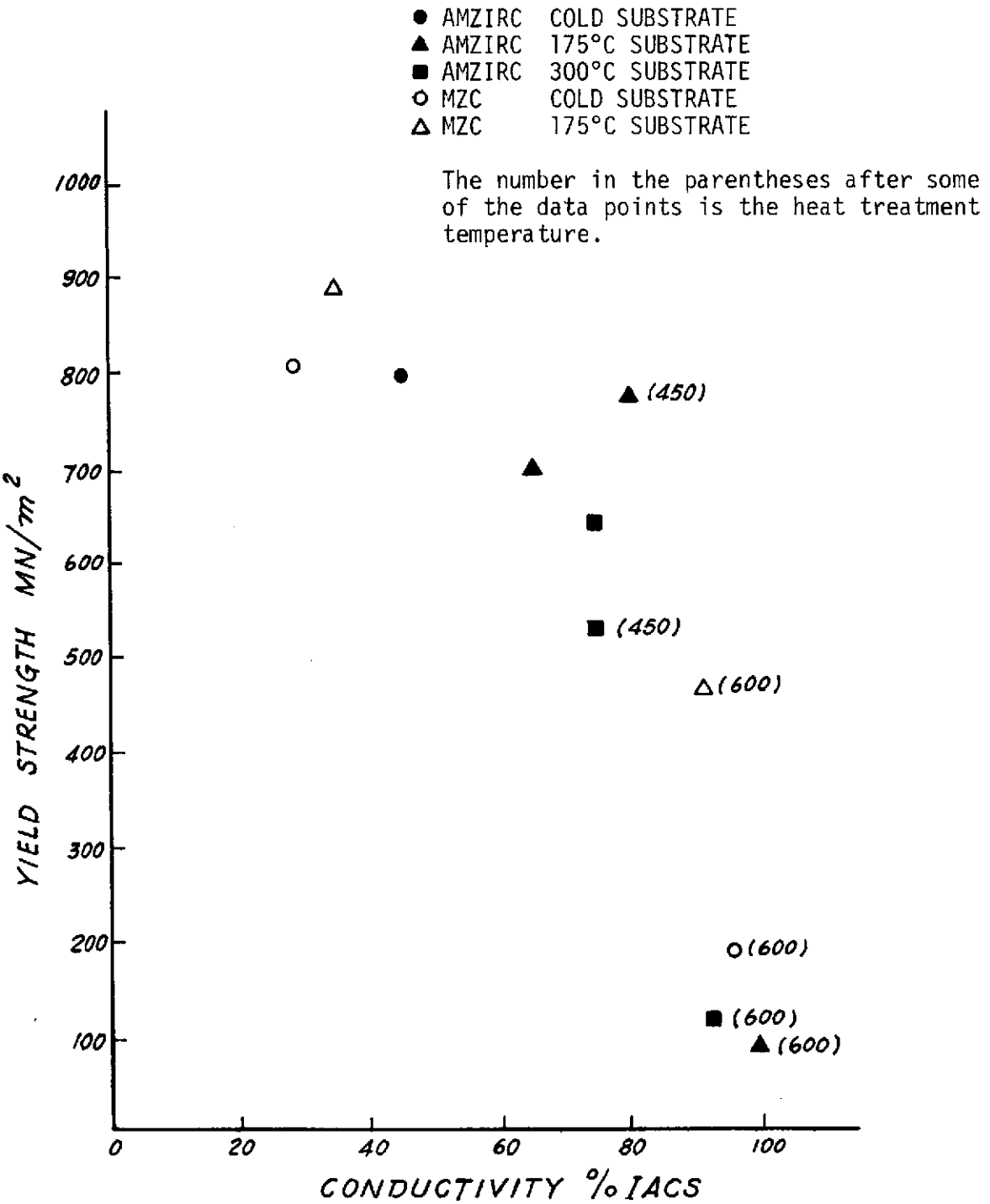
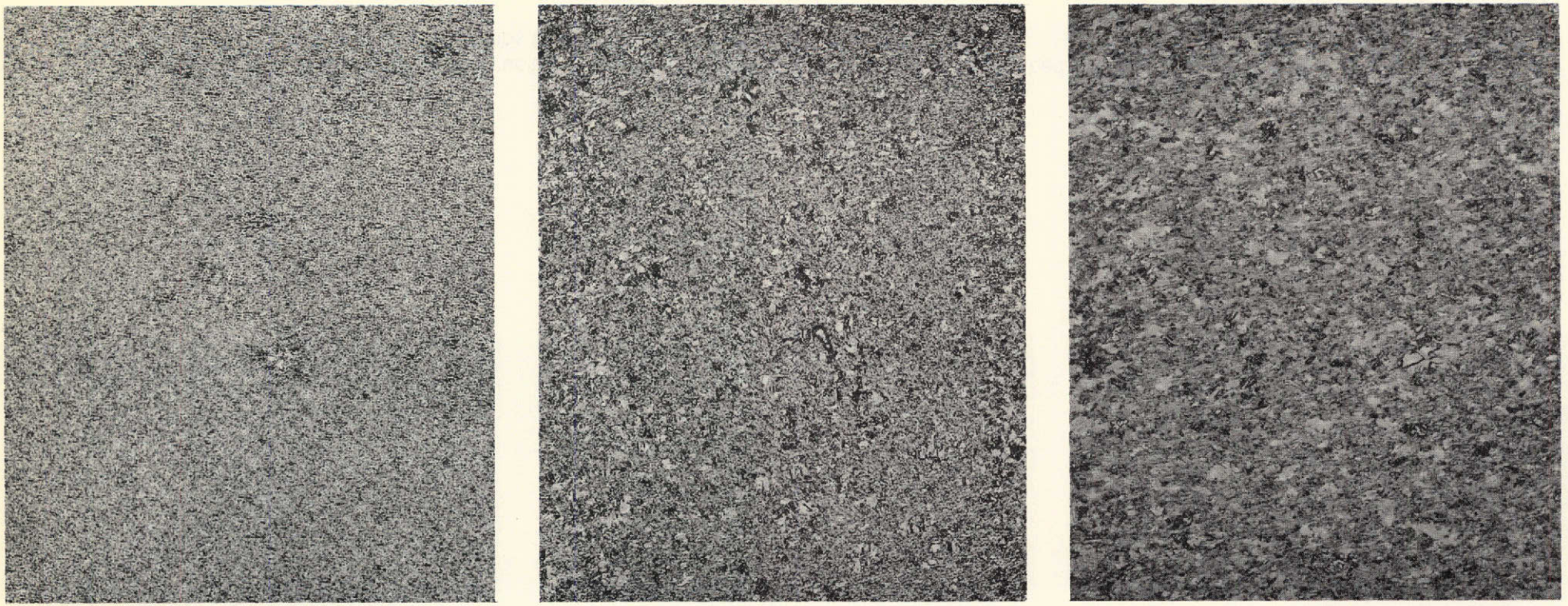


FIGURE 7. Relationship between yield strength and conductivity for sputtered AMZIRC and MZC copper alloy.

