WVT-TR-74005

DEVELOPMENT OF HIGH STRENGTH FILAMENT REINFORCED SUPERALLOY COMPOSITES

I.AHMAD
W.J.HEFFERNAN
J.M.BARRANCO
F.SAEGUSA
R.HASKELL

BENET WEAPONS LABORATORY
WATERVLIET ARSENAL
WATERVLIET, N.Y. 12189

MARCH 1974

TECHNICAL REPORT

AMCMS No. 612105.11.H8400

DA Project No. 1T162105AH84

Pron No. A1-4-RM006-03-AW-M7

DISPOSITION

Destroy this report when it is no longer needed. Do not return it to the originator.

DISCLAIMER

The findings in this report are not to be construed as an official Department of the Army position unless so designated by other authorized documents.

UNCLASSIFIED

SECURITY CLASSIFICATION OF THIS PAGE *(When Data Entered)*

REPORT DOCUMENTATION PAGE

READ INSTRUCTIONS BEFORE COMPLETING FORM

1. REPORT NUMBER: WVT-TR-74005	2. GOVT ACCESSION NO.
3. RECIPIENT'S CATALOG NUMBER	
4. TITLE *(and Subtitle)*: DEVELOPMENT OF HIGH STRENGTH FILAMENT REINFORCED SUPERALLOY COMPOSITES	5. TYPE OF REPORT & PERIOD COVERED
	6. PERFORMING ORG. REPORT NUMBER
7. AUTHOR(s): I. Ahmad, R. Haskell, W. J. Heffernan, J. M. Barranco, F. Saegusa	8. CONTRACT OR GRANT NUMBER(s): AMCMS No. 612105.11.H8400; DA Project No. 1T162105AH84; Pron No. A1-4-RM006-03-AW-M7
9. PERFORMING ORGANIZATION NAME AND ADDRESS: Benet Weapons Laboratory, Watervliet Arsenal, Watervliet, N.Y. 12189, SARWV-RDT	10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS
11. CONTROLLING OFFICE NAME AND ADDRESS: U.S. Army Armament Command, Rock Island, Illinois 61201	12. REPORT DATE: March 1974
	13. NUMBER OF PAGES: 74
14. MONITORING AGENCY NAME & ADDRESS *(if different from Controlling Office)*	15. SECURITY CLASS. *(of this report)*: Unclassified
	15a. DECLASSIFICATION/DOWNGRADING SCHEDULE

16. DISTRIBUTION STATEMENT *(of this Report)*

Approved for public release; distribution unlimited.

17. DISTRIBUTION STATEMENT *(of the abstract entered in Block 20, if different from Report)*

18. SUPPLEMENTARY NOTES

19. KEY WORDS *(Continue on reverse side if necessary and identify by block number)*

Composites	Silicon Carbide	Stress Rupture
Superalloys	Chemical Vapor Deposition	Cyclic Oxidation
Filaments	Tungsten	
Turbine Vanes	Tantalum Carbide	
Turbine Blades	Compatibility	

20. ABSTRACT *(Continue on reverse side if necessary and identify by block number)*

The report describes the progress made during FY 73 on the subject project, the objective of which is to develop high strength filament (tungsten alloys and silicon carbide) reinforced superalloy composites with a rupture life of 100 hours under 30 ksi at 2000°F. Prior studies had shown that W-1%ThO_2 filament or W coated SiC filament can be infiltrated with Mar M-322 (20%W) alloy without significant filament-matrix interaction. Also TaC was found to have very little interaction with molten Mar M-302. Therefore, CVD techniques

SEE REVERSE SIDE

DD FORM 1 JAN 73 1473 EDITION OF 1 NOV 65 IS OBSOLETE

UNCLASSIFIED

SECURITY CLASSIFICATION OF THIS PAGE *(When Data Entered)*

ABSTRACT (Continued)

Block No. 20

to coat filaments with these phases were optimized. W coating on SiC filament was affected by the interaction of WF_6 and H_2 at 730°C on the filament passing through a steel reactor. Conditions for coating TaC were optimized on 0.006" dia. W filament substrate. The filament was first coated with Ta by the reduction of $TaCl_5$ and H_2, and then with TaC by the interaction of $TaCl_5 + CH_4 + H_2$ + He in the temperature range of 950°-1100°C. The stoichiometric and homogeneous TaC was obtained at 950°C.

These filaments were successfully incorporated in the alloy matrices by investment casting technique. Also, a vane of W-1%ThO_2-Mar M-322 (20%W) was successfully cast. Composites of W-1%ThO_2-Mar M-322 (20%W) with 12-16 volume % of the filament had a 100-hour rupture strength of 16.5 ksi at 2000°F, as compared with 7.5 ksi for the commercial Mar M-322 alloy. Results of low volume % composites of tungsten coated silicon carbide and TaC coated tungsten filaments, respectively, in Mar M-322 (20%W) and Mar M-302 are also discussed.

Silicon carbide filament (W core) obtained from AVCO was found to have 2000°F 100-hour rupture strength of 140 ksi (the highest so far reported for SiC filament), as compared with about 85 ksi for W-1%ThO_2 filaments. Cyclic oxidation at 2000°F of the various alloy matrices showed Mar M-322 (20%W) superior to Mar M-322 (20%W), Mar M-302, and Mar M-509.

TABLE OF CONTENTS

	Page
DD FORM 1473	
INTRODUCTION	1
EXPERIMENTAL PROCEDURES	6
RESULTS AND DISCUSSION	13
GENERAL DISCUSSION	23
CONCLUSIONS AND FUTURE PLANS	29
ACKNOWLEDGMENT	30
REFERENCES	31

TABLES

I.	Composition of the Alloy Matrices Used.	32
II.	X-ray Diffraction Data and Microhardness Values of Tantalum Carbon Alloy Coatings Obtained Under Various Experimental Conditions.	33
III.	Short-time Tensile Properties of the Cobalt Alloy Matrices and Composites.	34
IV.	2000°F Stress Rupture Data for SiC (W) Filaments.	36
V.	2000°F Stress Rupture Life of the Alloy Matrices.	37
VI.	Stress Rupture Data of Composite Specimens at 2000°F.	39
VII.	Filament Matrix Zone Thickness as a Function of Time in Mar M-322 (20%W)-W-1%ThO_2 Composite (Investment Cast).	40

FIGURES

		Page
1.	W-1%ThO_2 filaments in Mar M-322 with 25%W.	41
2.	Showing interface between molten Mar M-302 matrix and a TaC disc.	41
3.	Continuous CVD apparatus for coating W on SiC filament: R-steel reactor, L-removable liner, F-furnace, S-spool D-thickness gauge, Hg-mercury seal, LNT-liquid nitrogen trap, V-valve, M-mixer, P-purifier, U-manometer.	42
4.	(a) Shell mold assembly. (b) The cast alloy tree after the refractory shell has been removed.	43
5.	Micrographs of the Mar M-302 alloy cast in the form of bars (a) and tensile specimens x 500.	44
6.	(a) A view of the high vac-high temperature unit incorporated in the Tinius Olsen EH machine.	45
	(b) SATEC stress rupture machines.	45
7.	(a) Showing filament pullout in button shaped specimen.	46
	(b) Final specimen design adopted for stress-rupture tests.	46
8.	DTA crucibles assembly.	47
9.	Effect of gas flow rates on the deposition rate of Ta.	47
10.	Effect of the addition of HCl on the deposition rate of Ta.	48
11.	Effect of temperature on the deposition rate of Ta.	49
12.	Tantalum content of tantalum carbide coating as a function of CH_4 flow rate.	50
13.	Deposition rate of TaC for different CH_4 concentrations in the gas mixture.	51

FIGURES (Cont'd)

		Page
14.	Sectional views of TaC_x coatings deposited at 1100°C, using various CH_4 concentrations in the gas mixture.	52
	(a) CH_4 4:HCl 40: He 255 cc/min. Deposition rate 0.12 mil/min.	52
	(b) CH_4 20:HCl 40: He 240 cc/min. Deposition rate 0.336 mil/min.	52
	(c) CH_4 30:HCl 40: He 230 cc/min. Deposition rate 0.432 mil/min.	52
	(d) CH_4 200:HCl:40:He 60 cc/min. Deposition rate 0.828 mil/min.	52
15.	(a) A TaC coated W filament in Mar M-302 matrix.	53
	(b) Showing the homogeneous TaC coating x 1000.	53
16.	Micrograph of W coating on SiC filament x 1000.	54
17.	Microstructure of as-cast W-1%ThO_2/Mar M-322 (20%W).	55
18.	Section view of a W coated SiC filament-Mar M-322 (20%W) composite.	56
19.	TaC coated W-filaments in Mar M-302 matrix. Notice absence of interaction.	56
20.	A view of a W-1%ThO_2-Mar M-322 (20%W) vane made by investment casting.	57
21.	Typical stress-strain curves of Mar M-322, Mar M-322 (20%W) and Mar M-322 (25%W) alloys and Mar M-322 (20%W)/0.22 V_f W-1%ThO_2 filaments.	57
22.	Fracture mode of room temperature and 2000°F tensile specimens of (a) Mar M-322 (9%W), (b) Mar M-322 (20%W) and (c) Mar M-322 (20%W) + 22-25 volume % W-1%ThO_2 filament.	58
23.	Stress rupture data of SiC (W) at 2000, 2200 and 2400°F.	59
24.	Results of the stress rupture tests on the alloys and composites of W-1%ThO_2/Mar M-322 (20%W).	60

FIGURES (Cont'd)

		Page
25.	Longitudinal section of SiC filament-Mar M-322 (20%W) composite after stress rupture test.	61
26.	TaC coated W filament-Mar M-302 composite after stress rupture test.	62
27.	(a) A sectional view of a TaC coated W filament-Mar M-302 composite specimen after 294 hours at 2000°F.	63
	(b) The same composite specimen after 294 hours at 2000°F.	63
28.	Cyclic oxidation rate of matrix alloys.	64
29.	Weight gain vs. time in the initial stage of oxidation of various alloys shown in Figure 27.	65
30.	Oxidation behavior of composites.	66
31.	A sectional view of a composite specimen after cyclic oxidation showing absence of cracks due to thermal fatigue.	67
32.	A view of the fracture surface of a composite after a 270-hour stress rupture test.	67
33.	An enlarged view of the structure of the oxide layer on the specimen shown in Figure 32.	68

INTRODUCTION

This is the third yearly progress report on the project, the objective of which is to develop filament reinforced superalloy composites suitable for application in advanced jet engine components. The immediate goal is to achieve 100-hour stress rupture life of 30 ksi at 2000°F.

As compared with nickel base alloys, cobalt base alloys have relatively higher m.p. and hot corrosion resistance. Therefore, they were selected as matrix material. (Chromium base alloys are very brittle and thus were not included in this study.) Silicon carbide (AVCO) and tungsten alloy (W-1%ThO_2) filaments, because of their high, elevated temperature properties (at 2000°F, 100-hour stress rupture of approximately 140 and 85 ksi, respectively) were considered to be the best candidates as reinforcements. Incorporation of silicon carbide filament with a density of only 0.125 lb/in^3 could give a composite material with very attractive specific rupture strength. For example, with a Vf = 0.40, using Mar M-322 (at 2000°F, 100-hour rupture stress of approximately 10 ksi, and density approximately 0.3 lb/in^3), the specific rupture strength can be estimated to be [1] 0.87×10^5 and 2.7×10^5 in., respectively, for W-1%ThO_2/Mar M-322, and SiC/Mar M-322 composites. This is to be compared with approximately 0.33×10^5 in for Mar M-322. It will be noted that, even with

---

[1] McDanels, D.L., Signorelli, R.A. and Weeton, J.W. "Analysis of stress-rupture and creep properties of tungsten-fiber-reinforced copper composites." NASA TND-4173, September 1967.

tungsten filament, which is quite dense, specific rupture strength of the alloy can be increased considerably. The objective of this project can be achieved by incorporating approximately 25 vol % of SiC of 35 vol % of W-1%ThO_2 filaments in the alloy matrix.

Studies of the compatibility of these filaments with cobalt base alloys reported in two previous annual reports [2,3] had indicated the following potential composite systems for developments.

A = W-1%ThO_2/Mar M-322* (20-25%W)

B = SiC filament coated with W/Mar M-322 (20-25%W)

C = SiC filament coated with TaC/Mar M-302**

D = W-1%ThO_2 filament coated with TaC/Mar M-302

In A and B, increase of W content in the matrix reduced the interaction of the filament-molten matrix as shown in Figure 1. TaC was found to show very little interaction with Mar M-302 (Fig.2) and was therefore considered to be a potential protective coating for the SiC filament in Mar M-302. In FY 72, some SiC filaments (they were experimental filaments obtained from the General Technology

---

*Nominal Composition of Commercial Alloy: 1.0C, 0.1Mn, 0.1Si, 21.5Cr, 9.0W, 0.75Ti, 2.0Zr, 4.5Ta, balance Co.

** " " " " " 0.85C, 0.1Mn, 0.2Si, 21.5Cr, 10W, .005B, 0.20Zr, 9.0Ta, balance Co.

[2] Ahmad, I., Barranco, J.M., Loomis, K.E. and Heffernan, W.J. "Metal Matrix Composites for High Temperature Application." An interim report FY 1971. WVT 7155, October 1971.

[3] Ahmad, I., Barranco, J.M., Heffernan, W.J. and Loomis, K.E. "Metal Matrix Composites for High Temperature Application." An interim report FY 1972. WVT 7266, December 1972.

Corp., Md.) were coated with W by CVD on contract with the San Fernando Labs and were successfully incorporated in Mar M-322 (25%W) by infiltration. A continuous process for CVD coating of tantalum carbide on 6 mil tungsten filament was successfully developed. By the end of FY 72, while adherent coating on the filament was obtained, it was not, however, of desired stoichiometry and showed interaction with molten Mar M-302.

The composites of A and B systems were fabricated by the infiltration technique in the laboratory. The 900°C tensile strength and 2000°F rupture strength (one value) of some of these composites were also reported. Some preliminary results on the long period stability (at 2000°F) and oxidation resistance of W-1%ThO_2/Mar M-322 (25%W) were also discussed.

During FY 73 some of the salient accomplishments were:

Development of CVD Coating Processes

a. Apparatus for the coating of W on the continuous silicon carbide filament was set up and the process was optimized.

b. TaC coating: Conditions for achieving TaC coating of desired stoichiometry on continuous 6.0 mil tungsten filament was optimized. The quality of the coating was proven by incorporating the filament in Mar M-302 by the commercial investment casting process. No interaction of the matrix with the coating was observed

(Fig. 19). Current studies are addressed to achieving homogeneity of the TaC coating by controlling the temperature profile along the filament in the reactor.

Fabrication of Composites

a. Composites of W-1%ThO_2 filament/Mar M-322 (9, 20, and 25%W), tungsten coated SiC filament/Mar M-322 (20%W), and TaC coated 6.0 mil W filament/Mar M-302 have been successfully fabricated by the commercial investment casting technique.

b. Attempts to cast turbine vanes from W-1%ThO_2/Mar M-322 (20%W) were also successful. Presently, dies are being designed to cast vanes and blades from these composites.

Testing and Fractography

1. In FY 72, equipment for tensile testing above 900°C was not available. During FY 73, a high temperature-high vacuum equipment was installed and tensile data at room temperature (R.T.) and 2000°F were obtained on Mar M-322 (20%W) and W-1%ThO_2/Mar M-322 (20%W). The latter showed, essentially, a ductile fracture and the 2000°F tensile strength of the composite followed rule of mixtures.

2. Rupture stress: Stress rupture properties of AVCO silicon carbide filament were measured at 2000° and 2200°F. This filament was found to be superior to the GTC filament. It had a 100-hour rupture strength of 140 ksi at 2000°F, as compared with 100 ksi for GTC filament mentioned in the 1972 report. Data were also obtained at 2200°F.

Three new Satec Stress Rupture machines were installed. Composites of W-1%ThO_2/Mar M-322 (20%W) containing 12-18 vol % filament tested in air at 2000°F showed a 100-hour rupture stress of 16.5 ksi. A specimen with 16.6 Vf filament had a rupture life exceeding 1800 hours, indicating an improvement of 18 times over the conventional Mar M-322 alloy. Also, incorporation of only 5% tungsten coated silicon carbide filament in Mar M-322 (20%) matrix showed a considerable improvement in life of unreinforced matrix. Metallography of sectioned specimens showed multiple fracture in the body of the composite. Similarly, an incorporation of 5 vol % TaC coated W-filament improved the rupture life of Mar M-302 by a factor of 3, at 2000°F and 10 ksi load.

Long-Period Stability and Oxidation Studies

1. The growth rate of the interaction zone of W-1%ThO_2 filament in Mar M-322 (20%W) matrix specimens maintained for 250-500 hours at 1900 and 2100°C were measured.

2. Oxidation (cyclic) behavior of Mar M-322 with 9, 15, 20, and 25%W, Mar M-509, Mar M-302, and IN713C alloys at 2000°F in air saturated with water vapor (60°C) was studied. Mar M-322, with 20%W but no Zr, was found to be superior to Mar M-322 (9 and 25%W), Mar-302, and Mar M-509.

In the following, the experimental details and results obtained will be briefly described and discussed.

EXPERIMENTAL PROCEDURES

Materials

Matrix alloys: Mar M-322 (9%W), Mar M-322 (20%W), Mar M-322 (25%W), and Mar M-302 were prepared under contract with the General Electric Company, Schenectady, New York. Compositions as given in Table I were vacuum melted and cast in the form of bars.

A few alloys were prepared in the laboratory from the constituent powders as described in the previous report [2].

Filaments: Mainly, 0.030" dia. W-1%ThO_2 and 0.004" dia. SiC filaments were used. The former were procured from General Electric, Cleveland, Ohio, and the latter were supplied by AVCO. According to the supplier, the room temperature tensile strength of the two filaments were 200 ksi and 450 ksi, respectively.

Chemical vapor deposition of TaC: The process and equipment were described in the previous report. Essentially, 0.006" dia. tungsten filament was continuously passed through (5"/min) a reactor (25" long) where it was resistively heated to 900-1100°C. Electrical connections to the filament were through mercury seals. A mixture of $TaCl_{5(g)}$ (made in situ by passing of $HCl_{(g)}$ through a column of Ta chipsat 800°C), CH_4, and He were introduced in the reactor through a side tube. The components reacted at the hot filament to form the

---

[2] Ahmad, I., Barranco, J.M., Loomis, K.E., and Heffernan, W.J. "Metal Matrix Composites for High Temperature Application." An interim report FY 1971. WVT 7155, October 1971.

carbide. The gaseous products and unused reactants were condensed in a liquid N_2 trap. During FY 73, the setup was improved by providing a variable speed (0.06-2 rpm) motor to drive an 8" clutch control take-up spool and a similar clutch controlled 8" feed spool. Also, to monitor the thickness of the filament, a General Electric diameter gage was placed in between the reactor and take-up spool. However, for data reported here, the diameter measurements were made with a Vickers image-splitting eyepiece. Using this setup it was possible to study the effect of the variation of the composition of the reactant gases, temperature and flow rates on the composition and rate of deposition of the coating.

To determine the phases present, coating removed from the filament was powdered and subjected to X-ray diffraction analysis by using a Debye-Scherrer camera with Cu K α radiation and a 7-hour exposure. Lattice parameters of selected specimens were also calculated from these diffraction patterns.

The Ta content of the deposit was determined by chemical analysis [4] in which powdered specimen was converted to Ta_2O_5 by heating in air in a muffle furnace at 1000°C for one hour. From the weight of the oxide, the Ta content and, consequently, carbon content of the coating were calculated. As a check, the total carbon of a specimen from the same coating was also determined by volumetric analysis [5]

---

[4] Samsonov, G.V. and Pilipenko, A.T. "Analysis of the high temperature melting compounds," Clearing House for Federal Scientific and Technical Information, U.S. Department of Commerce (AD 603009).

[5] Kazunobu Kodama. "Methods of Quantitative Inorganic Analysis," Interscience Publishers, John Wiley, New York, p. 460, 1963.

which consisted of burning the sample in an iron-tin bath at 1500°C and then determining the CO_2 content in the combustion products by absorbing it in known volume of standardized KOH solution. The results from the two methods agreed reasonably.

CVD tungsten coating: Reduction of $WF_{6(g)}$ with H_2 at the heated filament was the process used to deposit tungsten on silicon carbide filament. Helium was used as carrier gas. Preliminary runs made to resistively heat SiC filament were not successful, as the latter is a poor conductor of electricity. It was therefore decided to apply an initial flash of tungsten on the filament surface by externally heating the reactor through which $WF_6 + H_2 + He$ gas mixtures were introduced. This made the filament electrically conducting, whereby it could be resistively heated and coated with tungsten. The filament from the take-up spool was led through the first reactor which was a 1" dia, 20" long stainless steel tube heated externally by means of a split Hoskins furnace. Then it went into the second (pyrex glass) reactor through mercury seals which were also used as electrical connections. WF_6, H_2, and He measured with suitable flowmeters were introduced in the second reactor first, and then through the first on a counter-current principle. The unused reactants and the products were condensed in liquid N_2 trap. A mass flowmeter was used for $WF_{6(g)}$. The copper lines and valves bringing WF_6 into the reactor were kept hot by means of heating tapes to avoid condensation.

He gas jets provided as shown, helped keep the filament from developing hot spots near the mercury seals. At a later stage only one reactor (first) was used. The setup is schematically illustrated in Figure 3.

Fabrication of composites: The procedure for the fabrication of W-1%ThO_2 filament in Mar M-322 in the laboratory has been described in reference [3]. In this process, pre-mixed powders were compressed into slugs under pressure (10-20 ksi) and melted under vacuum in a graphite crucible-mold assembly with alumina refractory lining and contained in a water-cooled glass envelope. The crucible-mold assembly was inductively heated. For composite fabrication, premelted slugs (sometimes melted twice to homogenize the composition) were used. The filaments were pre-aligned in the mold. When the charge melted in the crucible,it flowed into the mold encapsulating the filaments.

This process was time-consuming. Therefore, in FY 73, investment casting technique [6] was used to cast the specimens. In this technique, patterns of the specimens were made in wax. They were added to the wax pattern of the main assembly (tree) which included gates and runners. The assembly was then dipped in a thin slurry of mold refractory. This was repeated 8-10 times until the desired thickness (3/8") was achieved. It was then covered with dry stucco

---

[3] Ahmad, I., Barranco, J.M., Heffernan, W.J., and Loomis, K.E. "Metal Matrix Composites for High Temperature Application." An interim report FY 1972. WVT 7266, December 1972.

[6] Heibeisen, M.C. et al. "Vacuum Melting and Casting of Superalloys," NASA SP-5095, 1971.

grains. This shell mold was dried (24 hours) and heated to melt out the wax. The shell was baked for one hour at 900°C in a 10^{-4} torr vacuum. Prior to casting, while the charge was being heated in the vacuum induction melting unit, dry sand contained in a ceramic lined can was heated to 1000°C in a gas-fired furnace. It was then quickly taken out and the shell mold was inserted in the sand and the can was then transferred to the vacuum chamber of the vacuum induction unit. The chamber was evacuated rapidly (within one minute) to a pressure of 10^{-3} torr. The molten metal was then poured into the mold. A super-heat temperature of about 250°C was used in all these castings. After five minutes, the chamber was brought back to atmospheric pressure. The mold was taken out. The mold was allowed to cool for 24 hours after which the shell was broken off by light hammering. Figures 4(a) and (b) show the shell mold after casting and the casting after the shell had been removed.

In the initial runs the castings were in the form of 3/4" dia. and 4" long cylinders from which the specimens were machined. Later, the appropriate die was made to cast the alloys and composites directly into the form of tensile specimens. However, this presented problems. The gauge length area of the specimen did not have complete infiltration because of the rapid cooling of the melt. To solve this problem, introduction of the melt through the side of the mold is being investigated.

For composites, arrangements in the wax pattern were made to align bundles of filaments in the center of each specimen.

Figure 5 shows the micrographs of the sections of both cylindrical and tensile configuration castings of Mar M-302. It will be noticed, the former have a more developed structure than the latter. This may result in different mechanical properties for the two castings. In fact, as will be described later, this was found to be the case.

Determination of Mechanical Properties

Short-time tensile strength: In FY 73 a high vacuum-high temperature unit was incorporated in the Tinius Olsen electrohydraulic testing machine (Fig. 6(a)) with which it was possible to determine short-time tensile strength of the composite at 2000°F. In these tests the grips were machined from TZM. Button-end type of specimens were used. No pullout was observed. All the test data reported here were obtained at 2000°F and 10^{-4} torr. Initially, seizing of the grips became a problem. It was successfully solved by using a thin alcoholic slurry of fine polishing alumina at the contact surfaces.

Stress rupture: Three additional machines (SATEC) of 5000 psi capacity were installed (Fig. 6(b)) to determine rupture strength of the specimens at 2000°-2200°F. The tests were conducted in air. Mar M-509 was used as the grip material. In these tests with the

button-end specimens, filament pullout was observed. Figure 7 shows a W-1%ThO_2/Mar M-322 (20%W) specimen which was tested under 10 ksi at 2000°F. The specimen did not fracture, but the grips of the specimen sheared off from the filament. Thereafter, the tapered end type of specimens were used in all these tests. Figure 7(b) illustrates the grip assembly that is currently being used.

The equipment for the measurement of rupture stress of silicon carbide filament was described in the previous report [3].

Oxidation studies: Cyclic oxidation behavior of the matrix alloys used in this study and composites was investigated at 2000°F [7] by exposing specimens (3/8" dia. x 1/8" thick) to air which was saturated with water vapor at 60°C at a flow rate of 4 cu ft/hr. At one-hour intervals the specimen was removed from the furnace, cooled to room temperature, weighed, rotated, and returned to the furnace. The specimen was weighed every hour for the first five hours then at the seventh and tenth hours, and every five hours thereafter. After a total of fifty hours of exposure, the specimen was examined metallographically.

Long-period filament-matrix interface stability: Composite specimens in the form of 0.5" long slugs were exposed to 2000° and 2100°F in He in a resistively heated furnace for periods of time ranging from 50-500 hours. After they were taken out they were

---

[3] Ahmad, I., Barranco, J.M., Heffernan, W.J. and Loomis, K.E. "Metal Matrix Composites for High Temperature Application." An interim report FY 1972. WVT 7266, December 1972.

[7] Ohnysty, B. et al. "Test manual evaluation of Composite Materials for Gas Turbine Engines," AFML TR-66-156, Part III, March 1968.

sectioned, polished, and examined metallographically. Reaction zone thicknesses were measured from enlarged micrographs at five random locations. Also, electron microprobe scanning was used to gain information on the nature of the interaction zone.

Determination of m.p. and Other Phase Transitions

The differential thermal analysis (DTA) technique was used to determine the m.p. of the matrix alloys. The measurements were made using a microcrucible of aluminum oxide, 4 mm dia., placed in a platinum cup to which thermocouple wires were welded. The whole assembly is shown in Fig. 8. The alloy samples were crushed and pulverized to -60 mesh. Ten mg of the specimen were weighed and loaded in the crucible. For reference material platinum powder was used. The sample was pre-melted in the apparatus under argon and DTA and TG (thermogravimetric) traces were then recorded simultaneously at the heating rate of 4°C/min.

RESULTS AND DISCUSSION

Chemical Vapor Deposition of TaC

In Reference [3], the elimination of the brittleness of tungsten substrate (0.006" dia.) by initial application of thin Ta coating, by the reduction of $TaCl_5$ with H_2 on the filament, was reported. Study of the variation of CH_4:HCl molar ratio in the reacting gases had shown that good TaC coating free of Ta_2C phase was obtained at 1100°C using 100cc/min He:50cc/min CH_4:25cc/min HCl.

---

[3] Ahmad, I., Barranco, J.M., Heffernan, W.J. and Loomis, K.E. "Metal Matrix Composites for High Temperature Application." An interim report FY 1972. WVT 7266, December 1972.

During FY 73, to achieve the optimum conditions for the deposition of Ta, the effect of the total flow rate on the deposition rate of Ta (Fig. 9) was investigated. The decrease of deposition rate for high flow rate was thought to be caused by free HCl entering the deposition chamber. The possibility was checked and confirmed by adding free HCl to the deposition chamber. The results of this experiment are shown in Figure 10. From these runs it was decided to deposit tantalum at 1000°C using molar ratio of 5 HCl:20 H_2:40 He at a flow rate of 325cc/min. Figure 11 shows the effect of temperature on the deposition rate of Ta. The figure also shows the Arrhenius plot for tantalum carbide, but it was not stoichiometric, because it was deposited from high methane gas mixtures.

Further studies were then made to achieve stoichiometric TaC. Some runs with varying flow of HCl (5-25cc/min) into the chlorinator had indicated that this parameter did not affect either the rate of deposition or the composition of TaC. Therefore, the major effort was focused on varying CH_4 while maintaining HCl concentration rates constant. The sum of the flow rates of CH_4, HCl (in the chlorinator) and He was also kept constant. Runs were made both at 1100°C and 950°C using HCl in the chlorinator and also at 1100°C using chlorine gas in the chlorinator. The speed of the filament was kept constant at 5.5" per minute. The thickness of the coating was measured by an image splitting eyepiece and the tantalum content of the coating was determined, as described in the previous section. The composition of the coatings obtained at various CH_4 flow rates is

shown in Figure 12. The deposition rates obtained in these runs are plotted in Figure 13. It will be noticed that at 1100°C, the rate of deposition for both HCl and Cl_2 series are identical. During these runs the color of the coating was observed to change from silver to golden yellow to carbon black as the CH_4 concentration was increased. The chemical composition and the data from X-ray diffraction analysis are summarized in Table II. Figure 14 (a)-(d) shows the enlarged view of the transverse section of the filaments, coated under different conditions. Some optical activity was observed under polarized light in specimens containing large amounts of Ta_2C. The best coating with stoichiometric composition was obtained under conditions (25-30cc/min CH_4) indicated in Figure 12 as hashed region which is the TaC phase field calculated from the equilibrium phase diagram.

Currently work is in progress to solve the problem of in-homogeneity of these coatings. Some runs made at 950°C and corresponding CH_4 flow rate read from Figure 12, have given a relatively homogeneous coating as is shown in Figure 15 (b). This coating is being evaluated.

To confirm if the desired TaC coating had been achieved, some filaments under these conditions were infiltrated with molten Mar M-302 (by investment casting). The sectional view of one of these filaments is shown in Figure 15 (a). The sharp filament-matrix interface shows absence of noticeable interaction. Microhardness measurements made with a 5 g. load, indicated that the outermost layer was TaC. Data on the microhardness measurements on filaments shown in Figure 14 are summarized in Table II.

CVD of W Coating on Silicon Carbide Filament

In the initial runs the temperature of the furnace around the first reactor (steel tube) was first brought to 550°C, followed by applying direct power to the filament through the mercury seals. The furnace temperature was then decreased to 350°C. Under conditions of 140cc/min He, 15cc/min WF_6, 45cc/min H_2, and the filament speed of 5.5 in/min, a coating of 0.0015" thickness was obtained. However, it was brittle and did not adhere to the filament satisfactorily.

Subsequently, the problem was solved by increasing the furnace temperature to 730°C to achieve initial W coating in the first reactor by simple radiative heating and then in the second reactor applying power to the filament through the mercury seals for further buildup. The flow rate of the reactive gas had also to be increased because much of the W was being deposited on the walls of the first reactor due to the increase of the temperature. Typical run conditions were:

Resistive Power (Second Reactor)	Gas Flow cc/min			Furnace Temp. °C (First Reactor)	Buildup
	WF_6	H_2	He		
0	70	560	200	730°	0.0009"
38V, 2 amp	"	"	"	"	0.0017"

For the protection of the filament from molten matrix (Mar M-322 20%W), roughly .0003" thickness of tungsten coating is required. It is believed that this thickness could be easily accomplished by increasing the speed of the filament. A typical microstructure of the

W coating on SiC filament is shown in Figure 16.

Fabrication of Composites and Testing

The following type of castings were made by the investment casting technique:

1.	W-1%ThO_2/Mar M-322 (25%W)	Cylindrical specimen
2.	W-1%ThO_2/Mar M-322 (20%W)	" "
3.	W-1%ThO_2/Mar M-322 (20%W)	Tensile specimen
4.	W coated SiC filament/Mar M-322 (20%W)	" "
5.	TaC coated tungsten filament (0.006"dia)/Mar M-302	" "

Each of these castings had twelve specimens on the tree. On each tree a number of specimens were without filament. These were used to obtain data on the matrix. The W-1%ThO_2/Mar M-322 (20%W) composite specimen came out nearly flawless (Figure 17), while those with Mar M-322 (25%W) showed some microcracks. Casting of all tensile shaped specimens did not result in proper infiltration of the filament. This may be due to the relatively thinner gage section which did not allow the melt enough time to infiltrate because of relatively quicker solidification. The same was observed when TaC coated W filament/Mar M-302 was cast into tensile specimen configuration. However, in the grip section there was good infiltration. The micrographs of the as-cast composites of W-coated SiC filament and TaC coated W filament are shown in Figure 18 and in Figure 19. Notice the lack of any excessive filament matrix interaction.

Casting of Turbine Vanes

Encouraged by the successful casting of W-1%ThO_2 filament composites, it was considered of interest to show the feasibility of casting a composite vane or blade. To achieve this, wax patterns of a turbine vane were hollowed in the middle with a sharp knife and bundles of tungsten filament were inserted in each. These patterns were then fixed on the tree and by using the process described earlier, a vane was successfully cast using Mar M-322 (20%W) alloy. Micrograph of a section of such a blade is shown in Figure 20.

Testing and Fractography

Tensile tests: Short-time tensile strength of the matrix alloys and composites was determined both at room temperature and 2000°F (in vacuum). The data are summarized in Table III. Typical room temperature stress-strain curves for Mar M-322 (9%W), Mar M-322 (25%W), a blank Mar M-322 (20%W) and Mar M-322 (20%W) composite are reproduced in Fig. 21. The elongation was determined by measuring the total length of the two fractured pieces of the specimen. The room temperature fracture of both the blank alloy and the composites were essentially brittle. However, at 2000°F, 25.5Vf% W-1%ThO_2 filament/Mar M-322 (20%W) composite showed a ductile fracture (% elongation 7.1) (Fig.22). Also, the data indicate that Mar M-322 (20%W) was at least as good as Mar M-322 in short-time tensile properties. For comparison, tensile property data on Mar M-322 (25%W), with and without filaments, taken from the previous year's report are also included. Also, the tensile strength values of W-1%ThO_2 filament determined in the laboratory are recorded.

Stress Rupture Tests

SiC filament: The mean values of the stress rupture obtained to date at 2000°F, 2200°F, and 2400°F are given in Table IV. They are also plotted in Figure 23.