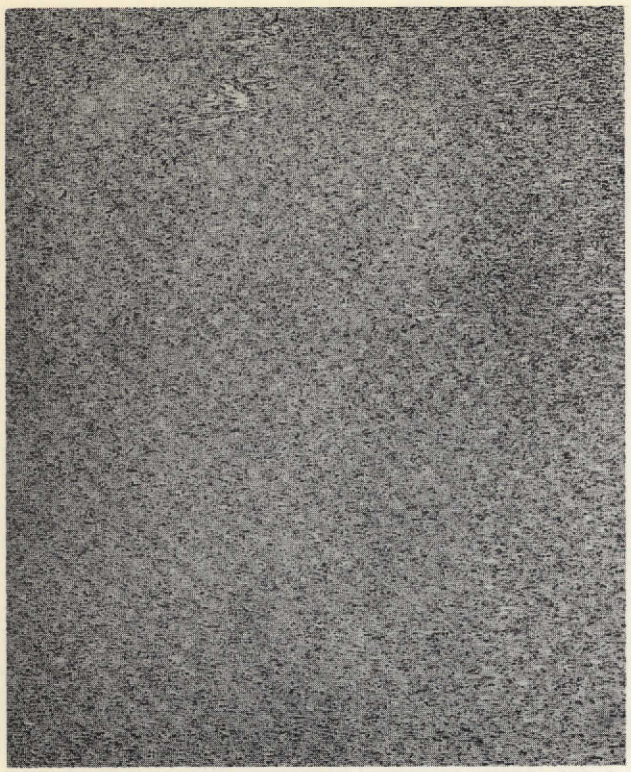


As-deposited

After 450°C heat treatment

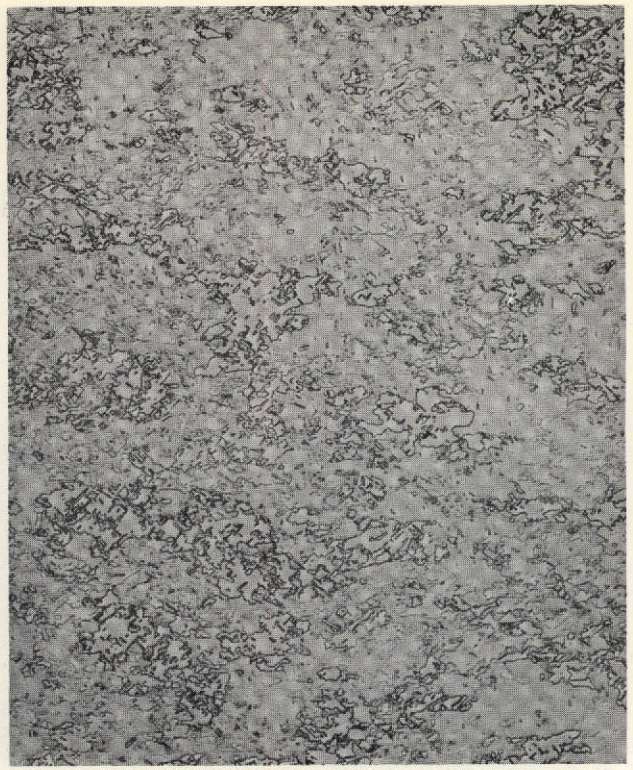
After 600°C heat treatment

FIGURE 8. Optical microstructure of Cu-0.25 vol% SiC sputter deposited on 175°C substrate. Direction of deposition left to right. Etched, 250X.



As-deposited

After 450°C heat treatment



After 600°C heat treatment

FIGURE 9. Optical microstructure of Cu-0.50 vol% SiC sputter deposited on 175°C substrate. Direction of deposition left to right. Etched, 250X.

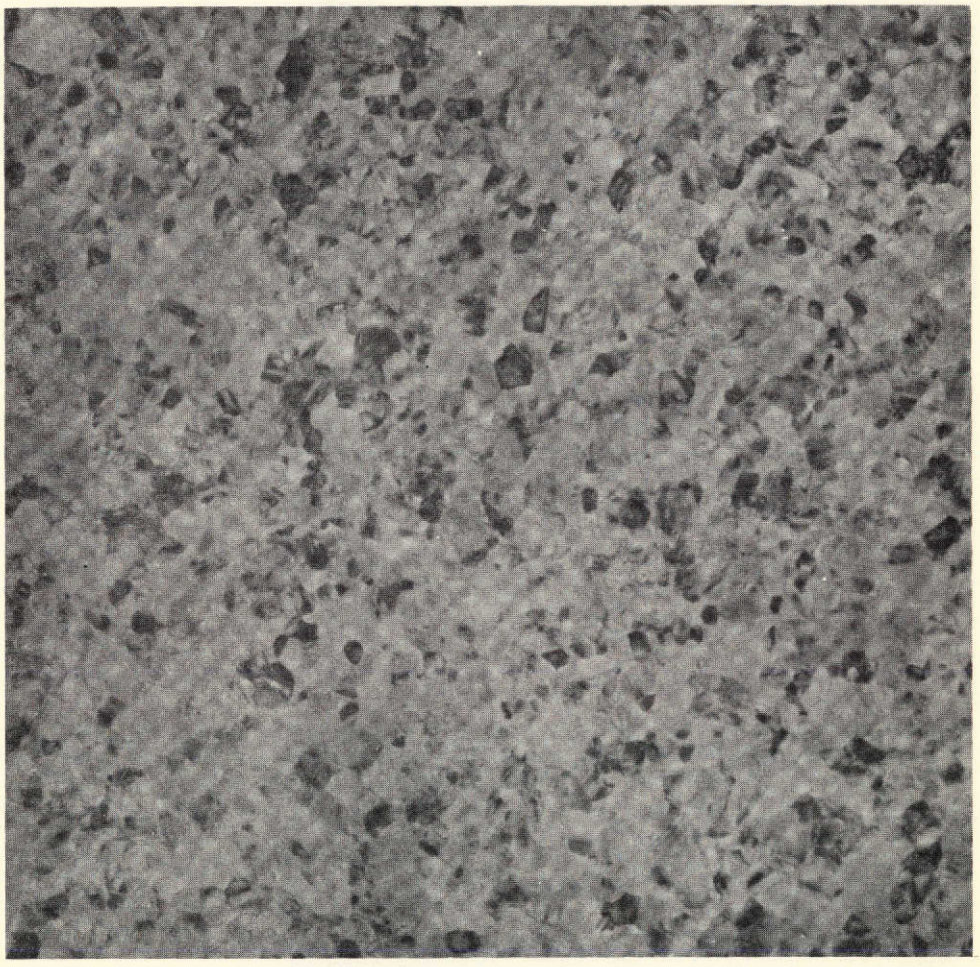
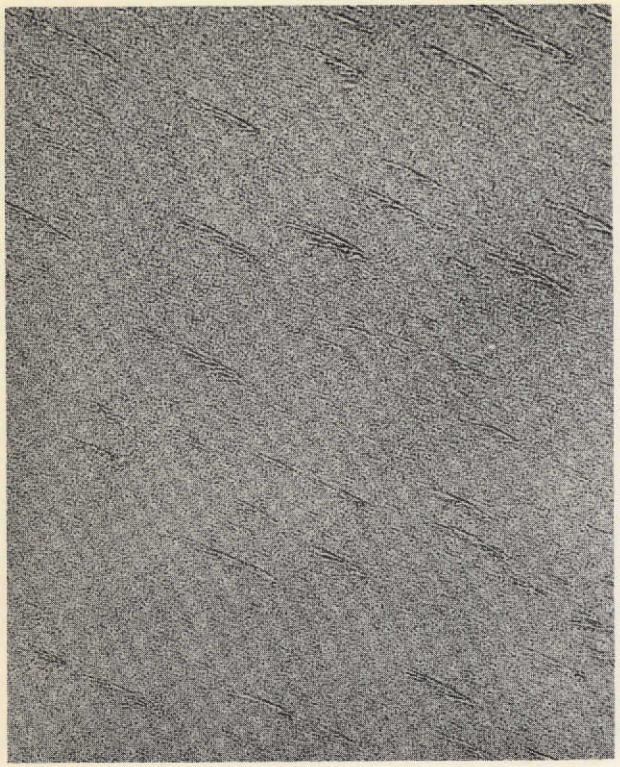
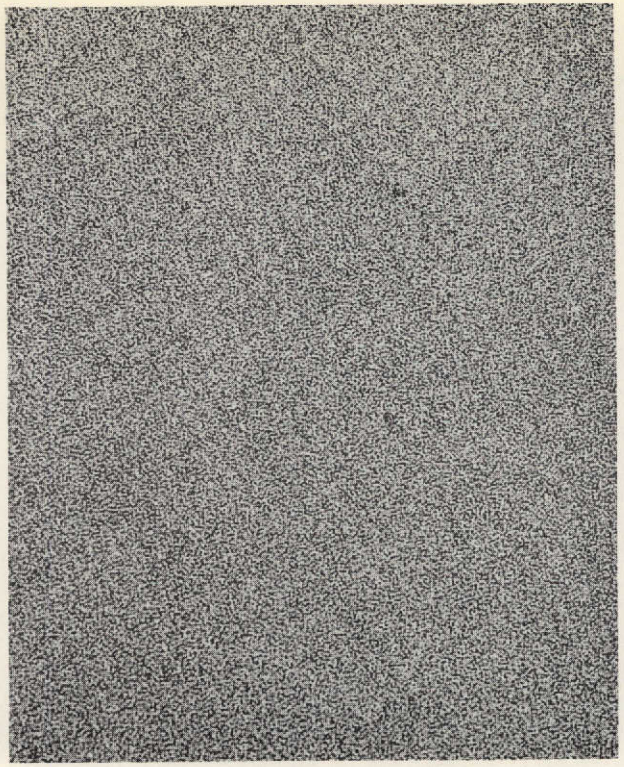