Alloys: The 2000°F stress rupture tests on the alloy matrices are summarized in Table V and shown in Figure 24. As will be seen, the average stress to fracture in 100 hours for the Mar M-322 (9%W) i.e., commercial alloy, is 7.5 ksi as compared with the published value of 10 ksi. During these tests it became clear that, except for those specimens with filaments not completely encapsulated in the matrix, there was no special advantage of testing the specimen in helium. Therefore, most of the data reported here were obtained in air. All the data in helium was obtained on a 0.125" dia. specimen prepared in the laboratory, while those tested in air were investment cast and had a diameter of 0.25".

Mar M-302 alloy required for TaC coated filaments was also tested. The 2000°F value in air for specimen 36 was close to the literature value. However, this specimen was machined from a cylindrical bar 3/4" diameter, prepared by investment casting. The second value for specimen 33 was lower. This specimen was cast directly into tensile specimen geometry with 0.25" diameter. Micrographs of the polished sections of these specimens, in Figure 5(a) and 5(b), show that in the former the carbide precipitates were relatively more developed than the latter.

Composites

As mentioned earlier, composite specimens cast directly into tensile geometry were defective. These included W-coated SiC filament/Mar M-322 (20%W), and TaC coated W filament Mar M-302. Therefore, the data reported here are mostly on the specimens of W-1%ThO_2 filament machined from cast composite bars. A few specimens of silicon carbide, although defective, were also subjected to stress rupture tests. The data will be briefly discussed in the following.

W-1%ThO_2/Mar M-322 (20%W): These specimens were machined from composite bars. In some cases the filaments were exposed in the gage area and oxidized during the run; therefore, the filament Vf was determined after the test from the micrograph of a section of the specimen. The data are summarized in Table VI and shown in Figure 23. Because of machining requirements the Vf in these composites has been, in general, low. However, even at 16.6 vol % filament, the life of the composite was more than 18 times that of the commercial alloy. This specimen, in fact, did not fracture. The test was voluntarily stopped.

At higher stress levels, the grip fixtures gave trouble. Initially, grips made from 713C alloy were used, but they deformed and failed when a 15 ksi load was used. Mar M-509 was found to be better but, still, in longer runs, some deformation was apparent.

Only a limited supply of W-coated SiC filament was available. Therefore, in the initial stage, a few composites containing only 5.6 vol % of the coated filament in Mar M-322 (20%W) were cast.

A transverse section examined metallographically showed a majority of the filaments unaffected. Some with perhaps poor coating were attacked by the molten matrix. This composite survived for more than nine hours under 10 ksi at 2000°F. Longitudinal section of the fractured specimen polished metallographically (Figure 25) shows multiple fracture in the body of the composite. The cracks in the filament were essentially normal to the direction of the applied stress. However, they did not propagate in the body of the matrix. Similarly, specimens of Mar M-302 containing very low volume fraction of TaC coated W filament were subjected to stress rupture tests at 2000°F. The data are included in Table VI. In spite of the poor infiltration of these filaments, as mentioned under "Fabrication of Composites", the composites had a life roughly (290 hours) three times that of the standard Mar M-302 (100 hours). Figure 26 shows filament pullout in a fractured specimen showing lack of matrix infiltration in the body of the filament bundle. Metallographic examination of the filament-matrix interface in specimen 34 (which lasted 294 hours), showed no recognizable increase in the interaction zone thickness (Fig. 27 (a) and (b). This may be compared with the long period filament-matrix interaction data on W-1%ThO_2-Mar M-322 (20%W) composites, presented in Table VII.

Oxidation Behavior of the Matrix Alloys

In the FY-72 report, preliminary data on the oxidation of Mar M-322 with 9%, 20%, 25%W, and Mar M-302 in dry air at 2000°F was reported. In FY-73, cyclic oxidation studies of these alloys in air with 10-14 vol % moisture were made. Figure 28 shows a plot of weight gain against

time. It is seen that the resistance to oxidation is in order Mar M-322 (20%W) > Mar M-322 (25%W) > Mar M-302 > Mar M-322. It must be pointed out here that the Mar M series of alloys were prepared in the laboratory without the addition of Zr. A plot of the square of weight gain vs. time during the initial stage, shown in Figure 29, indicates that the oxidation kinetics are governed by the parabolic rate law.

Some specimens of W-1%ThO_2/Mar M-322 (25%W) were also subjected to the cyclic test. The preferential oxidation of the filament resulted in weight loss after about five hours (Fig. 30). This was solved by sputtering platinum on the ends of the specimen. The main conclusion to be drawn was that after fifty hours of thermal cycling involved in this test, the filament-matrix interface did not show formation of cracks due to thermal mismatch (Fig. 31).

In the first ten hours or so, Mar M-322 alloys containing Zr (2%) behaved essentially similar to the ones without it; but then the oxidation kinetics became essentially linear, indicating cracking of the oxide filament or high porosity. Examination of specimen 20, (Table VI), which lasted more than 1800 hours, showed, however (Fig. 31) a dense film growth. Figure 33 is a composite picture of the magnified views of the oxide layer. At this time no effort was made to identify the various zones in this micrograph. Apparently, the outermost layer (Zone 1, amorphous) is CoO. Beneath it (Zone 2) is probably a mixture of CoO and $CoCr_2O_4$ (and perhaps some $CoWO_4$). Adjacent to this layer

is an internal oxidation zone (Zone 3) in which the carbide precipitates have been oxidized. Some preferential oxidation along the grain boundaries was also observed. Zone 4 is the alloy, Zone 5 is the filament-alloy interaction zone, and Zone 6 is the tungsten filament.

Melting Points of the Alloy Matrices

A series of DTA/TG curves of Mar M-322 and Mar M-302 (20%W) were obtained at a heating and cooling rate of 4° per minute. Distinct endothermic breaks were observed for both the alloys, which gave the melting points of 1425° and 1445°C, respectively. No other transition during heating or cooling was observed.

GENERAL DISCUSSION

W-1%ThO_2 - Mar M-322 (20%W) Composites

It can easily be shown that by introducing approximately 35 volume % of W-1%ThO_2 filament or 20 volume % of SiC filament in the cobalt alloy matrix, the goals of this study could be achieved. Significant progress has been made this year in this direction, in that the conventional investment casting technique was applied to fabricate these composites. It was particularly successful when the specimens were in the form of cylindrical bars. However, in the initial stage of this development, there was a problem of centering the filaments. Therefore, after machining these bars into tensile specimens the filament volume fraction in the gauge section was not constant and was generally between 12-18 volume %. This is reflected in the

stress-rupture curves shown in Figure 24.

Major changes in the technique will be required to achieve good infiltration to cast composites directly into the tensile specimen. One of the possibilities that is being explored is pouring the melt from the side of the mold, so that the gauge area in the bundle of the filament sees the melt at its optimum temperature for infiltration.

At this time the authors believe that except for a few minor improvements of the casting technique, there is no major hurdle in fabricating .35 Vf W-1%ThO_2/Mar M-322 (20%W) composites. Even with .12-.16 Vf, the 100 hour rupture stress of the composite is 16.5 ksi as compared with 7.5 ksi for the standard alloy. Also a composite containing 16.6 volume % filament showed 10 ksi rupture life in excess of 1800 hours, which is 18 times better than the commercially quoted value for Mar M-322.

The stress rupture data on the Mar M-322 (20%W) at 2000°F shows that the addition of tungsten decreases the rupture stress but not greatly. Considerable influence of the microstructure of the matrix on the rupture life was noticed. For example, Mar M-322 (20%W) alloy specimen machined from the bar had a life of 707 hours under five ksi load at 2000°F as compared with 589 hours for the one cast directly into a tensile specimen. The same was true with Mar M-302 alloy (table). As shown in Figure 5(a), in the bar specimen the microstructure is relatively more fully developed because of the longer

cooling time involved than the other specimen 5(b). This may also be the reason of low rupture life for the standard Mar M-322 alloy obtained in this study as compared with that reported in the commercial literature. The values in the commercial literature could be for large specimens, with fully developed microstructure.

The authors are cognizant of the possibility of making the Mar M-322 matrix more prone to TCP phase formation by increasing its tungsten content. For example, the $\overline{N}_V$, calculated for the Mar M-322 composition with 20%W used in this study is 2.78 which is slightly higher than the critical value of 2.7 for cobalt base alloys [8]. It is estimated that by decreasing the W content to 15 W-%, the $\overline{N}_V$ number can be brought below this critical value. However, at this time, it is not clear how the embrittling effect of sigma phase will influence the performance of the composites containing filaments.

More work is necessary to optimize the composition of the matrix required for these composites. In particular, it will be worthwhile to modify the alloy composition (as for example by the addition of rare earth metals like Ya, La) to improve their oxidation resistance. In the present study Mar M-322 (20%W) containing no Zr has been found to be relatively more resistant to cyclic oxidation than the Mar M-322 or Mar M-302 alloy. The reason for this improvement is not understood as yet. One of the encouraging results of these oxidation studies is that exposure to cyclic heating and cooling did not induce cracking at the filament-matrix interface of the composite specimen (Fig. 31).

---

[8] Sims, Chester T., J. Metals, pp. 27-42, December (1969).

Silicon Carbide Filaments

In spite of the statement in the introduction, with effect to the high specific rupture stress of tungsten filament-Mar M322 (20%W) composite, as compared with the unreinforced matrix, the use of lighter filament reinforcement such as silicon carbide is much more preferable. In FY 1972, the stress rupture data on an experimental batch of silicon carbide filaments manufactured by General Technology Corporation was reported. Since then AVCO optimized the process with which they could produce silicon carbide filament of uniform quality with tensile strengths between 450-500 x 10^3 psi (as compared with 250-300 psi for GTC filament). Stress rupture data shown in Figure 23 clearly shows the superiority of these filaments both to the GTC filament and W-1%ThO_2. Even at 2200°F the rupture stress of these filaments is superior to W-1%ThO_2. At the time of the writing of this report AVCO reported the successful preparation of silicon carbide filament with graphite core, with room temperature strengths approaching 600,000 psi, which makes this filament an extremely attractive reinforcement. Presently, 2000°F rupture life of these filaments is being measured by the authors.

Coated SiC Filaments - Cobalt Alloy Composites

Figure 25 (a) clearly demonstrates the feasibility of the incorporation of silicon carbide filaments coated with W in Mar M-322 (20%W). Because of the initial difficulty with investment casting of composites with tensile bars, sound specimens with 0.30 Vf filament could not be

prepared prior to this reporting. But even with very low filament content in a defective matrix specimen, improvement in the rupture life was achieved. Also, the longitudinal section shown in Figure 25 (b) indicates multiple random fracturing of the filament in the body of the composites, indicating efficient load transfer on the filaments. It is hoped that in the very near future it will be possible to obtain good composite specimens for further evaluation.

The tungsten coating process of the silicon carbide is not yet the optimum one. There are two major problems: (1) Silicon carbide is a poor conductor, requiring considerable electric power to bring the filament to the requisite temperature (600-700°C). But as soon as the tungsten coating is started, tungsten, being a good conductor, draws most of the current, thereby decreasing the surface temperature. Even two reactor systems, in which in the first reactor a flash of W coating was applied by radiative heating and in the second reactor the wire was resistively heated, did not work very well. (2) The second problem encountered was that resistive heating was found to degrade the tensile properties of the filament. While the reason for this degradation is being investigated, the coating is presently being applied essentially by radiative heating of the wire. This of course is wasteful because only a minor amount of W is recovered as coating; the rest is deposited on the walls of the heating tube, which results in periodic plugging up. In order to make this process economically feasible, it has to be considerably modified.

Considerable progress has been achieved in coating TaC on 6 mil tungsten wire, for which conditions were optimized for obtaining protective TaC coating as shown by lack of the reactions in Figure 18. However, the coating itself was inhomogeneous. This is apparently due to initial deposition occurring at a higher temperature in the reactor and final deposition occurring at a lower temperature and a relatively low $TaCl_5$ region in the reactor. When resistively heated wire enters the reactor, its diameter is minimum, hence its temperature is the highest, whereby the carbon deposition rate will be high. As the wire proceeds into the center portion of the reactor, its diameter increases and hence, its temperature is relatively lower. This reduces the carbon deposition rate. At the exit end, again the carbon content may be increasing because of the relative depletion of $TaCl_5$ from this region, possibly caused by the high efficiency of this component in the reactor and/or its slower transport in the gas phase as compared with CH_4. These considerations are evident in the micrographs shown in Figure 14(a)-(d). The next step in this study is to achieve a homogeneous coating. Some success has already been achieved in coating the filament at 950°C. It may be of interest to state here that, as far as TaC field is concerned in the coating reported in Table II, we observed almost entirely $\underline{a}$ parameter of 4.455° A, corresponding to TaC; however, it was always accompanied by a phase with $\underline{a}$ of 4.428°A corresponding to $TaC_{0.82}$. The latter may correspond to an as yet not clearly defined zeta phase [9].

---

[9] Storms, E.K. "The Refractory Carbides," p. 82, Academic Press, New York (1967).

Coating of silicon carbide filament directly with TaC is expected to present the same difficulties as in coating them with W. This aspect will be studied thoroughly in FY 74.

CONCLUSIONS AND FUTURE PLANS

FY 73 work has resulted in the application of investment casting to the fabrication of cobalt base composites containing W-1%ThO_2 and SiC filaments. Feasibility of the casting of a vane was also demonstrated. Although some problems in the mold design resulted in low V_f composites, it is hoped that in the very near future composites of Mar M-322 (20%W) reinforced both with W-1%ThO_2 and W coated silicon carbide filaments will be fabricated, leading to the achievement of the immediate goal of this study. In FY 74, major thrust of the work will be along the following lines:

1. Improvement of investment casting technique to obtain composites of W-1%ThO_2, and W and TaC coated SiC filaments in Mar M-322 (20%W) and Mar M-302, and measurements of the tensile and stress rupture properties in the temperature range 1500°-2200°F.

2. Optimize the W and TaC coating processes, and determine the effect of these coatings on the mechanical properties of the filaments.

3. Evaluate the high temperature properties of SiC filaments in the temperature range 2000°-2400°F.

4. Improvement of the composition of the cobalt base alloy such as Mar M-322 and 302, to achieve better structural stability and oxidation resistances under service conditions.

5. Improve the casting techniques of vanes and blades from the above composites and determine their thermal shock and environmental resistance.

6. Study the filament-matrix interface and alloy structure stability as a result of exposure to stress and temperature conditions for extended periods of time.

7. Investigate the oxidation and hot corrosion resistance of the composites.

ACKNOWLEDGMENT

The authors acknowledge with thanks the following: Mr. R. A. Warenchak for assistance in obtaining stress rupture data on SiC filaments and composites, and coating SiC filaments with CVD tungsten; Mr. R. Wharton for measuring the short time tensile properties of composites; Mrs. T. Brassard for metallographic work; and Miss Mary Anne Normile for typing the manuscript of this report.

REFERENCES

1. McDanels, D.L., Signorelli, R.A. and Weeton, J.W. "Analysis of stress-rupture and creep properties of tungsten-fiber-reinforced copper composites." NASA TND-4173, September 1967.

2. Ahmad, I., Barranco, J.M., Loomis, K.E.,and Heffernan, W.J. "Metal Matrix Composites for High Temperature Application." An interim report FY 1971. WVT 7155, October 1971.

3. Ahmad, I., Barranco, J.M., Heffernan, W.J., and Loomis, K.E. "Metal Matrix Composites for High Temperature Application." An interim report FY 1972. WVT 7266, December 1972.

4. Samsonov, G.V. and Pilipenko, A.T. "Analysis of the high temperature melting compounds," Clearing House for Federal Scientific and Technical Information, U.S. Department of Commerce (AD 603009).

5. Kazunobu Kodama. "Methods of Quantitative Inorganic Analysis," Interscience Publishers, John Wiley, New York, p. 460, 1963.

6. Heibeisen, M.C. et al. "Vacuum Melting and Casting of Superalloys," NASA SP-5095, 1971.

7. Ohnysty, B. et al. "Test manual evaluation of Composite Materials for Gas Turbine Engines," AFML TR-66-156, Part III, March 1968.

8. Sims, Chester T., J. Metals, pp. 27-42, December (1969).

9. Storms, E.K. "The Refractory Carbides," p. 82, Academic Press, New York (1967).

TABLE I. COMPOSITION OF THE ALLOY MATRICES

Mar M-322	1.0 C, 0.1 Mn, 0.1 Si, 21.5 Cr, 9.0 W, 0.75 Ti, 2.0 Zr, 4.5 Ta, balance Co.
Mar M-322 (20%W)	1.0 C, 0.1 Mn, 0.1 Si, 21.5 Cr, 2.0 W, 0.75 Ti, 2.0 Zr, 4.5 Ta, balance Co.
Mar M-322 (25%W)	1.0 C, 0.1 Mn, 0.1 Si, 21.5 Cr, 20 W, 0.75 Ti, 2.0 Zr, 4.5 Ta, balance Co.
Mar M-302	0.85 C, 0.1 Mn, 0.2 Si, 21.5 Cr, 10 W, 0.005 B, 0.2 Zr, 9.0 Ta, balance Co.
Mar M-509	0.6 C, 0.10 Mn, 0.1 Si, 21.5 Cr, 10 Ni, 7 W, 0.2 Ti, 0.10 B, 0.5 Zr, 1.0 Fe, 3.5 Ta, balance Co.

TABLE II

X-Ray Diffraction Data and Microhardness Values of Tantalum-Carbon Alloy Coatings, Obtained Under Various Experimental Conditions

Sample and Photomicrograph No.	CH_4 Flow Rate	Atom Percent Tantalum	X-ray Identification	Microhardness 25gm load (Kg/mm^2) Inside	Outside	Remarks
7a	5	85.5	Ta_2C, trace Ta	1340	571	Ta_2C, strongly oriented (001) fiber axis. Active under polarized light.
7b	20	60.0	TaC, Ta_2C, trace Ta	2412-1546-926-	1778	Same as above. TaC, weak (100) fiber axis. Broad lines for TaC.
7c	30	52.0	TaC, trace Ta_2C	2470-1546-1895		TaC: $a_o = 4.455$ ($TaC_{1.0}$) strong, $a_o = 4.428$ ($TaC_{0.82}$) weak
	40	45.5	TaC, trace Ta_2C			No photomicrograph given
7d	200	27.5	TaC	590-1111-2200		Broad lines for TaC. Slight optical activity in soft region.

* Samples are the 1100°C deposits using HCl in the chlorinator.

TABLE III. SHORT TIME TENSILE PROPERTIES OF COBALT ALLOY MATRICES AND COMPOSITES

Matrix	No. Specimens	Test Temp. °F	Fil. Vol %	UTS ksi	Y.S. (0.2%) ksi	Elong. %	G.L.	Atmos.
Mar M322 (9%W)	2	R.T.	-	123	95	2.7	1.00	air
Mar M322 (9%W)	1	1652	-	67.5	47	7.2	1.00	H_2
	1	2000	-	27.5	23.8	15.1	1.75	vac.
Mar M322 (20%W)	2	R.T.	-	121.2	100	1.5	1.0	air
Mar M322 (20%W)	1	1652	-	43.5	37	4.6	1.50	H_2
Mar M322 (20%W)	1	2000	-	28.4	28.0	21.4	1.75	vac.
Mar M322 (25%W)	4	R.T.	-	73.4	-	0.31	1.00	air
Mar M322 (25%W)	2	1652	-	45.9	-	3.21	1.00	H_2
Mar M322 (25%W)	1	2000	-	31.0	30.9	3.57	1.75	vac.
Mar M322 (20%W) + W-1%ThO_2 Fil	2	R.T.	22.3	105.2	92.4 (0.1%)	0.4	1.00	air
	2	2000	25.8	44.4	-	7.1		

TABLE III. SHORT TIME TENSILE PROPERTIES OF COBALT ALLOY MATRICES AND COMPOSITES (Cont'd)

Matrix	No. Specimens	Test Temp. °F	Fil. Vol %	UTS ksi	Y.S. (0.2%) ksi	Elong. %	G.L.	Atmos.
Mar M322 (25%W) + W-1%ThO_2 Fil	1	R.T.	33.4	50.0	-	.18	1.00	air
Mar M322 (25%W) + W-1%ThO_2 Fil	1	1652	31.0	75.0	34.0	4.3	1.00	air
Mar M302	1	R.T.	-	133.9	99.8	-	1.00	air
Mar M302	1	2000	-	30.2	30.1	17.9	1.75	vac.

TABLE IV. STRESS RUPTURE DATA FOR SiC FILAMENT (W-CORE)

Temp.	Stress ksi	Time to Fracture			No. of tests
		Mean Value	Highest Value	Lowest Value	
2000° F	250	0.53	1.0	0.1	12
	200	3.05	3.9	0.7	9
	165	34.0	46.1	26.2	11
	150	48.06	58.1	26.2	9
	140	1000	did not fracture		1
	130	1000	did not fracture		3
	125	tests stopped after 250 hrs			
	100				
2200° F	170	1.7	1.9	1.2	2
	160	12.5			1
	150	18.5	21.4	15.7	4
	110	286	298	- 273.6	2
	100	331	342	317	4
	75	1804			1
2400° F	100	1.9	2.3	- 1.6	7

Table V. 2000°F Stress Rupture Life of the Alloy Matrices

Alloy	Specimen Code	Run No.	Stress ksi	ATM.	Time (hrs)	Remarks
Mar M-322(9%W)	3-37-72	R6	10.0	He	0.6	Some porosity in specimen
Mar M-322(9%W)	3-2-72	R7	10.0	He	0.0	Some porosity in specimen
Mar M-322(9%W)	3-1-72	R8	10.0	He	0.0	Some porosity in specimen
Mar M-322(9%W)	3-CT-9W	18	7.5	Air	99.2	CT stands for investment cast
Mar M-322(9%W)	2-CT-9W	21	7.5	He	79.7	
Mar M-322(9%W)	7-CT-9W	22	7.5	Air	114.4	
Mar M-322(15%W)	9-29-72	12	10.0	He	0.0	
Mar M-322(15%W)	10-18-72	14	8.0	He	20.9	

Table V. 2000°F Stress Rupture Life of the Alloy Matrices (Cont'd)

Alloy	Specimen Code	Run No.	Stress ksi	ATM.	Time (hrs)	Remarks
Mar M-322(20%W)	5-15-17	2	10.0	He	2.4	Some porosity in specimens
Mar M-322(20%W)	8-KA-72	4	10.0	He	1.0	Some porosity in specimens
Mar M-322(20%W)	9-JP-72	11	10.0	He	0.4	Some porosity in specimens
Mar M-322(20%W)	3-CT-12-72	13	10.0	He	0.2	
Mar M-322(20%W)	22-CT-BS	44	5.0	Air	589.0	As cast
Mar M-322(20%W)	21-CT-BR	45	5.0	Air	707.0	Machined from 3/4" bar
Mar M-302	CT04-302-B3	32	5.0	Air	249.7	
Mar M-302	CT03-302-B3	33	10.0	Air	34.1	As cast (see fig 5b) (small grained)
Mar M-302	CT02-302-B3	36	10.0	Air	94.3	Machined from bar stock (large grained)

TABLE VI. STRESS RUPTURE DATA OF COMPOSITE SPECIMENS AT 2000°F

Filament/Matrix	Run No.	Fil. V_f	Stress (ksi)	Time to Rupture	ATM.	Remarks
W-1%ThO_2/Mar M-322 (20%W)	28	18.4	30	0.0	Air	
W-1%ThO_2/Mar M-322 (20%W)	29	18.3	20	0.2	Air	
W-1%ThO_2/Mar M-322 (20%W)	27	12.7	15	225.0	Air	
W-1%ThO_2/Mar M-322 (20%W)	25	15.5	15	821.0	Air	
W-1%ThO_2/Mar M-322 (20%W)	20	16.6	10	1875.0	Air	Test stopped
W-1%ThO_2/Mar M-322 (20%W)	23	27.0	15	131.0	Air	Button head specimen used. Filaments pullout from the button heads.
W-1%ThO_2/Mar M-322 (20%W)	16	30.0	10	121.0	Air	Test stopped, machine malfunction.
W coated SiC/Mar M-322 (20%W)	26	6.0	10	9.2	Air	
TaC coated W/Mar M-302	30	5.6	5	292.0	Air	Poor infiltration
TaC coated W/Mar M-302	34	5.6	10	294.0	Air	Poor infiltration

TABLE VII. FILAMENT-MATRIX INTERACTION ZONE THICKNESS AS A FUNCTION OF TIME IN MAR M-322 (20%W)/W-1% ThO_2 COMPOSITE

Temperature°C	Time(hrs)	Zone Thickness microns	Zone Growth Rate microns/hr
1000	250	9.3	0.0373
	500	17.1	0.0342
1100	250	25.0	0.1020
	500	39.1	0.0780
1150	100	26.3	0.2630
	500	66.8	0.1340

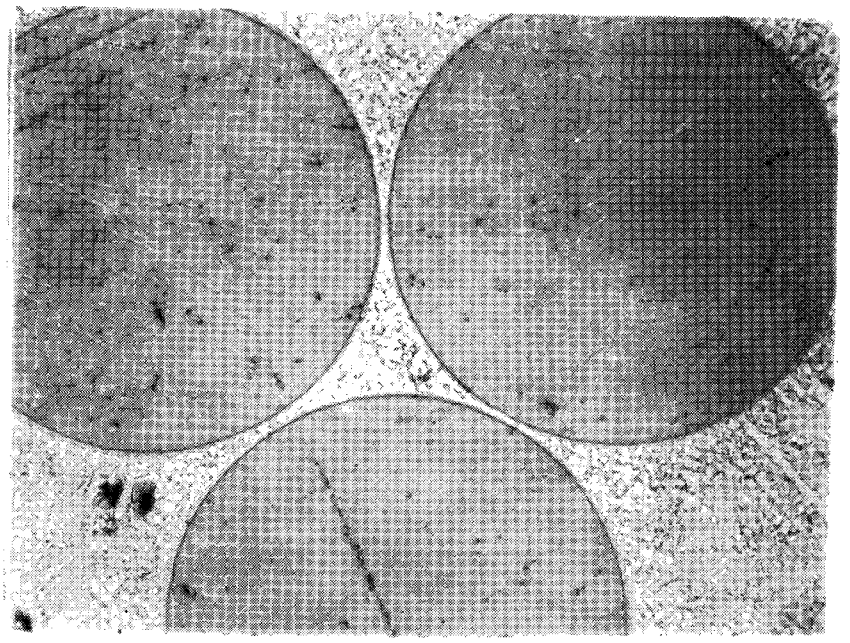


Figure 1. W-1%THO_2 filaments in Mar M-322 with 25%W.

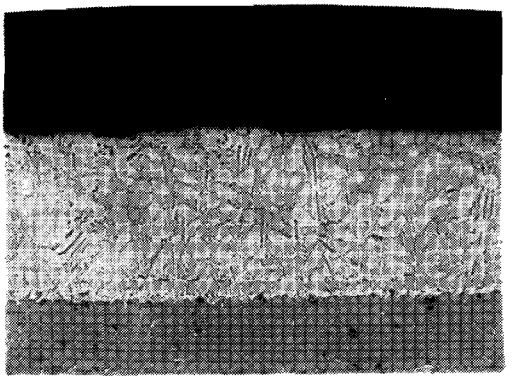


Figure 2. Showing interface between molten Mar M-302 matrix and a TaC disc.

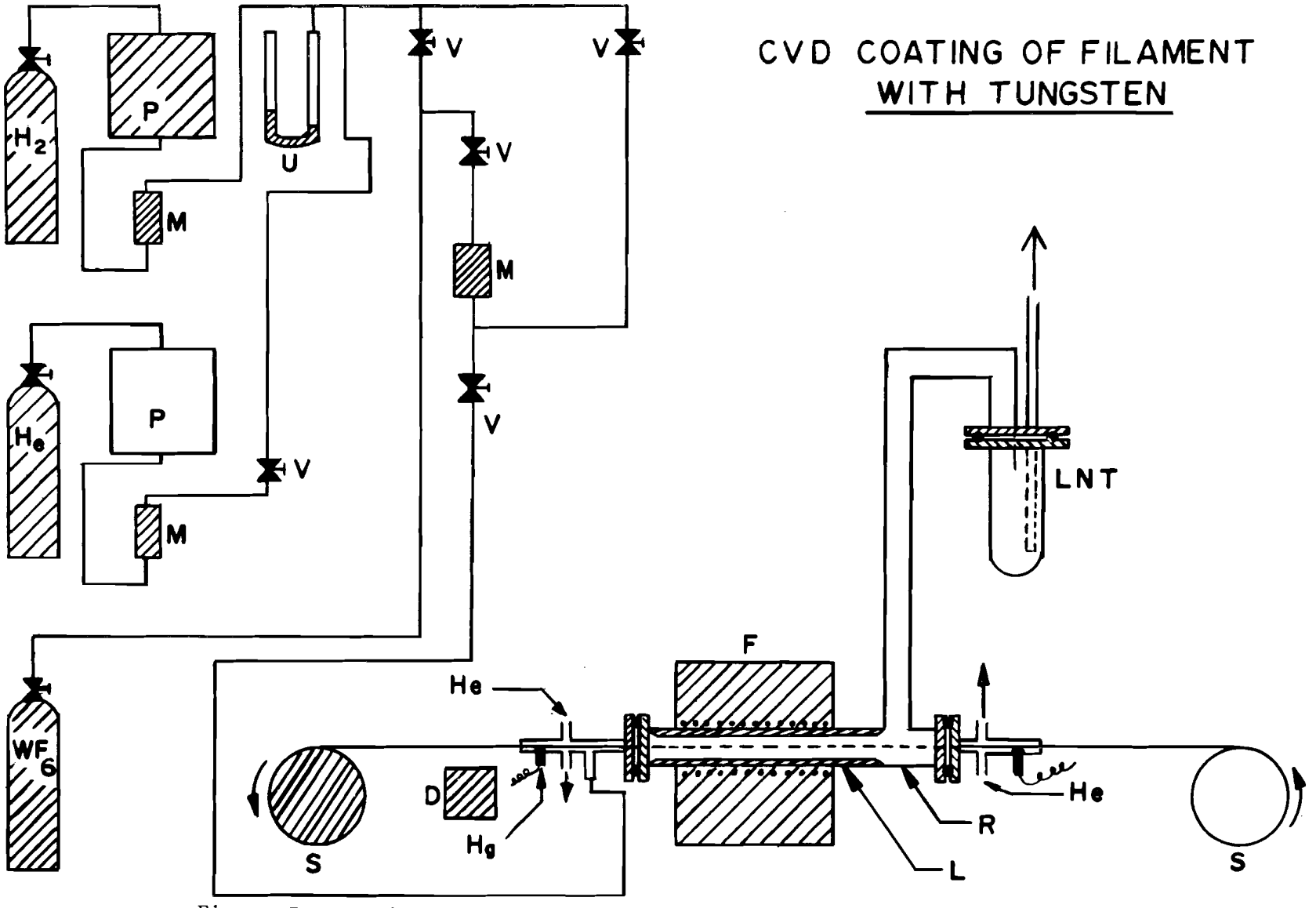


Figure 3. Continuous CVD apparatus for coating W on SiC filament: R-steel reactor, L-removable liner, F-furnace, S-spool, D-thickness guage, Hg-mercury seal, LNT-liquid nitrogen trap, V-valve, M-mixer, P-purifier, U-manometer.

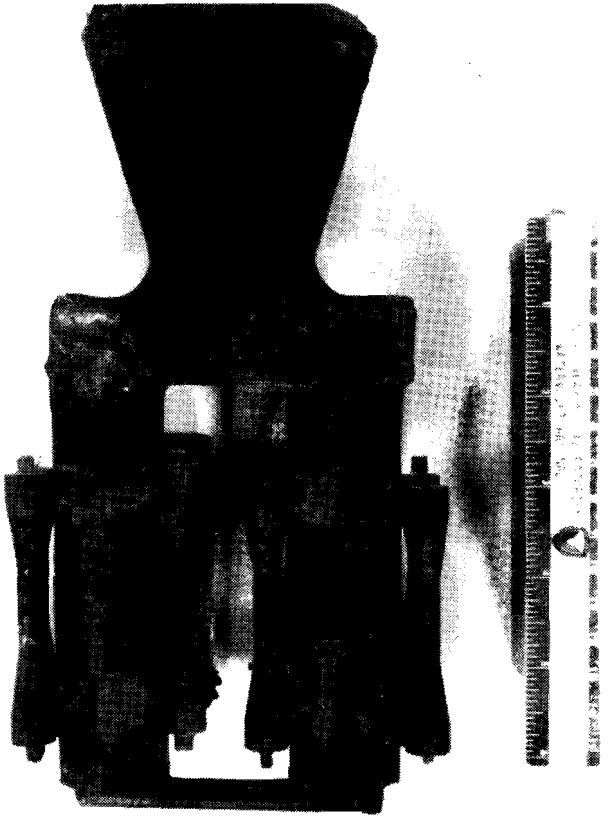
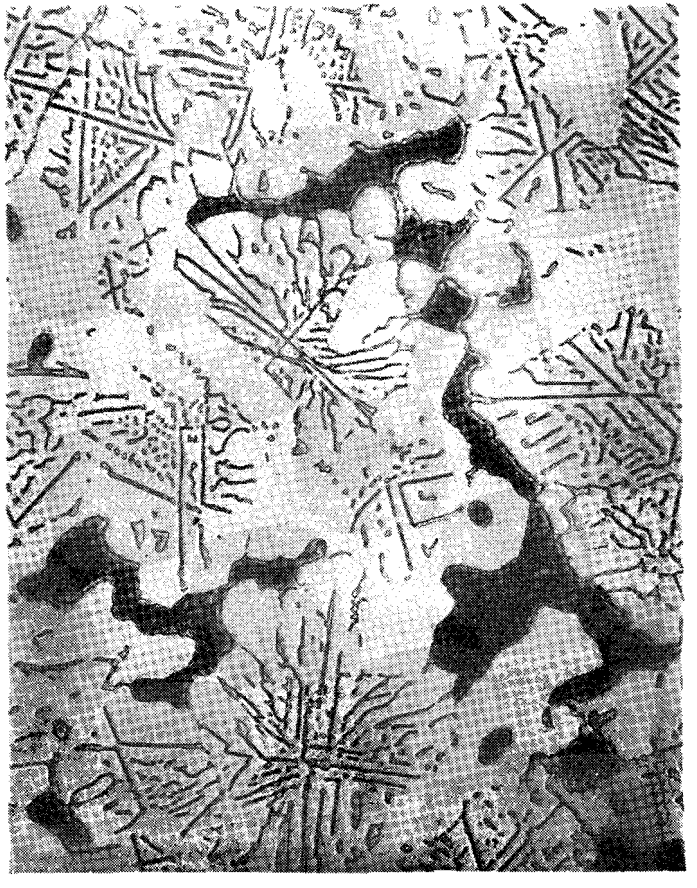


Figure 4. (a) Shell mold assembly. (b) The cast alloy tree after the refractory shell has been removed.

a



b

Figure 5. Micrographs of the Mar M-302 alloy cast in the form of bars (a) and tensile specimens x 500.