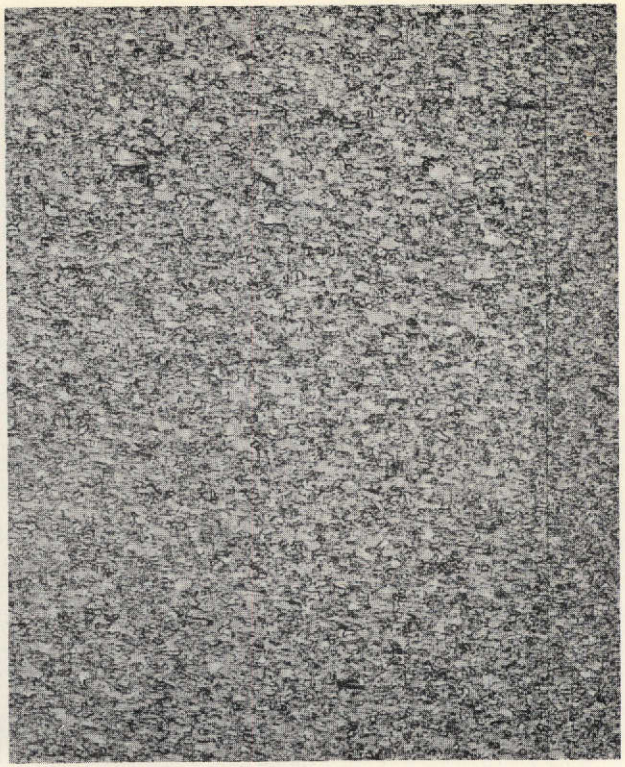
FIGURE 10. Microstructure of Cu-0.50 vol% SiC sputter deposited on cold substrate. The grain structure is viewed parallel to the growth direction. Grain diameters are in the range of 20 to 50 nm. Electron transmission micrograph, 100,000X.



As-deposited

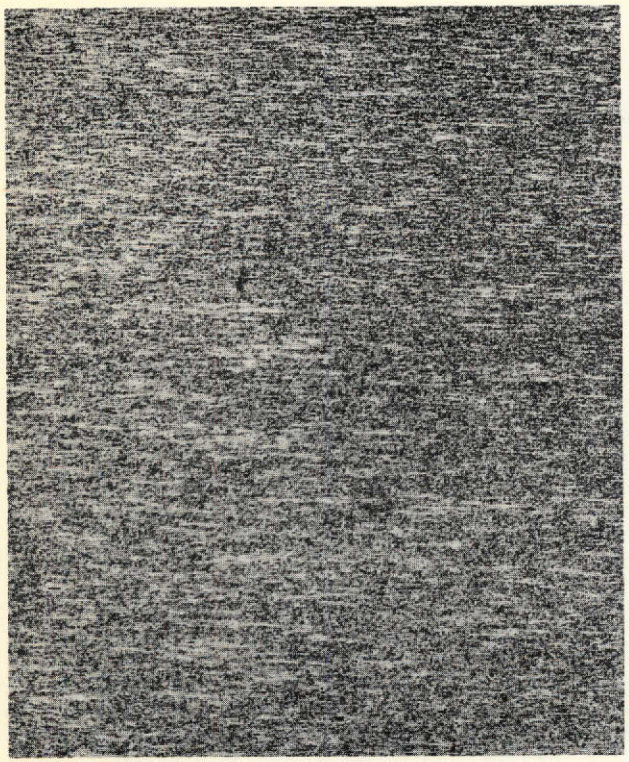


After 450°C heat treatment

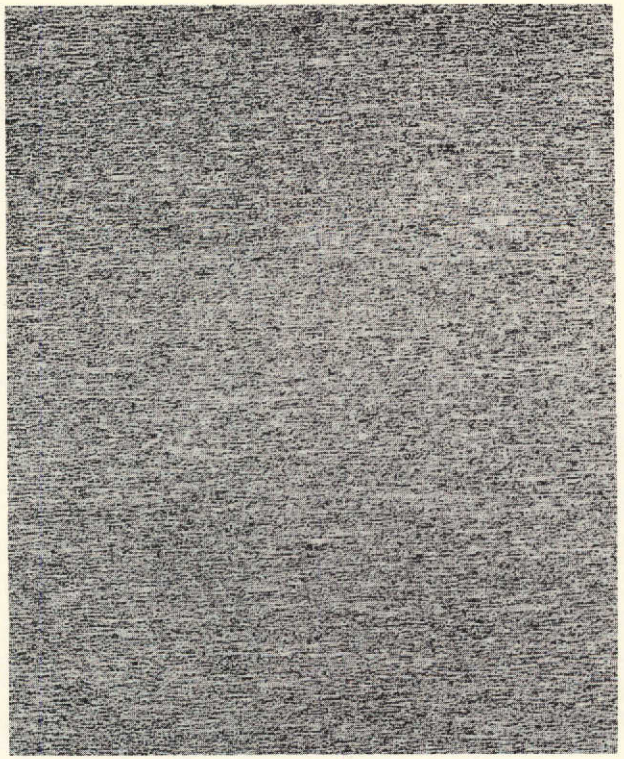


After 600°C heat treatment

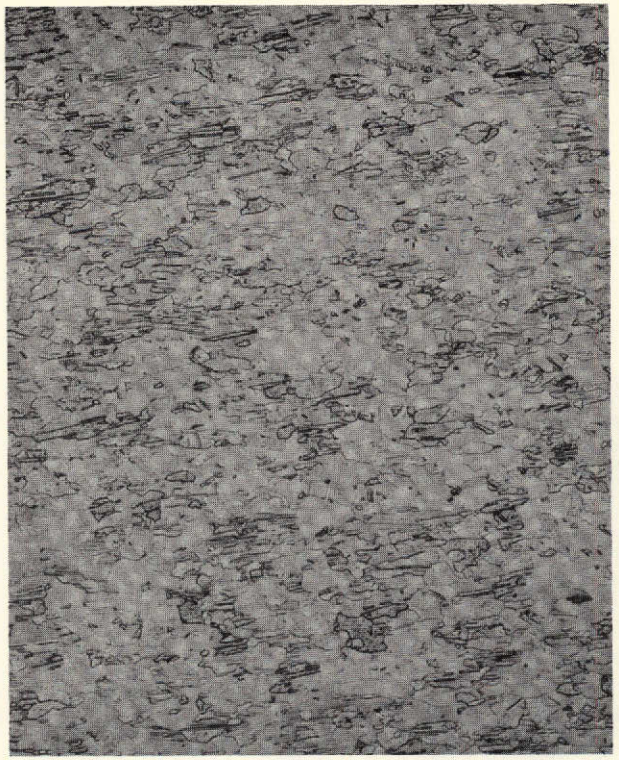
FIGURE 11. Optical microstructure of AMZIRC sputter deposited on cold substrate. Direction of deposition left to right. Etched, 250X.