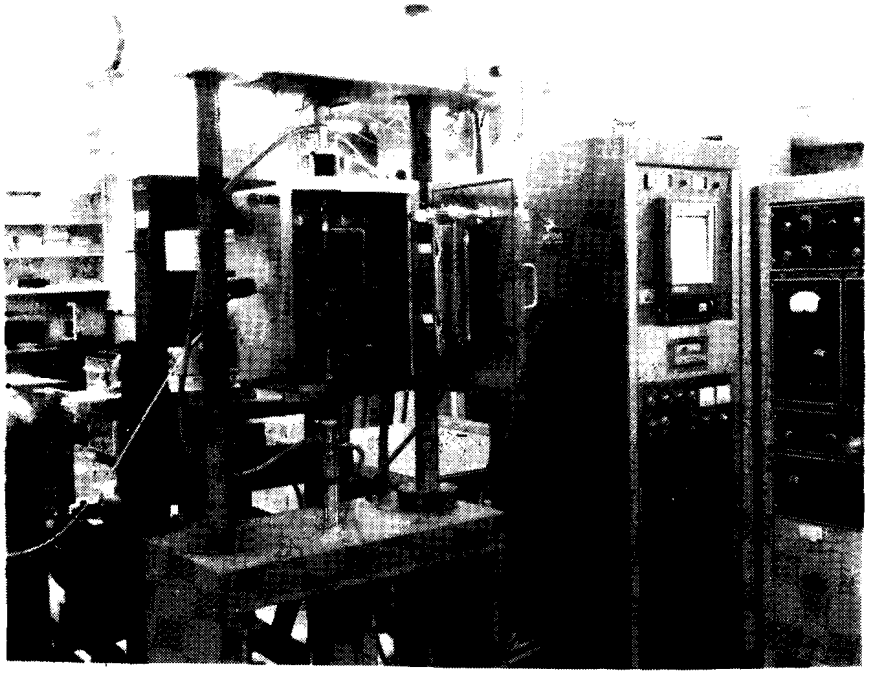
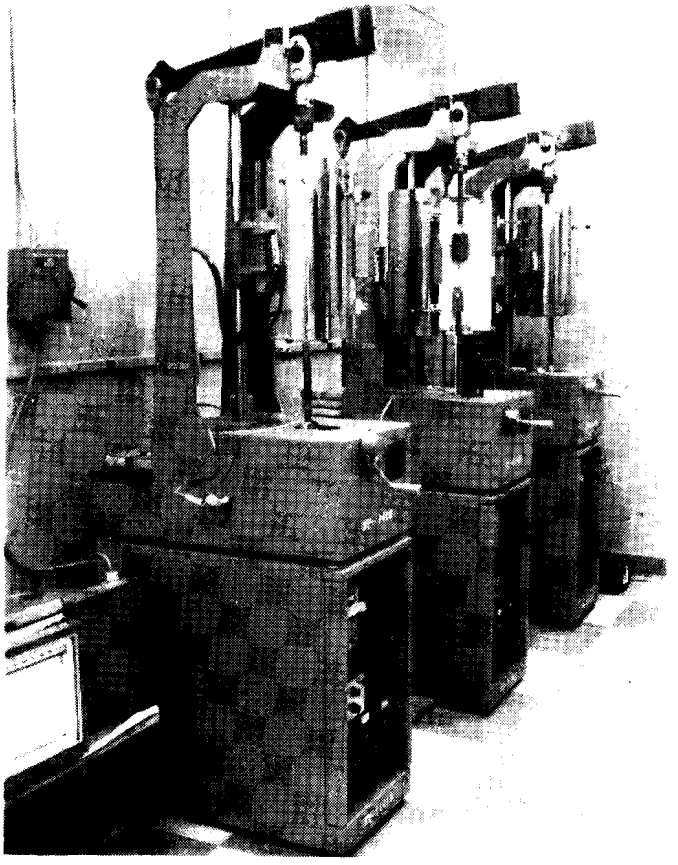


Figure 6. (a) A view of the high vac-high temperature unit incorporated in the Tinius Olsen EH machine.



(b) SATEC stress rupture machines.

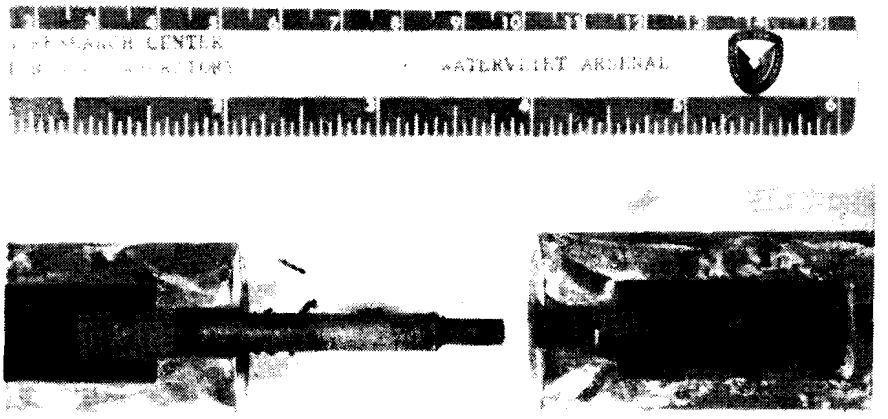


Figure 7. (a) Showing filament pullout in button shaped specimen.

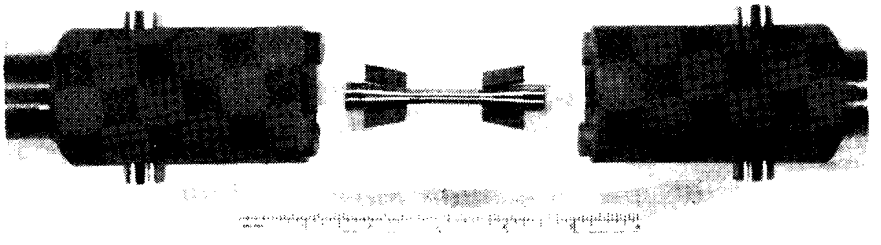


Figure 7 (b) Final specimen design adopted for stress-rupture tests.

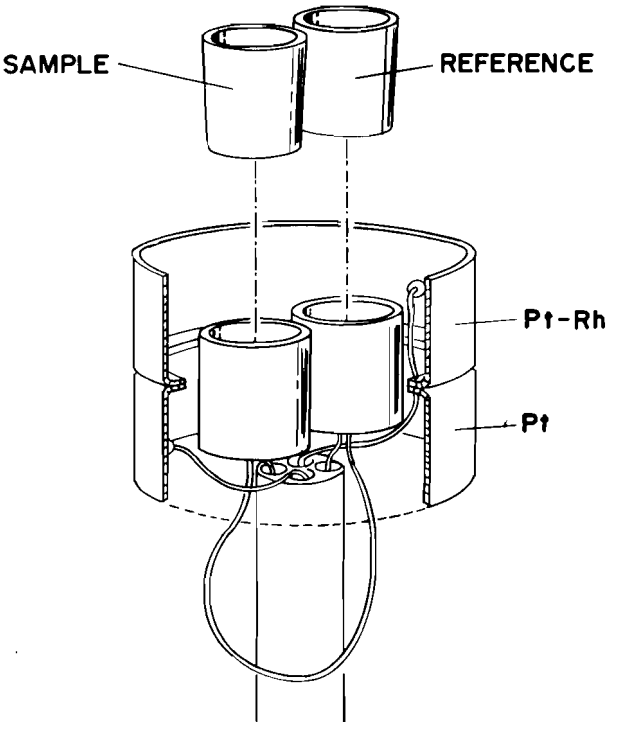


Figure 8. DTA crucibles assembly.

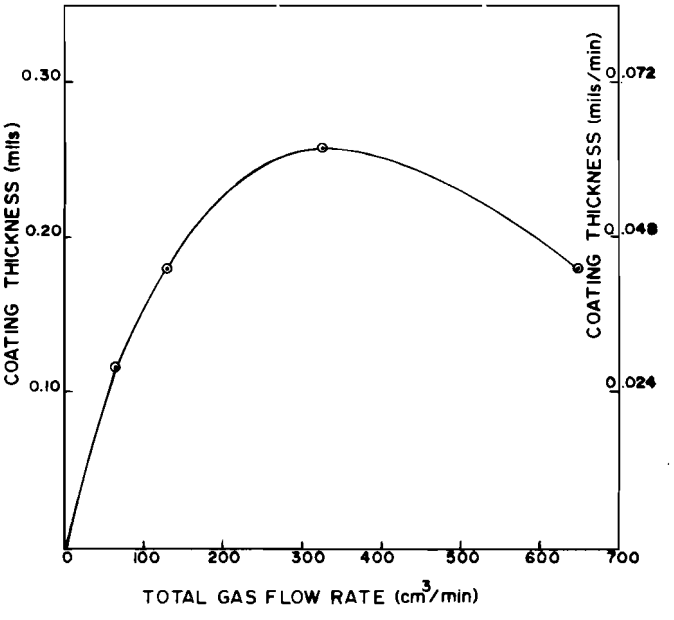


Figure 9. Effect of gas flow rates on the deposition rate of Ta.

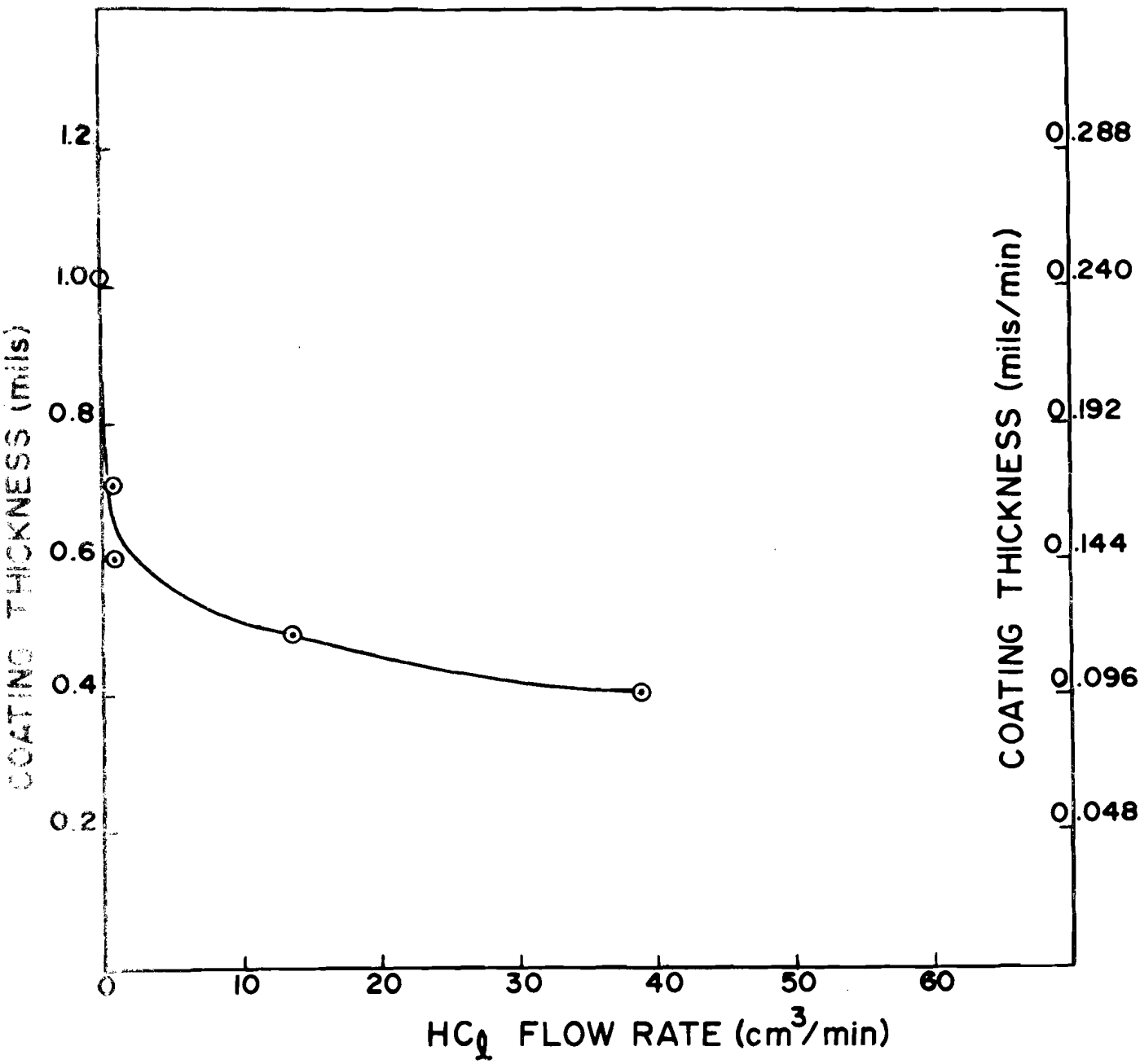


Figure 10. Effect of the addition of HCl on the deposition rate of Ta.

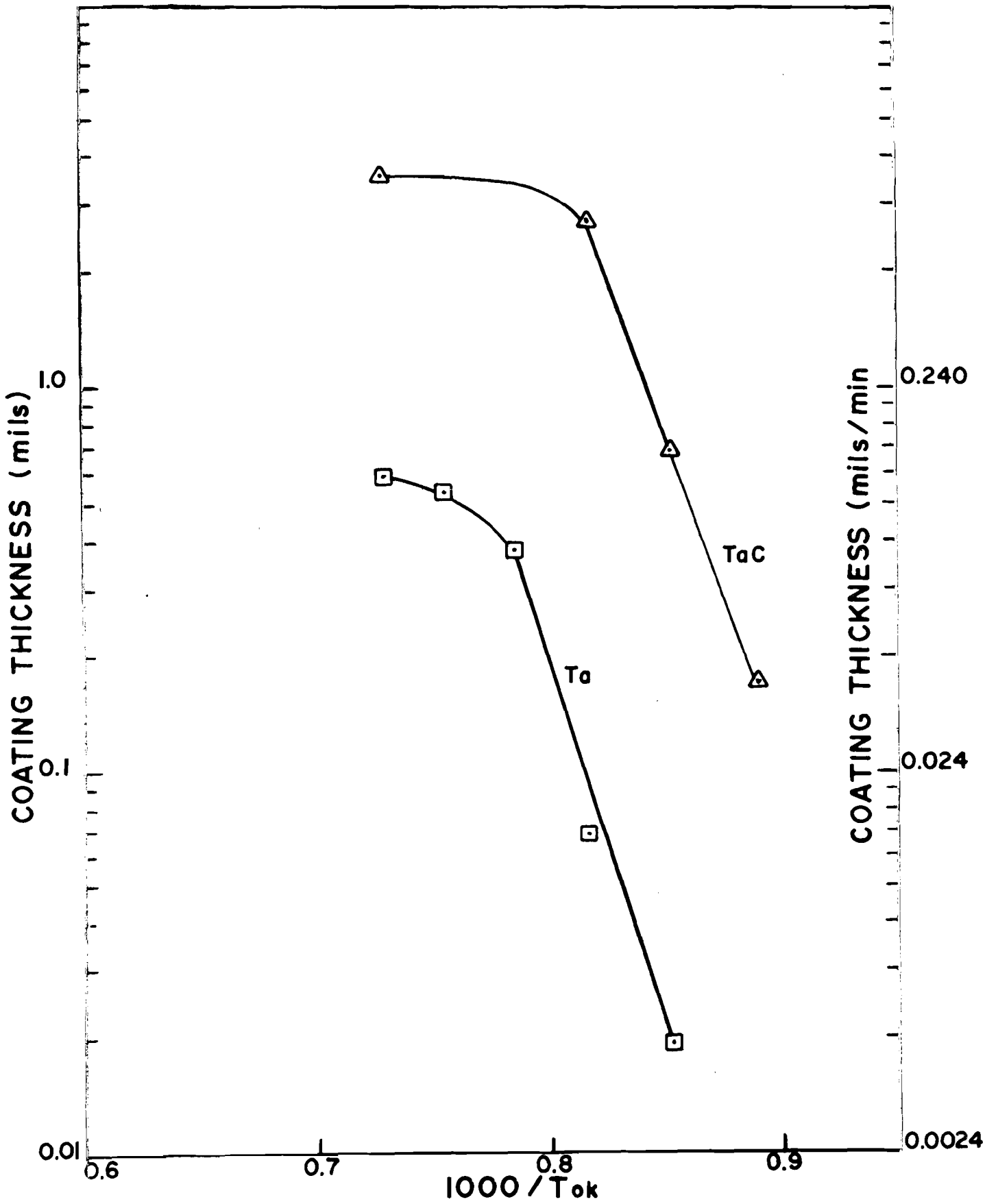


Figure 11. Effect of temperature on the deposition rate of Ta.

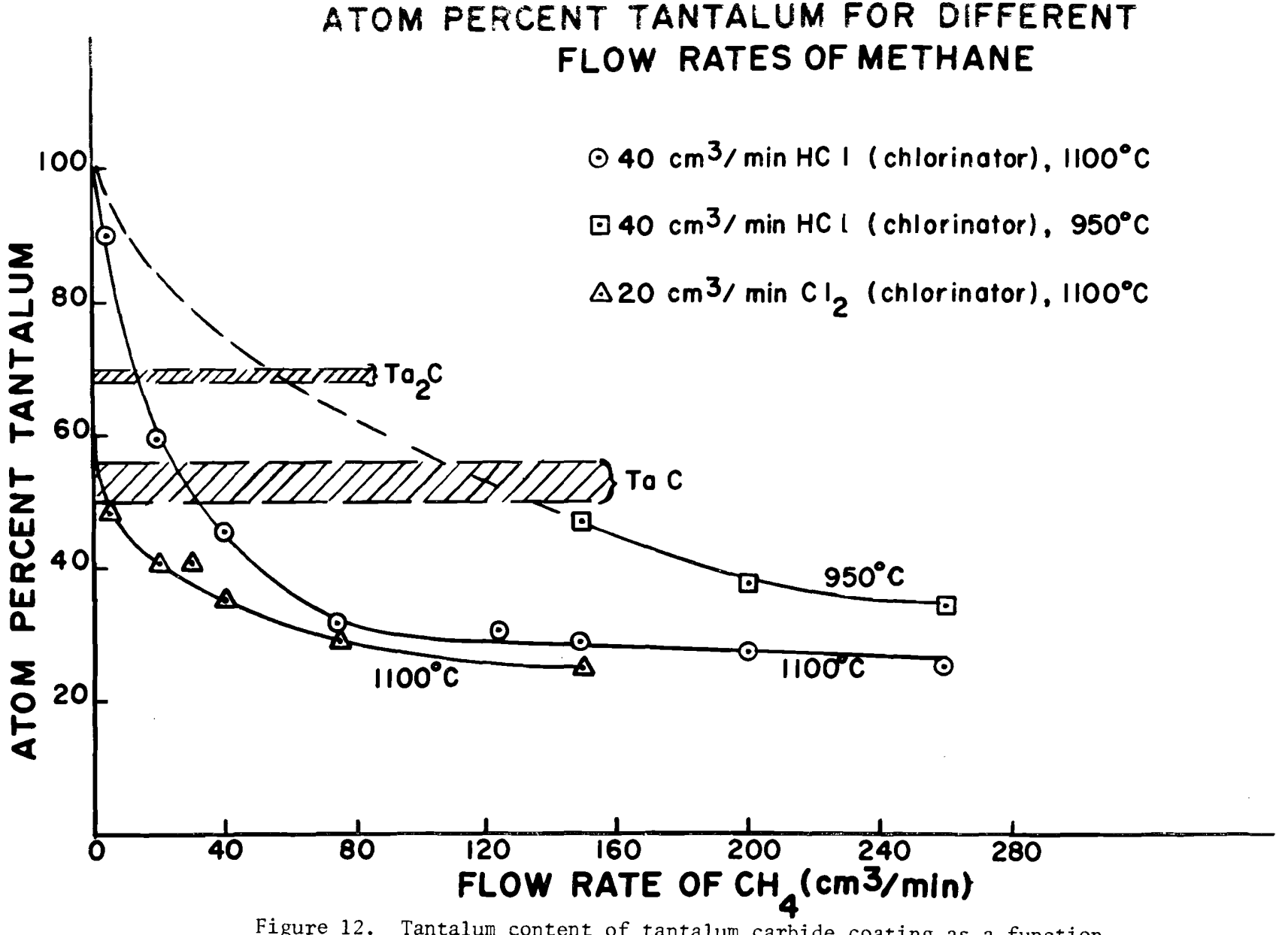


Figure 12. Tantalum content of tantalum carbide coating as a function of CH_4 flow rate.

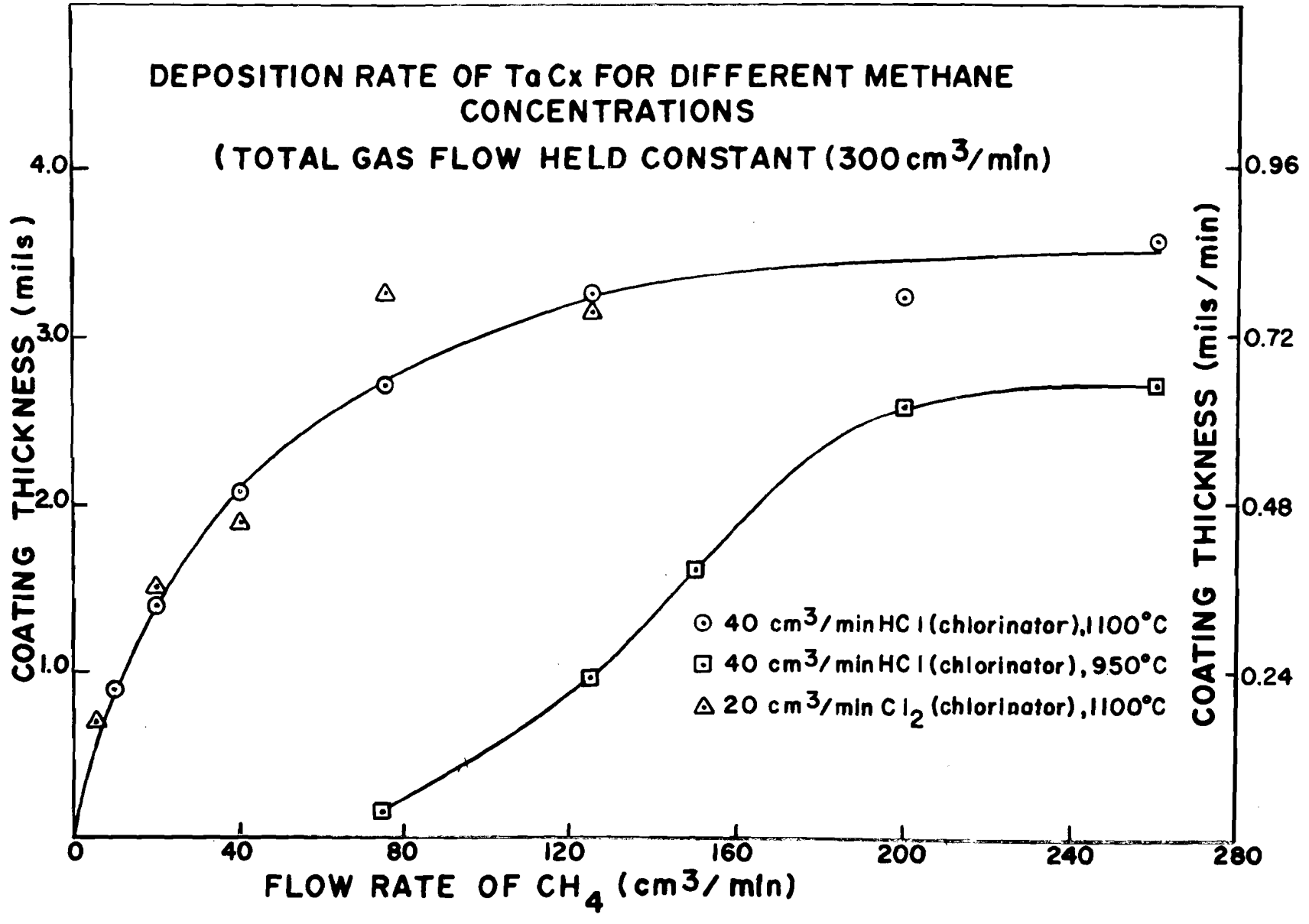
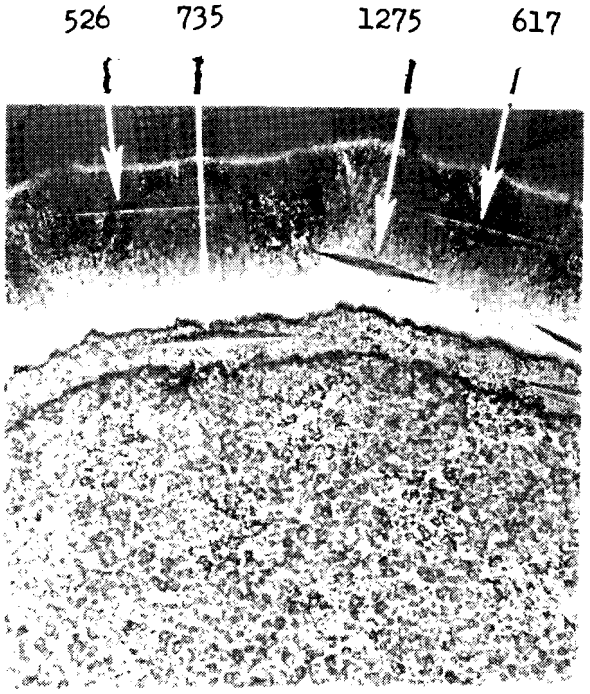
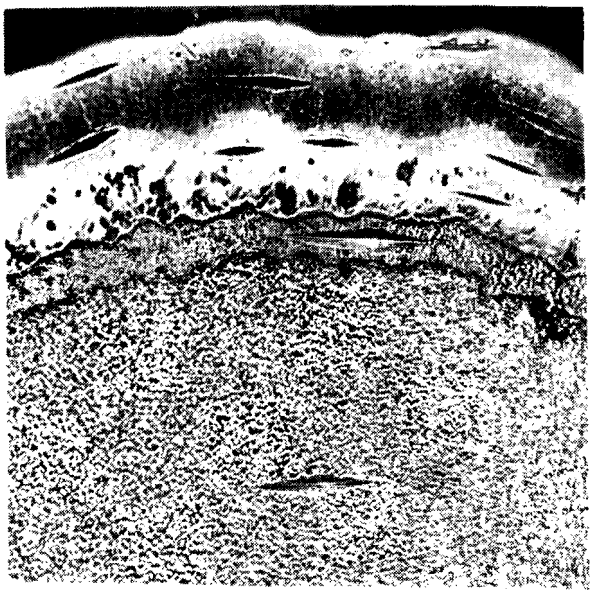


Figure 13. Deposition rate of TaC for different CH_4 concentrations in the gas mixture.

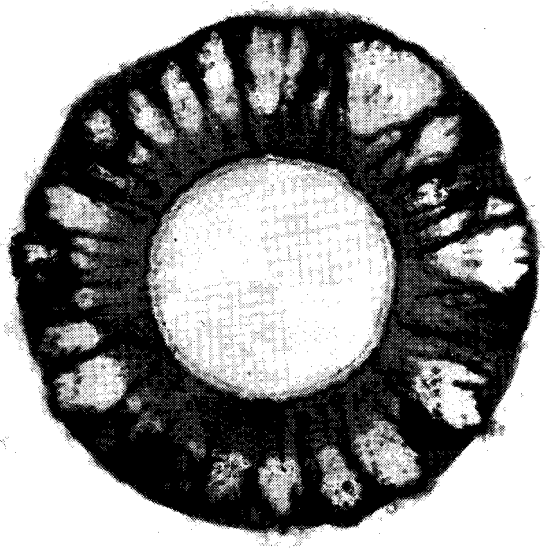


(a) CH 4:HC1 40: He 255 cc/min.
Deposition rate 0.12 mil/min.



(b) CH_4 20:HC1 40: He 240 cc/min.
Deposition rate 0.336 mil/min.

(c) CH_4 30:HCI 40: He 230 cc/min.
Deposition rate 0.432 mil/min.



(d) CH_4 200:HCI:40:HE 60 cc/min.
Deposition rate 0.828 mil/min.

Figure 14. Sectional views of TaC_x coatings deposited at 1100°C, using various CH_4 concentrations in the gas mixture.

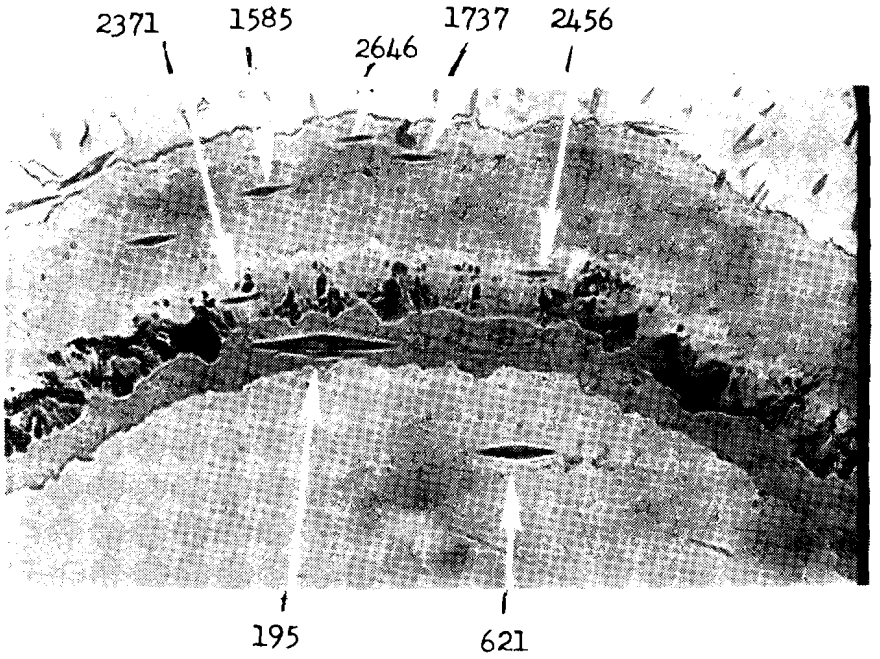


Figure 15. (a) A TaC coated W filament in Mar M-302 matrix.

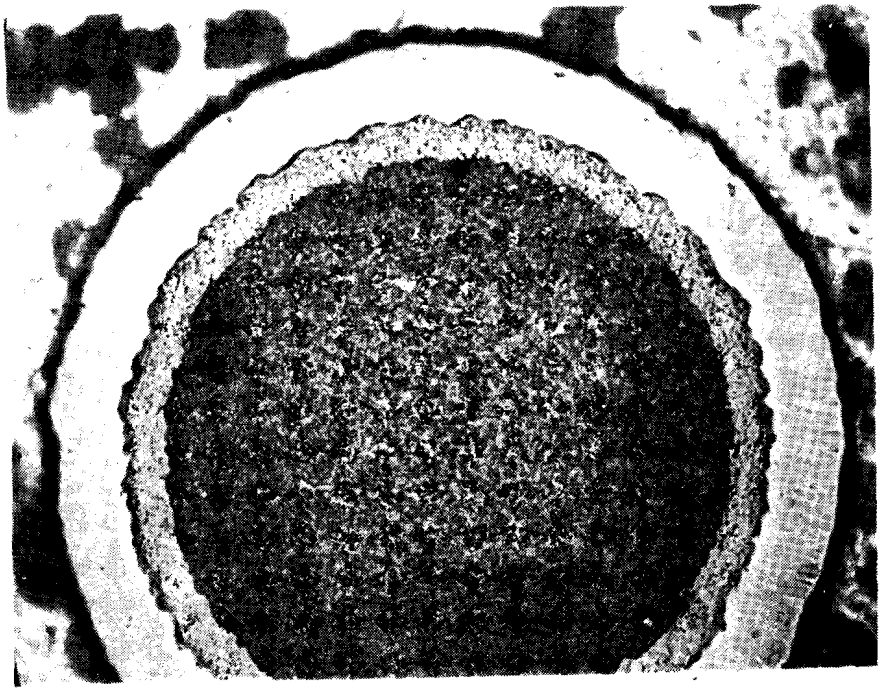


Figure 15. (b) Showing the homogeneous TaC coating x 1000.

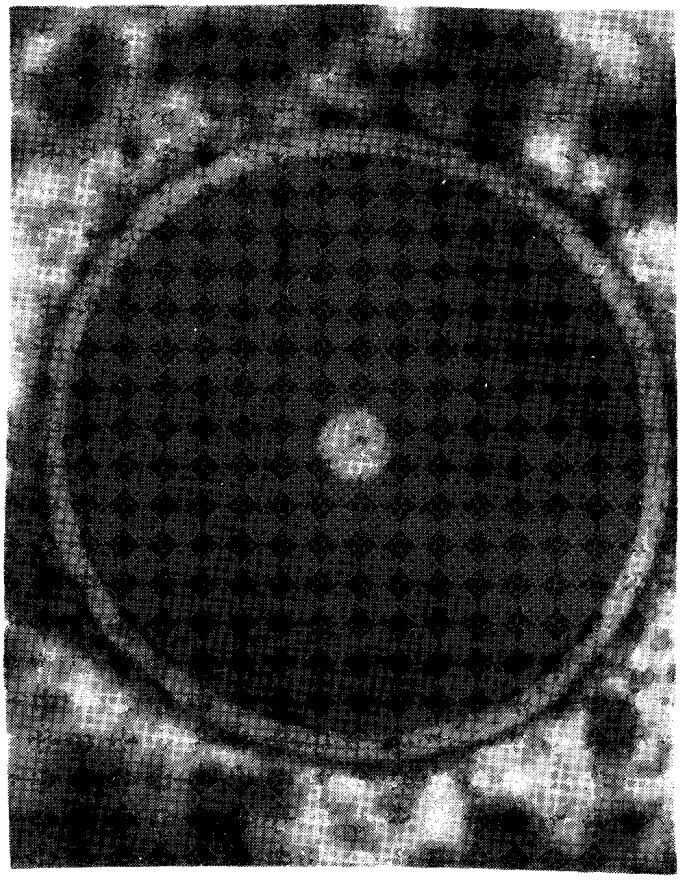


Figure 16. Micrograph of W coating on SiC filament x 1000.