As-deposited

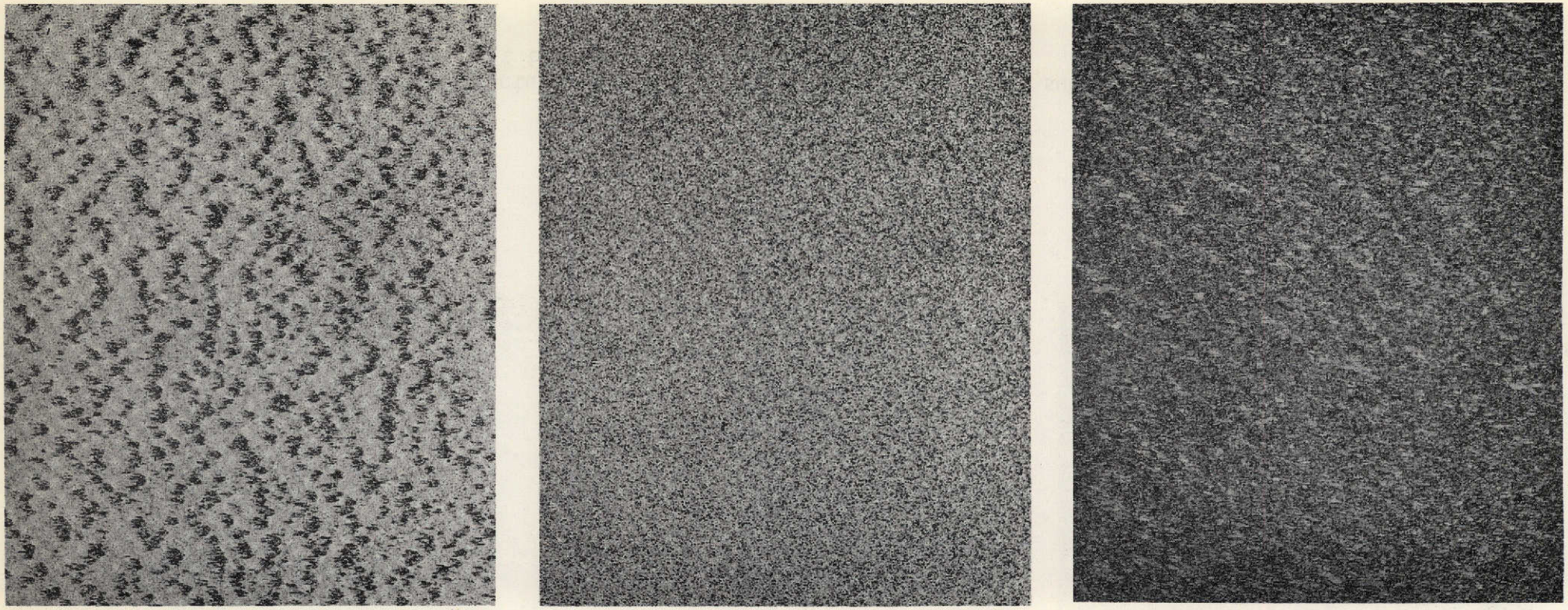


After 450°C heat treatment



After 600°C heat treatment

FIGURE 12. Optical microstructure of AMZIRC sputter deposited on 175°C substrate. Direction of deposition left to right. Etched, 250X.

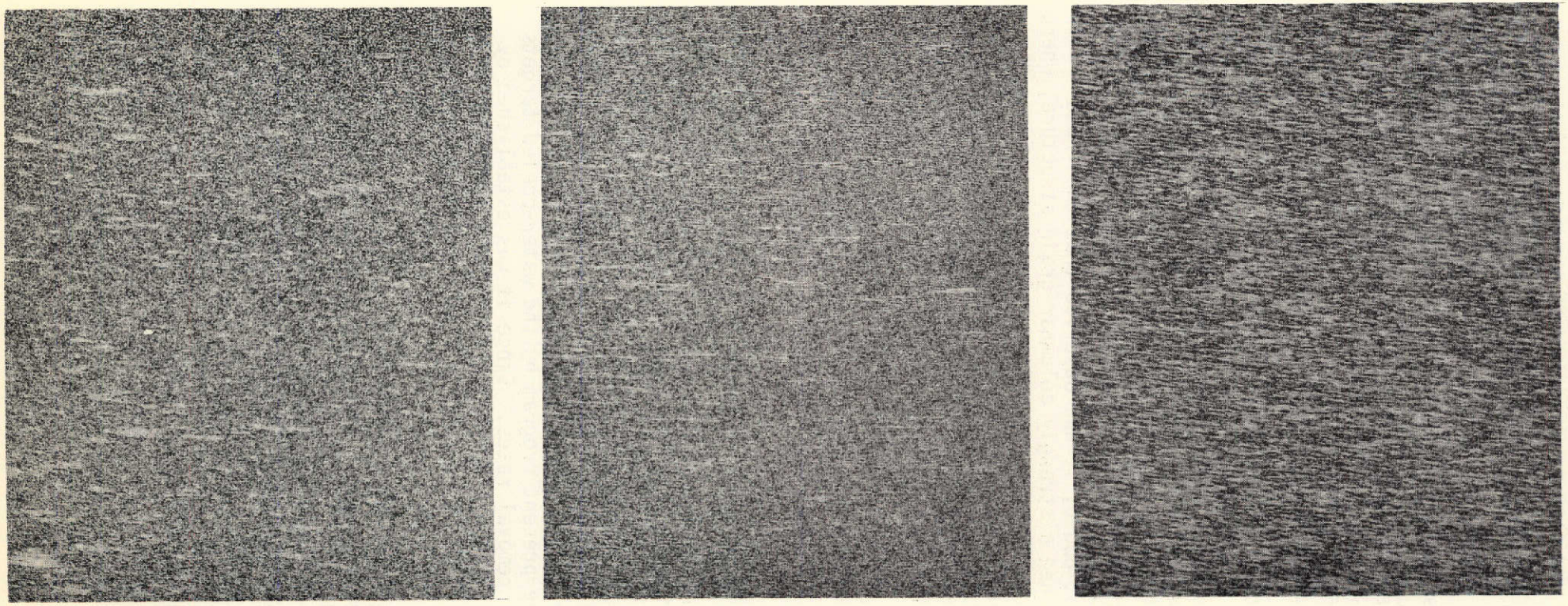


As-deposited

After 450°C heat treatment

After 600°C heat treatment

FIGURE 13. Optical microstructure of MZC sputter deposited on cold substrate. Direction of deposition left to right. Etched, 250X.



As-deposited

After 450°C heat treatment

After 600°C heat treatment

FIGURE 14. Optical microstructure of MZC sputter deposited on 175°C substrate. Direction of deposition left to right. Etched, 250X.

The AMZIRC microstructures are illustrated in Figures 11 and 12. The higher substrate temperature resulted in a coarser and more columnar grain structure. This difference persisted throughout the heat treatment schedule and can be associated with the slightly lower strengths and greater elongations of the 175°C substrate deposits. The microstructure of the AMZIRC deposit on a 300°C substrate was not examined as part of this program. The tensile properties of this deposit indicate a continuation of the trend observed above.

The effect of substrate temperature on grain structure in the MZC alloy was similar, Figures 13 and 14. The dark areas in the as-deposited, cold substrate sample (Figure 13) are believed to be artifacts, although they were reproducible. The apparent grain size of this sample can be seen between the dark areas and is small enough to be incompletely resolved. For samples heat treated at 600°C, it was observed that the 175°C substrate sample had retained a strongly columnar grain structure, whereas the cold substrate sample had a more equiaxed structure. Since the tensile axis is perpendicular to the columnar grain structure, this difference in grain morphology may account for the significantly higher yield strength of the 175°C substrate samples after this heat treatment (460 MN/m^2 versus 188 MN/m^2).

In summary, when allowance is made for the expected precipitation-hardening effects during heat treatment, the preceding comparisons between materials support the general relation between fine grain structure and high strength.

Composition of the SiC Deposits --

In general, if certain conditions are met, sputter deposition yields a stoichiometric transfer of material, i.e. the composition of the deposit is closely similar to that of the target. The primary requirement is that the target be kept sufficiently cold so that diffusion from the bulk to the ion bombarded surface proceeds at a lower rate than the migration of the surface due to the removal of material by sputtering. This requirement was met in the present program by the water-cooled targets operated at high material removal rates. Since it was established by chemical analysis that the compacted Cu-SiC targets were of the desired SiC content, the deposit composition was not considered an experimental variable.

The abrupt loss of strength of these deposits after heat treatments at 325 and 450°C suggested that SiC contents were less than expected. Also, the electrical conductivity did not increase with heat treatment as expected on the basis of the microstructural changes observed. This suggested that an insulating constituent was present, perhaps as a grain boundary film.

Chemical analysis of the as-deposited SiC samples was then performed; the fraction insoluble in 50% nitric acid, assumed to be SiC, was

less than 0.03% by weight. Emission spectroscopy indicated a silicon content of 0.2 wt% in a 0.50 SiC deposit. Since this silicon content corresponds to the amount of silicon in a 0.5 vol% SiC alloy, two possibilities were considered -- the silicon was present as SiC but with a particle size too small to be retained on the filter used in the analysis; and/or the silicon was present in another form, e.g. metallic or one of the oxides. A sample was heated to the melting point to coarsen the dispersed particles. Analysis of this sample (nominally 0.5 vol% SiC) resulted in 0.2 vol% SiC indicating that both of the above possibilities were in effect.

The residual gas analyses made during depositions with the compacted Cu-SiC targets exhibited higher partial pressures of carbon monoxide (CO) than the other depositions. It is hypothesized that these targets contain sufficient oxygen with the necessary energy being supplied by the plasma to promote the reaction $SiC + 1/2\ O_2 = CO + Si$. In addition, the silicon produced may have been partially oxidized, which would account for the low electrical conductivities observed. The correction of this situation will require the substitution of a higher vacuum process for target fabrication than the HERF process as used in this program. At the time of writing, hot isostatic pressing (HIP) has been used satisfactorily to fabricate targets with compositions similar to those used above.

PHASE II

Procedure and Discussion

Sputter deposition on the tubular substrates furnished by NASA required certain hardware to be fabricated. A schematic assembly of the necessary components is illustrated in Figure 15. For testing of the hardware a straight-sided tubular aluminum substrate and two targets, one of AMZIRC and one of OFHC copper, were fabricated. A total of eleven experiments[3] involving the deposition of 3 mm (0.118 in.) of AMZIRC and 3.68 mm (0.145 in.) of OFHC copper, were required to accomplish the following results:

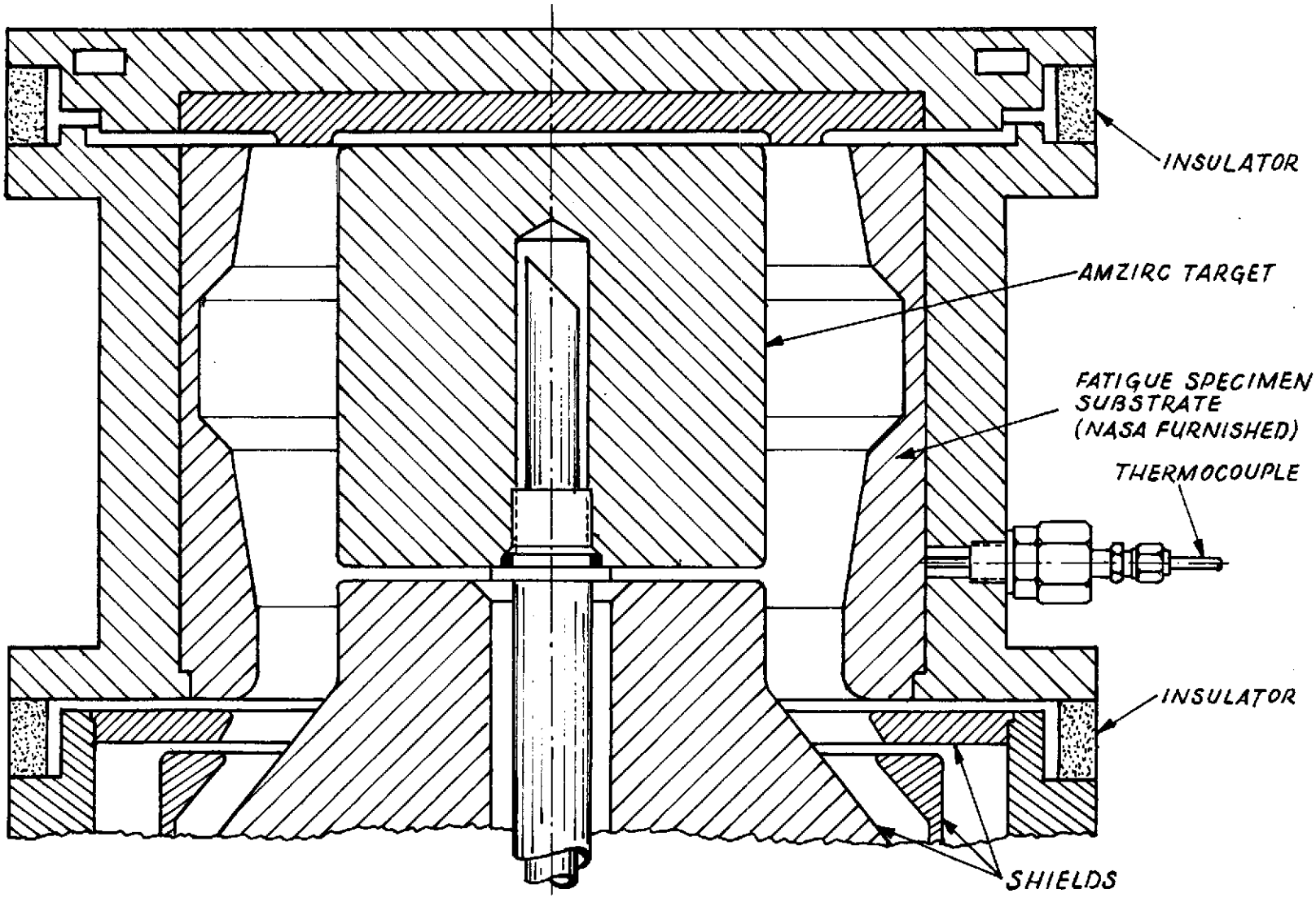


FIGURE 15. Sputtering hardware for deposition of AMZIRC on NASA-furnished copper substrate.