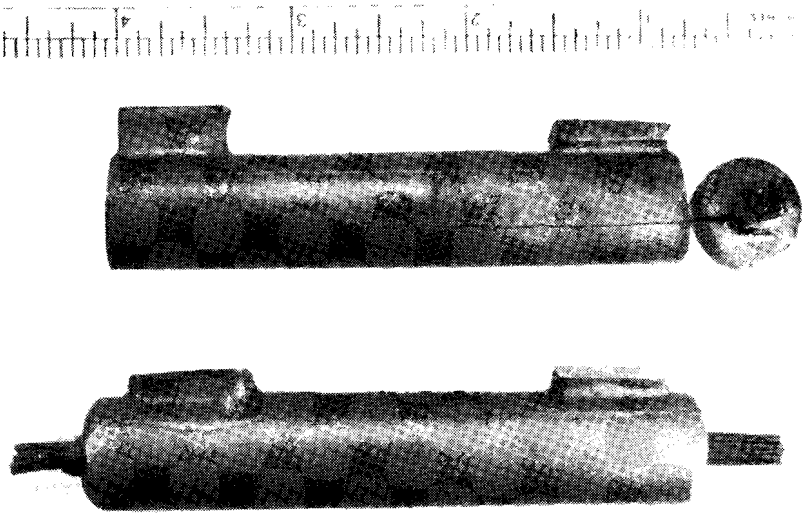


Figure 17.a Microstructure of as-cast W-1%ThO_2/Mar M-322 (20%W).

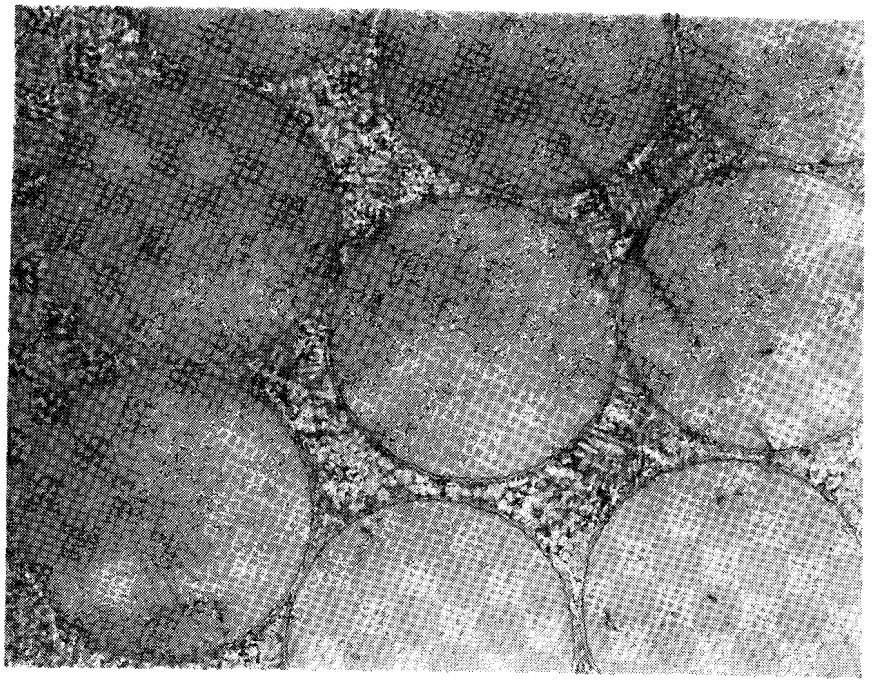


Figure 17.b Cross-sectional view of composite shown above in 17 (a)

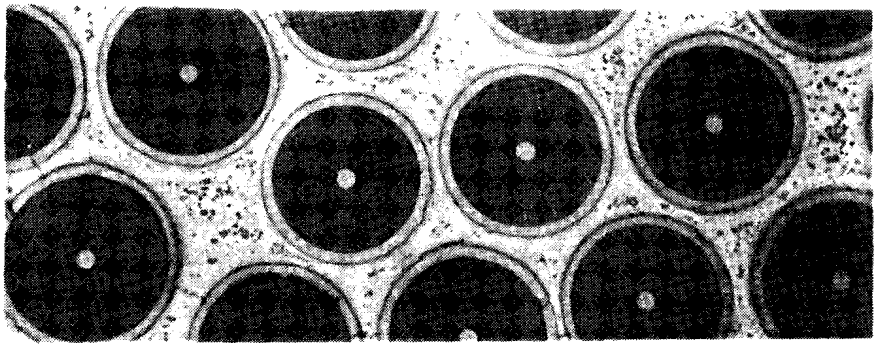


Figure 18. Section view of a W coated SiC filament-Mar M-322 (20%W) composite.

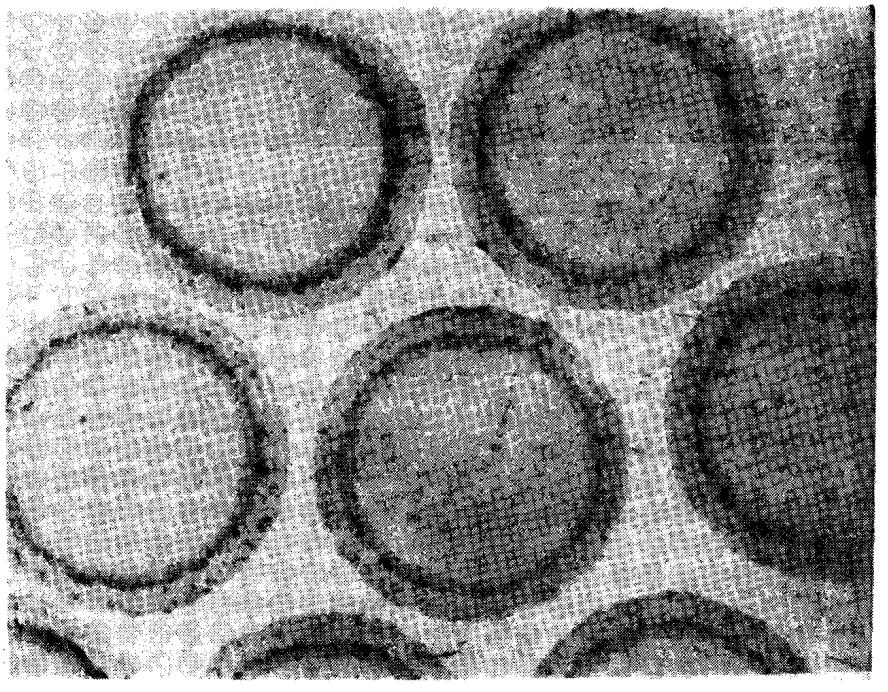


Figure 19. TaC coated W-filaments in Mar M-302 matrix. Notice absence of interaction.

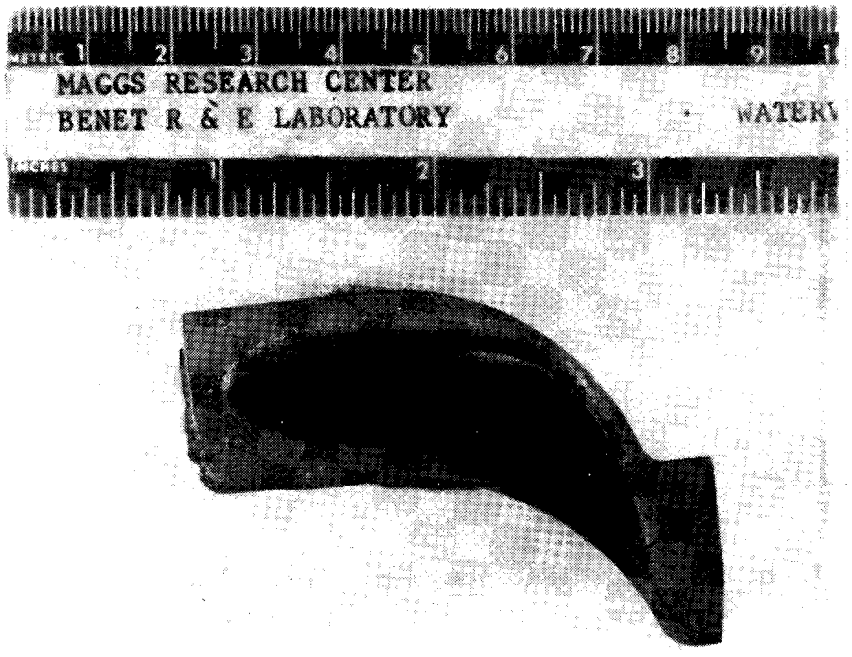


Figure 20. A view of a W-1%ThO_2-Mar M-322 (20%W) vane made by investment casting.

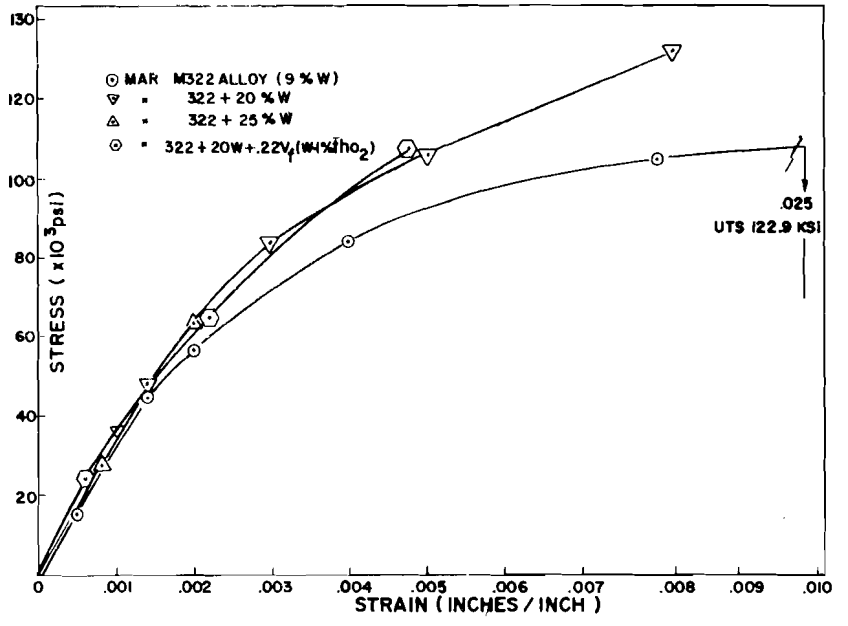


Figure 21. Typical stress-strain curves of Mar M-322, Mar M-322 (20%W) and Mar M-322 (20%W)/0.22 V_f W-1%ThO_2 filaments.

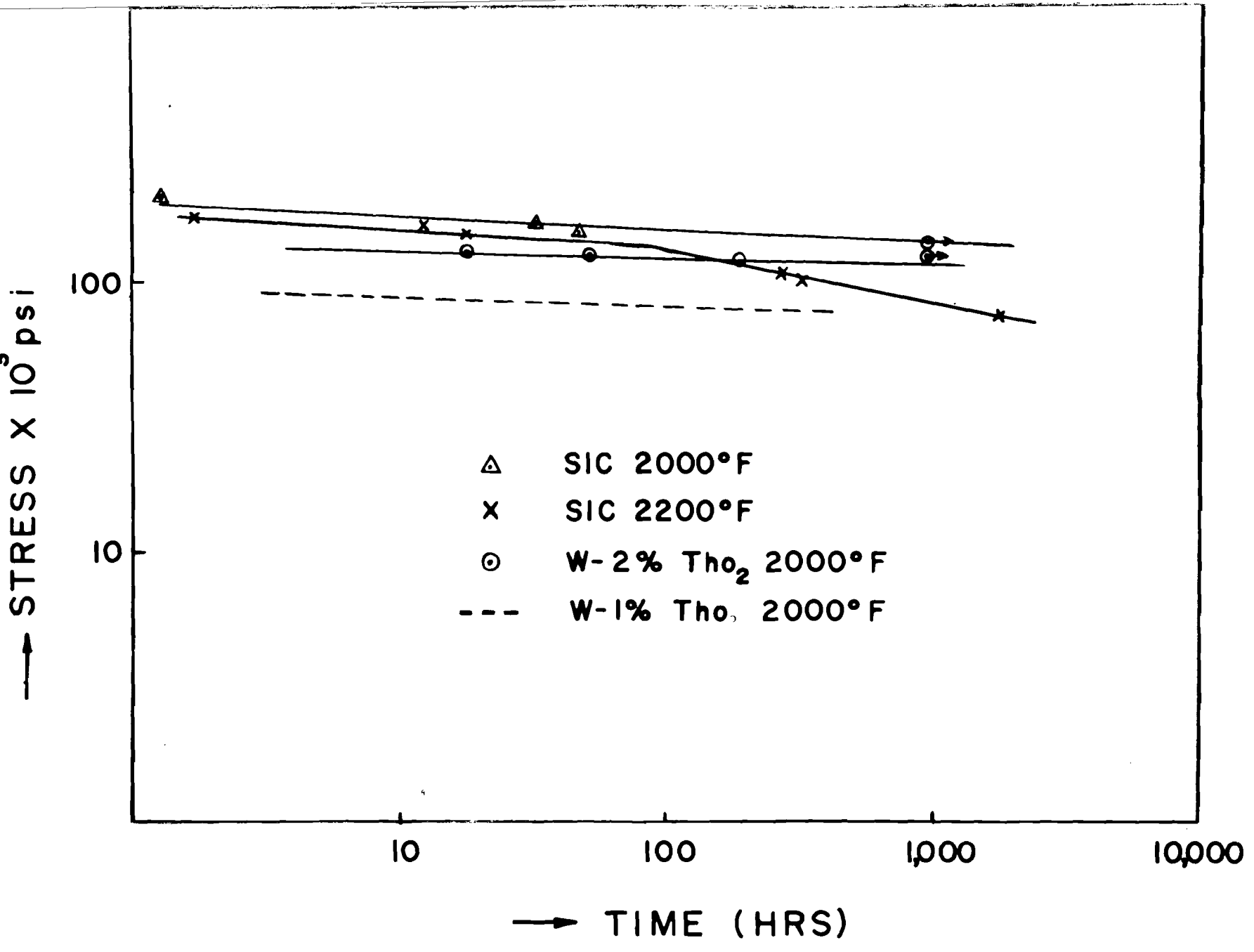


Figure 23. Stress rupture data of SiC (W) at 2000, 2200 and 2400°F.

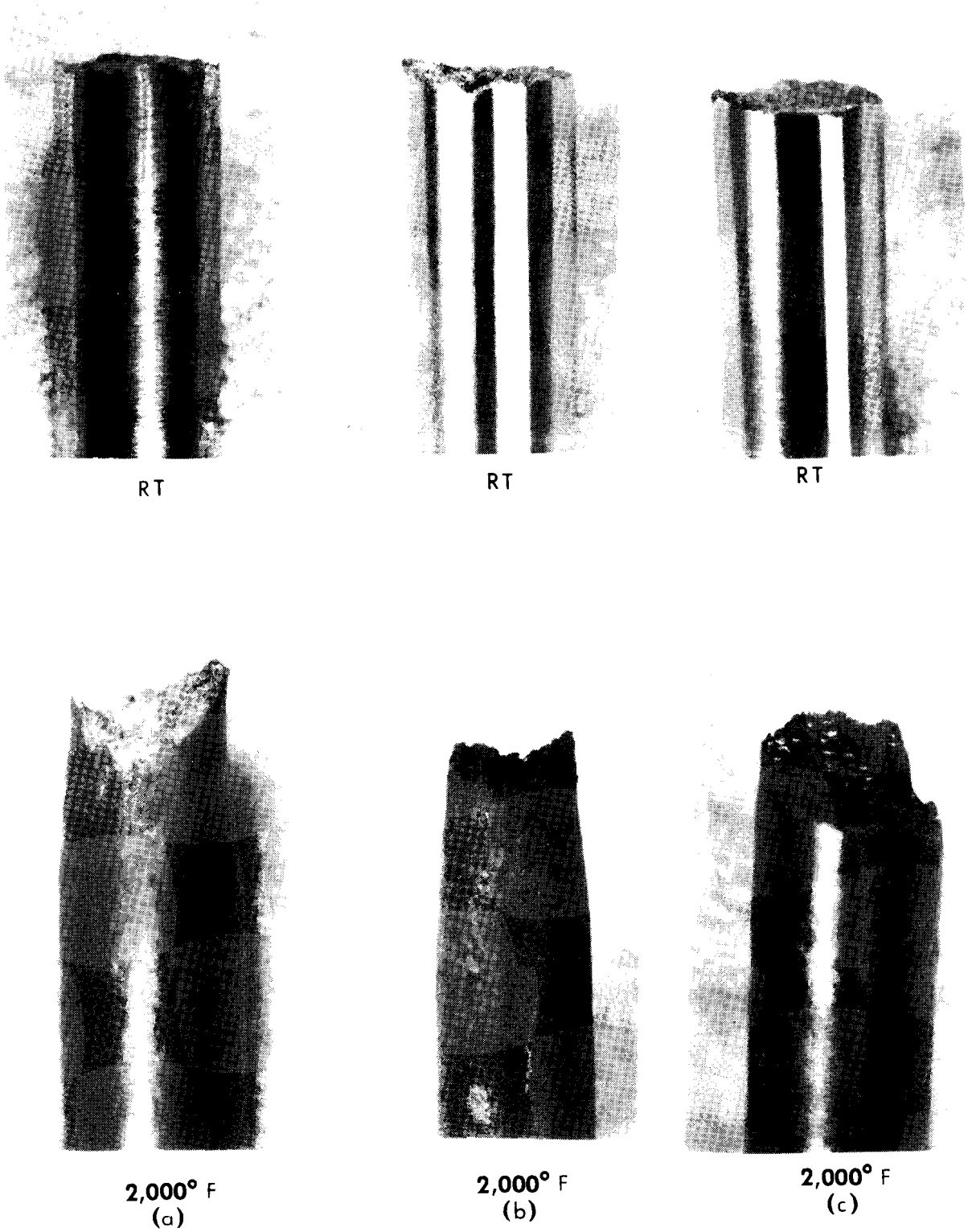


Figure 22. Fracture mode of room temperature and 2000°F tensile specimens of (a) Mar M-322 (9%W), (b) Mar M-322 (20%W) and (c) Mar M-322 (20%W) + 22-25 volume % W-1%ThO_2 filament.