1. Modify shield hardware and deposition parameters to obtain stable sputtering system operating conditions, improve plasma density, and increase deposition rate. It is significant that the ≈ 0.1 mm/hr (≈ 4 mil/hr) deposition rate found to be available was a factor of two higher than was originally thought to be obtainable in the system design used.

2. Establish that the positive ion flux around the target was nonuniform, and determine the substrate and target repositioning required for each run to optimize the deposit thickness and target erosion pattern.

3. Obtain a deposition temperature ≈ 200°C which would produce the deposit properties established in Phase I.

4. Demonstrate readiness to start Phase III by depositing 0.29 mm (11.5 mils) of AMZIRC on fatigue specimen substrate 1. The circumferential deposit distribution in the fatigue specimen gage length was ± 13% which was considered tolerable compared to the ± 16 to 24% values obtained in preceding experiments.

PHASE III

Upon successful completion of the Phase II work, preparations were made to sputter deposit the required thickness of AMZIRC on the inside of one of the NASA-furnished, contoured copper substrates.

Substrate Preparation --

The outer diameter on Fatigue Specimen substrate 2 was machined from 176.45 mm (6.947 in.) to 176.27 mm (6.940 in.) to achieve a substrate temperature of 210°C during deposition. After machining, the substrate was Summa* polished for four minutes. The thickness was measured at 40 mm (1-1/2 in.), 50 mm (2 in.), and 60 mm (2-1/2 in.) down from the top at 45° increments around the circumference and were found to be uniform within ± 0.025 mm (0.001 in.). The substrate was then Summa polished again for 2 minutes prior to cleaning. Approximately 0.0381 mm (0.0015 in.) was removed from the inner substrate surface during the two Summa-polishing steps. The procedure established to clean the substrate follows:

*Trademark of Molelectric, Inc.

1. Rinse in tap water.

2. Wash with cotton swabs in a solution of water and Ivory liquid detergent.

3. Rinse in running tap water until all detergent is removed, ≈ 5 minutes.

4. Rinse in distilled water.

5. Rinse well with best available grade methyl alcohol in laminar flow bench just prior to installation in substrate holder.

6. Cover substrate and remove with holder from the laminar flow bench to the sputtering system for installation.

Target Preparation --

The two freshly machined AMZIRC targets (from BNW stock) were sputter cleaned in a separate run just prior to installation for the first deposition run on the individual target. The targets did not require any additional cleaning between depositions.

Sputter Deposition --

Three deposition runs of ≈ 37 hours sputtering time each were planned to make the required 10.29 mm (0.405 in.) deposit thickness. The runs were made on a 3-shift, 24-hour-day basis to permit the total deposition to be accomplished within two 5-day work weeks. The total deposition could not be made in fewer runs because of excessive deposit buildup on the shields and the nonuniform metal removal from the target. Between each run the shields were cleaned and the target was rotated 180° to equalize the removal profile.

The deposition parameters used are presented in Table III. The run history is described on an individual basis as follows:

Run 1 - Approximately 1.7 kg of AMZIRC was deposited to an average thickness of 3.94 mm (0.155 in.) in the fatigue specimen gage length. The deposit was machined to a thickness of 2.997 mm (0.118 in.) to improve its surface and thereby minimize the formation of defects in succeeding runs.

Run 2 - Approximately 1.8 kg of AMZIRC was deposited to an average thickness of 4.19 mm (0.165 in.) as above. The substrate was not removed from the holder.

Run 3 - A new target was installed and 1.8 kg was deposited on it bringing the total average thickness of the deposit to 11.41 mm (0.449 in.). There was, however, one area at the 185° location which measured only 10.08 mm (0.397 in.).

Run 4 - To assure that all areas of the deposit met the thickness requirements, an average thickness of 0.89 mm (0.035 in.) of AMZIRC was deposited.

TABLE III. - Deposition Parameters for Fatigue Specimen 2

	Run			
	1	2	3	4
Deposition Rate (mm/hr)	0.114	0.117	0.10	0.101
Average Thickness Deposited (mm)	3.937*	4.191	4.216	0.889
Target Voltage (kV)	2	2	2	2
Target Current (amperes)	5.0	4.75	4.5	4.0
Plasma Voltage (volts)	46	47	49	49
Total Deposit Weight (grams)	1700	1800	1800	325
AMZIRC Target No.	2	2	1	1

*Calculated thickness. Machined to 2.997 mm (118 mils) thickness before start of Run 2.

Results and Discussion (Phase III) --

In the four runs a total of 5500 g of AMZIRC was deposited resulting in an average total thickness of 12.29 mm (0.484 in.). The average thickness for each layer and the nature of the interface receiving the deposit in the fatigue specimen gage length are illustrated in Figure 16. The measured thickness as a function of circumferential location is illustrated in Figure 17. The variation in inside contour is illustrated in Figure 18. This variation in thickness contour was the result of nonuniform positive ion flux at the target surface.

The as-deposited surface was rough in appearance, see Figure 19. This resulted primarily from the inability to obtain a satisfactorily machined surface on the first layer of sputter-deposited AMZIRC. Although attempts were made to hand polish the surface, it was still too rough to obtain uniform deposition; protrusions were therefore formed on the deposit. These then perpetuated themselves on succeeding depositions.

The erosion profile, i.e. a total metal removal corresponding to an average deposition of 8.128 mm (0.32 in.) on AMZIRC target 2 after the second use, is illustrated in Figure 20. The "hour-glass" contour was the result of more rapid erosion at the lower end of the target which necessitated end-for-end reversing after the first deposition to maximize utilization.

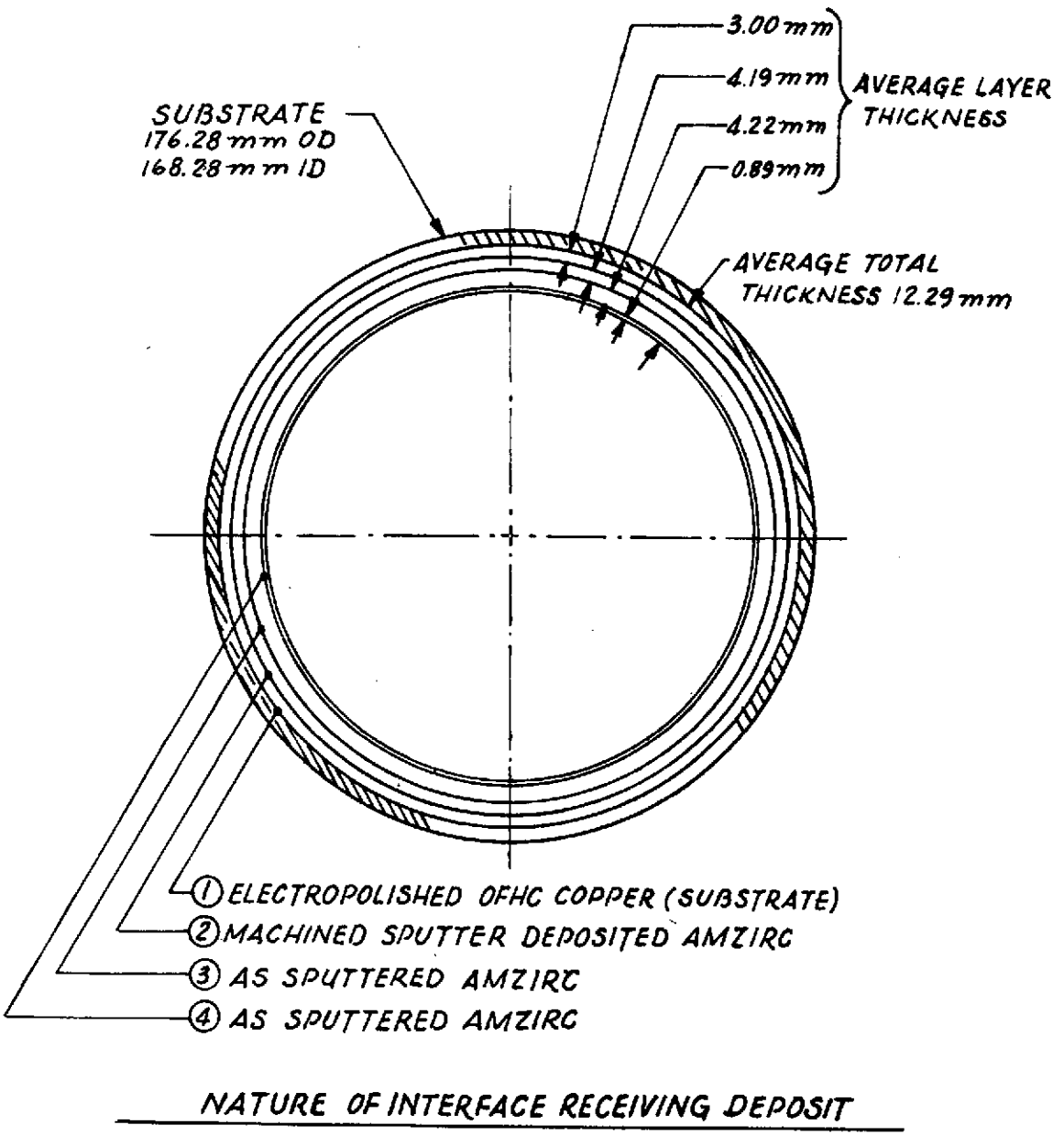


FIGURE 16. Average layer thickness and nature of interface receiving sputtered AMZIRC deposit in fatigue specimen gage length (Fatigue Specimen 2).

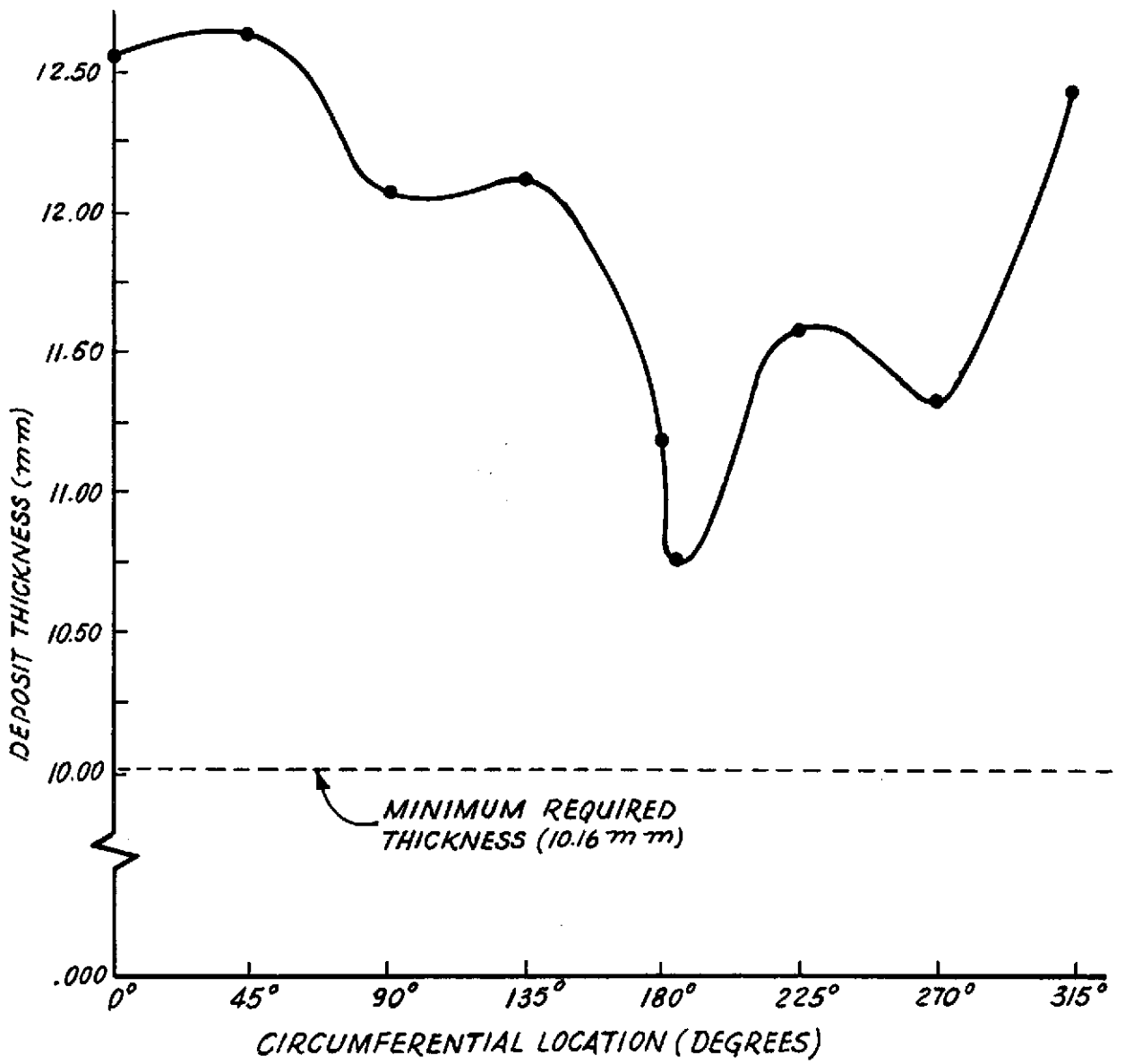


FIGURE 17. Deposit thickness as a function of circumferential location. Each point is the average of three measurements taken at the top, middle and bottom of the gage length (Fatigue Specimen 2).

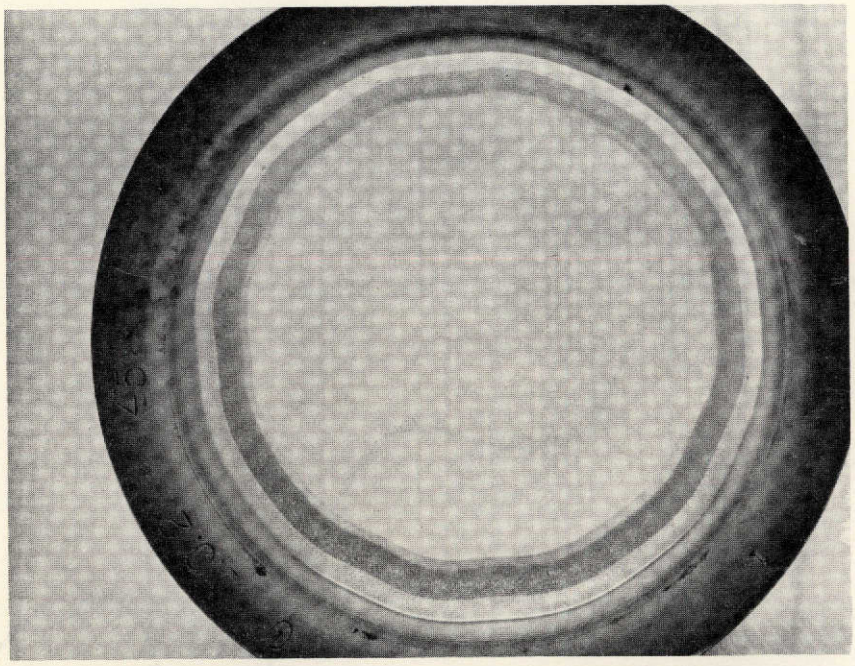


FIGURE 18. Deposit contour on inside of Fatigue Specimen 2 substrate, Irregular or scalloped effect was the result of nonuniform metal removal from the target during sputtering. Approximately 1/2X.

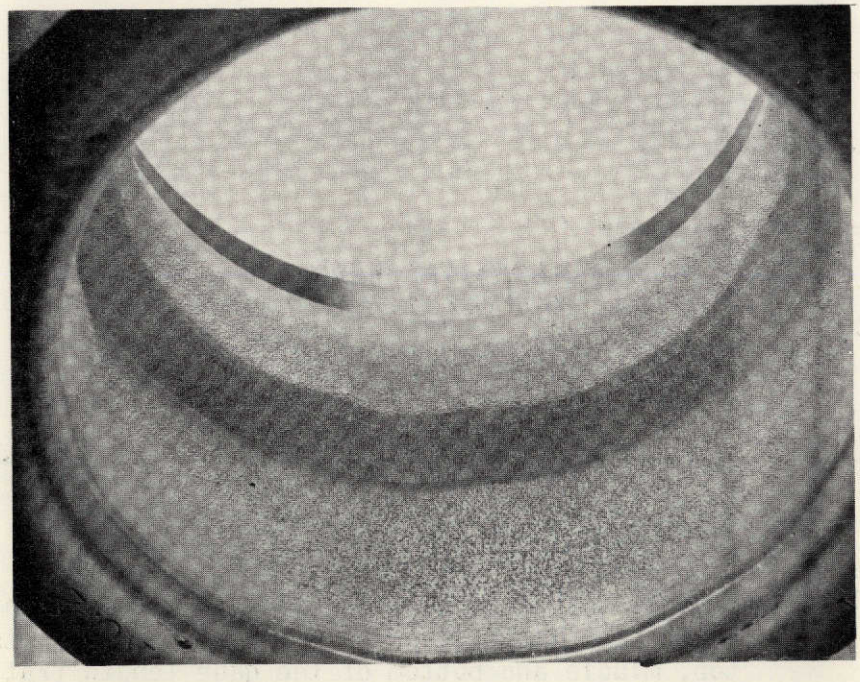


FIGURE 19. Rough or pebbly appearance of sputtered deposit resulted from poor surface finish after first layer of deposit was machined. Approximately 3/4X.

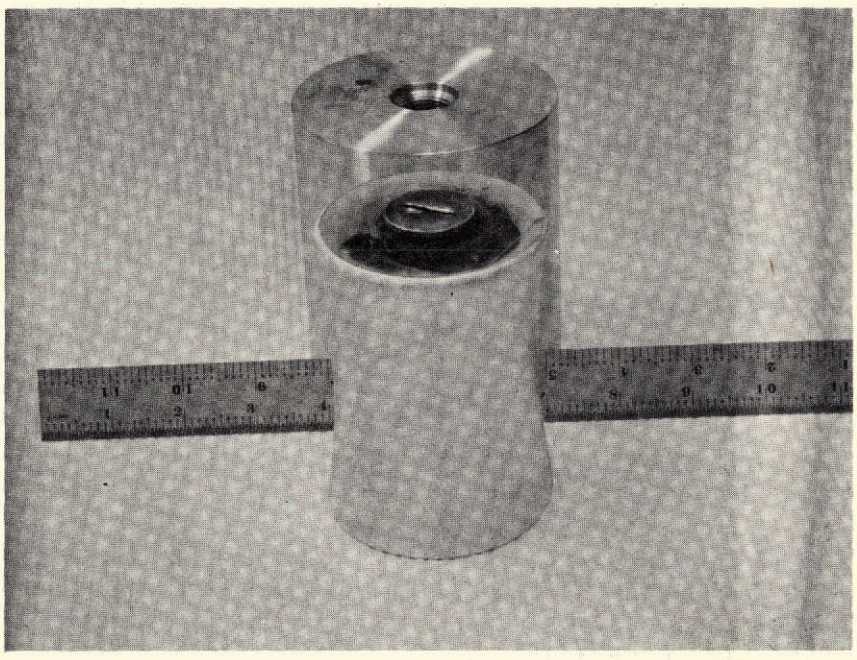


FIGURE 20. Erosion profile on AMZIRC target 2 after second use compared to unused target. Approximately 1/2X.

Sputter-deposited Fatigue Specimen 2 was shipped to NASA October 2, 1973. The three unused substrates were shipped to NASA the same week. Fatigue Specimen 1 has ≈ 0.254 mm (≈ 0.010 in.) of sputter-deposited AMZIRC from the last experiment in Phase II.

CONCLUSIONS

The results of the materials development work support the following conclusions:

- Yield strengths in excess of 900 MN/m^2 at room temperature can be routinely obtained in sputtered deposits of copper-base alloys or dispersion-hardened copper.
- Although these materials exhibit small uniform elongations, they are not generally brittle; this is indicated by reduction in area and fracture surface markings. In particular they are not sensitive to growth defects formed during deposition.
- The mechanical properties of these sputter-deposited materials are in large part due to the extremely fine grain structure and the high density of lattice defects produced by high rate deposition.
- The tensile properties are strongly dependent on the substrate temperature during deposition. In general the dependence is, as expected, to reduce strength and increase elongation with increased substrate temperature.
- The precipitation-hardened alloys exhibit a better combination of strength and electrical conductivity than the dispersion-hardened materials. This behavior was not believed to be intrinsic to these materials but rather was attributed to the effects of oxygen in the sputtering targets for the dispersion-hardened materials on the composition of the deposits.
- The copper 0.15 wt% zirconium alloy (AMZIRC) deposited at the 300°C substrate temperature was selected for the deposition of the required fatigue specimens. The selection of this substrate temperature was in part based on the desire expressed by NASA to avoid postdeposition heat treatment.

The results of the hardware development and fatigue specimen deposition phases of this program support the following conclusions:

- The major problem encountered was the nonuniform positive ion flux at the surface of the cylindrical target. A 37% variation was found along the axis of the target cylinder, being higher at the lower end of the target. A variation of about 20% in the positive ion flux existed around the circumference of the target.

- The surface roughness of the completed thick deposit was greater than desirable. The surface roughness was the result of a less than satisfactorily machined surface obtained on the first deposited layer.

- The suitability of the BNW numerically controlled sputter-deposition equipment for long-term operation at high deposition rates was demonstrated. The resulting deposit is by a factor of at least three the thickest and most massive sputtered deposit known to the authors.

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1. Patten, JW; McClanahan, ED; and Johnston, JW, Room-Temperature Recrystallization in Thick Bias-Sputtered Copper Deposits, J. Appl. Phys., 42, 4371 (1971).

2. Mar-Test Inc., 45 Novner Drive, Cincinnati, Ohio 45215; Report on Task 1 of Contract No. NAS3-16753 (NASA-Lewis), January 15, 1973.

3. McClanahan, ED; and Busch, R, Sputtered Fatigue Specimens, Monthly Technical Progress Narrative (May 4, June 25, August 2, September 4, October 1, and October 23, 1973), Battelle-Northwest, Richland, Washington.