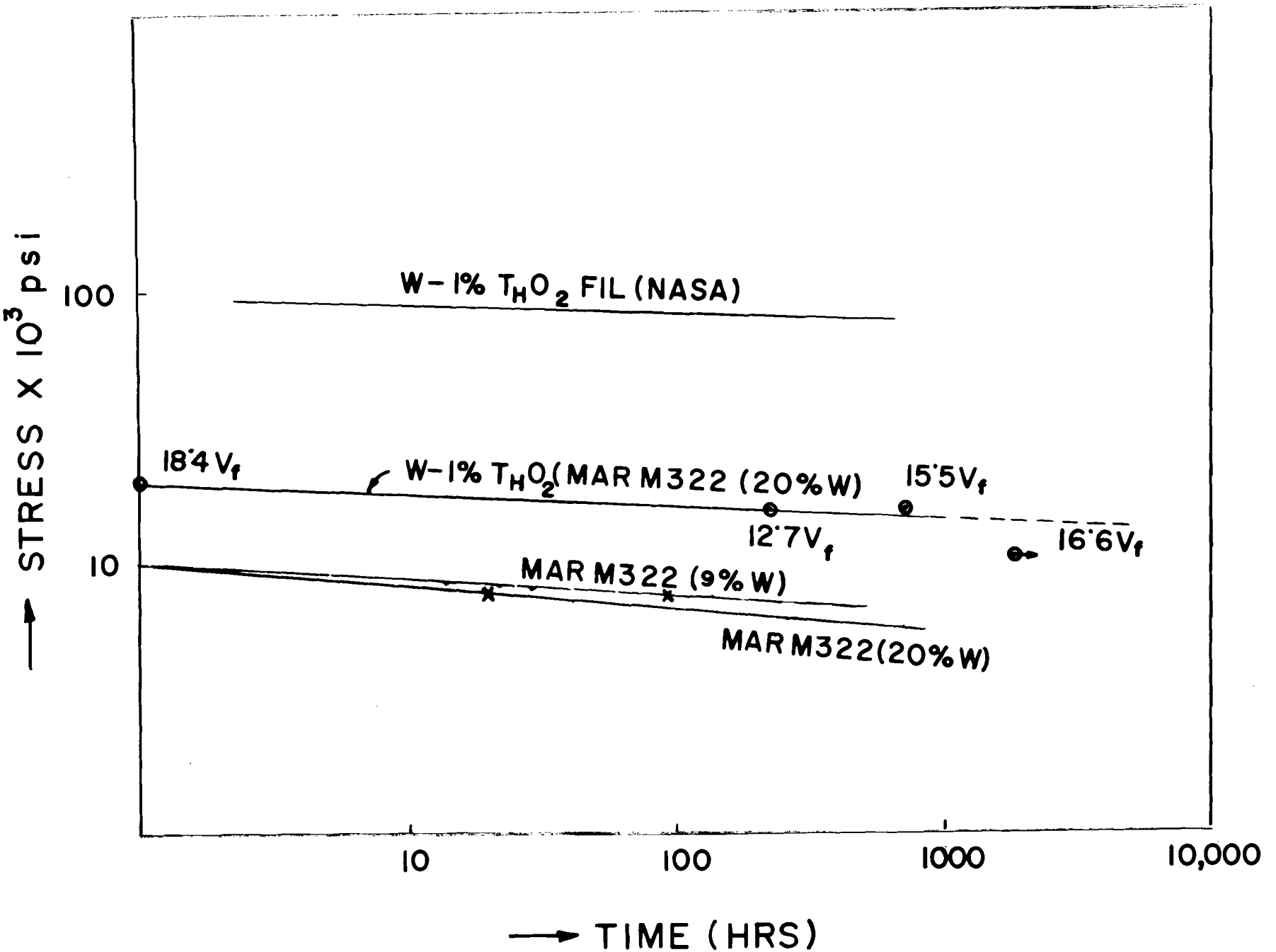


Figure 24. Results of the stress rupture tests on the alloys and composites of W-1%ThO_2/Mar M-322 (20%W).

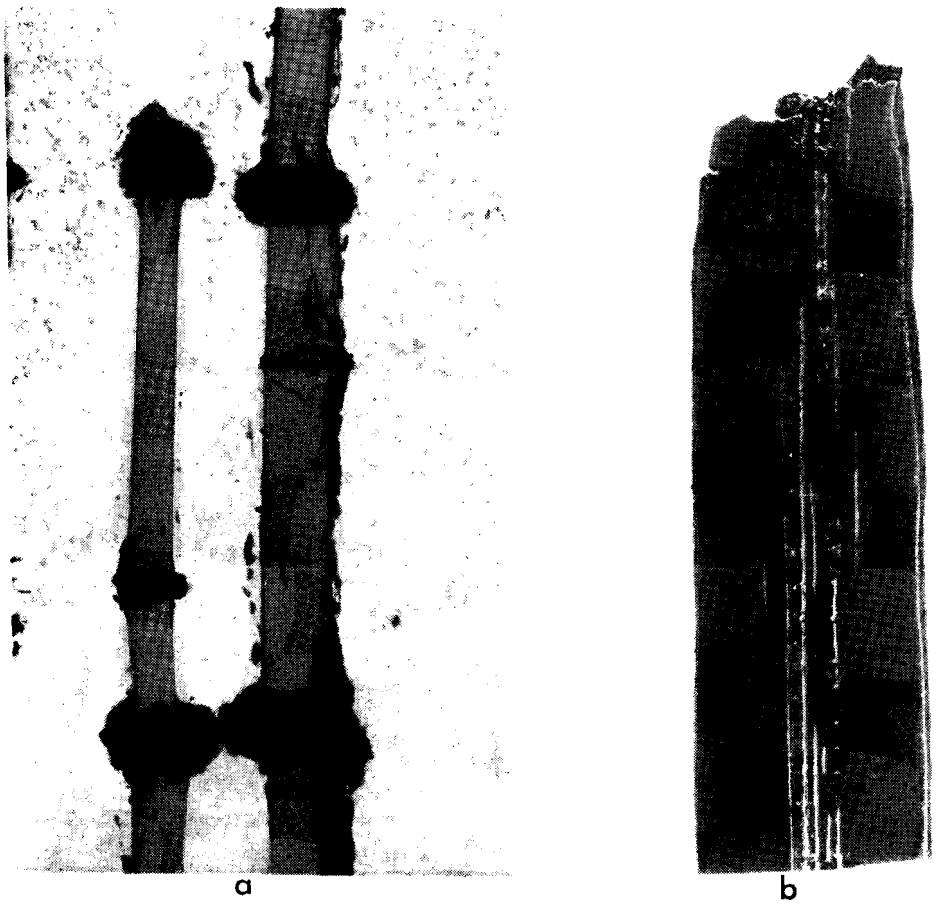


Figure 25. Longitudinal section of SiC filament-Mar M-322 (20%W) composite after stress rupture test.

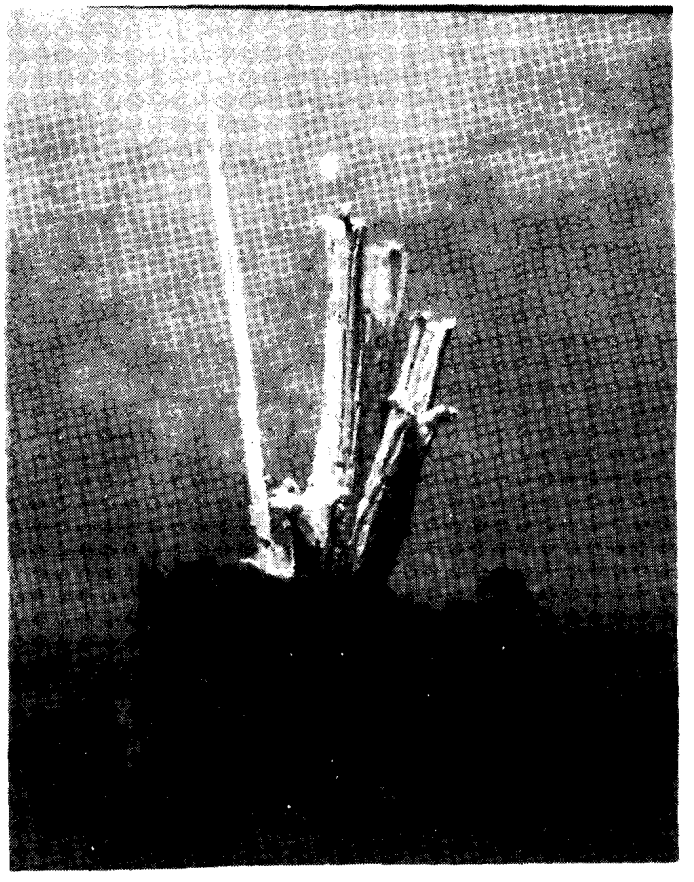
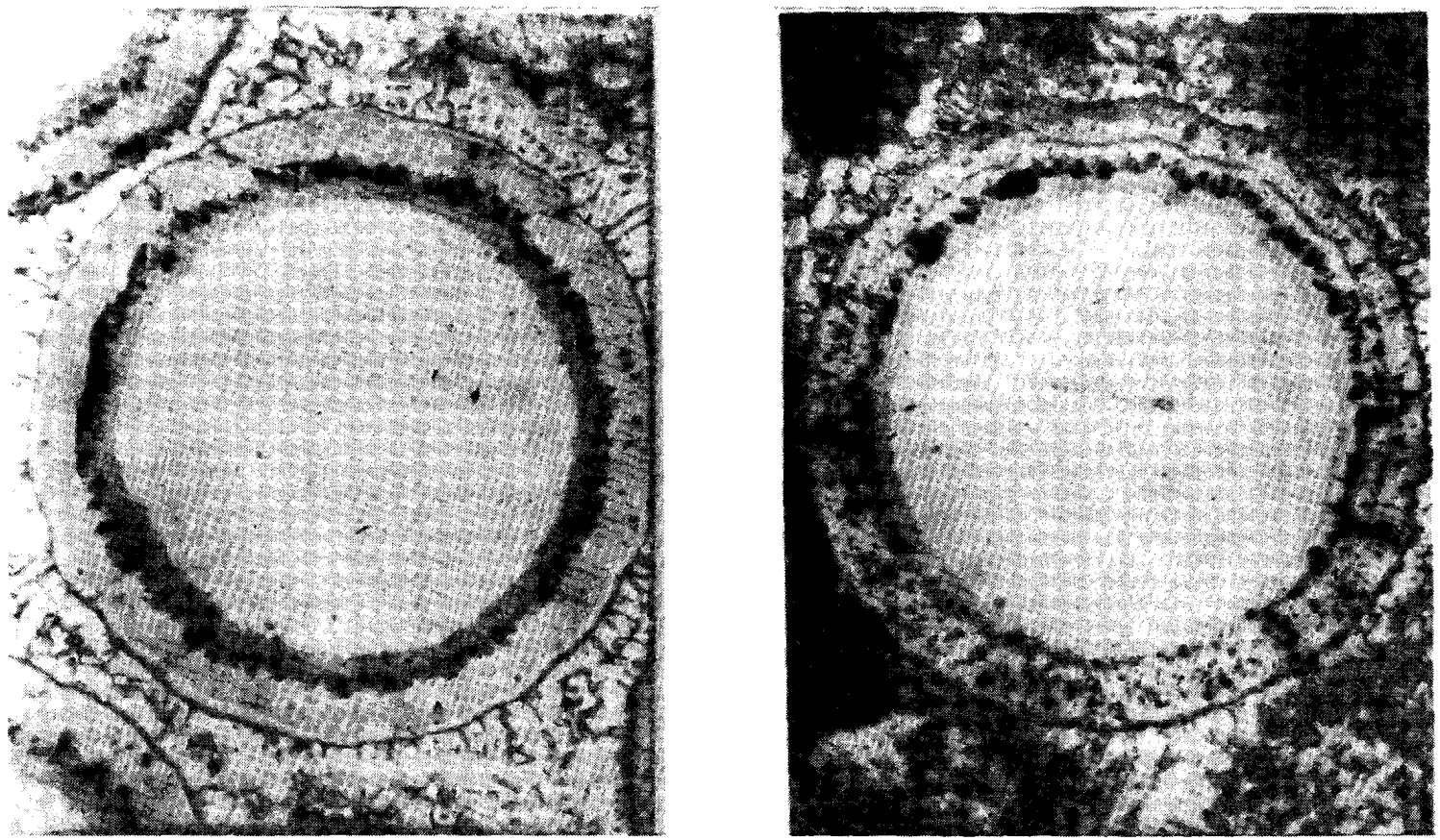


Figure 26. TaC coated W filament-Mar M-302 composite after stress rupture test.



a

b

Figure 27. (a) A sectional view of a TaC coated W filament-Mar M-302 composite specimen after 294 hours at 2000°F.

Figure 27. (b) The same composite specimen after 294 hours at 2000°F.

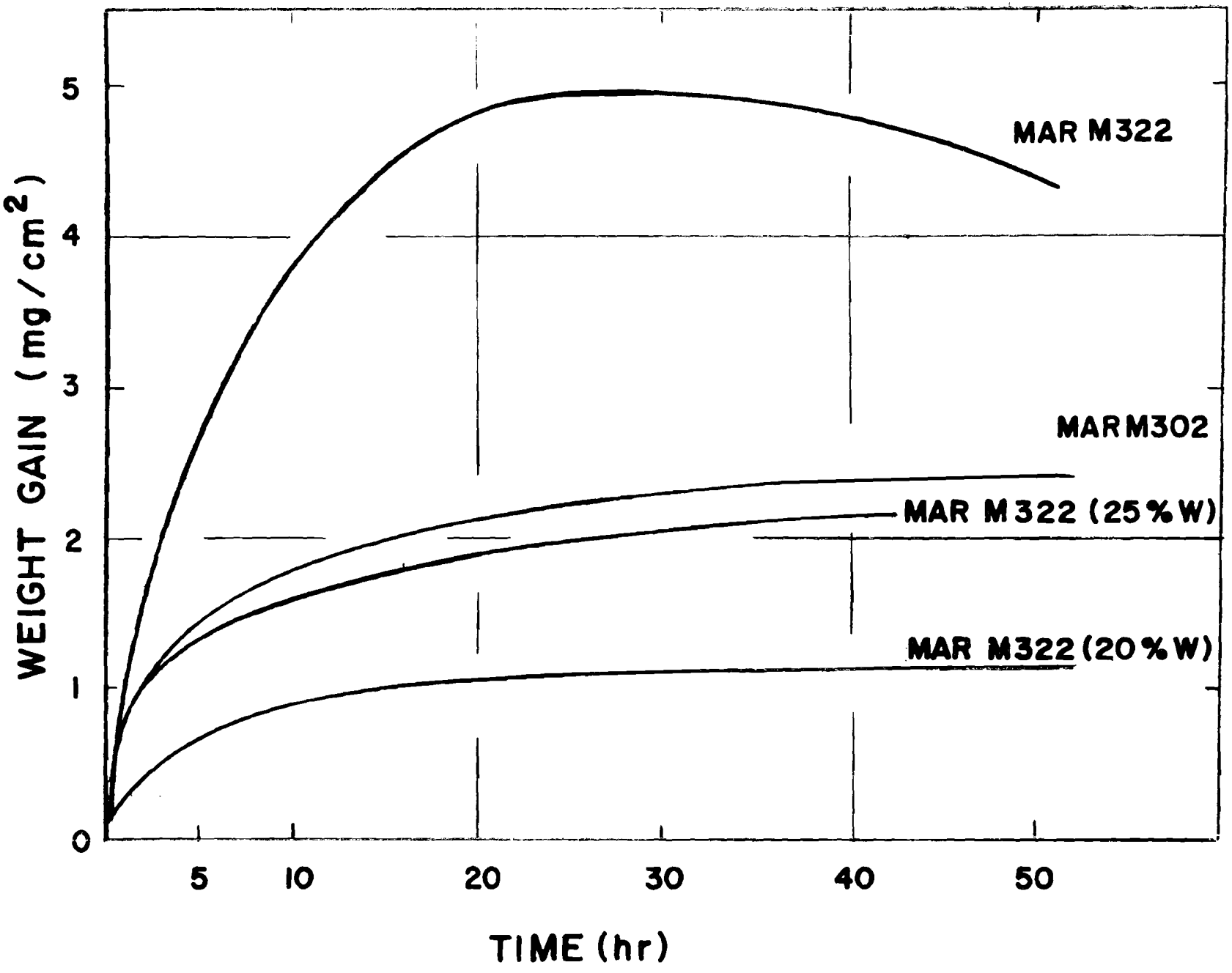


Figure 28. Cyclic oxidation rate of matrix alloys.

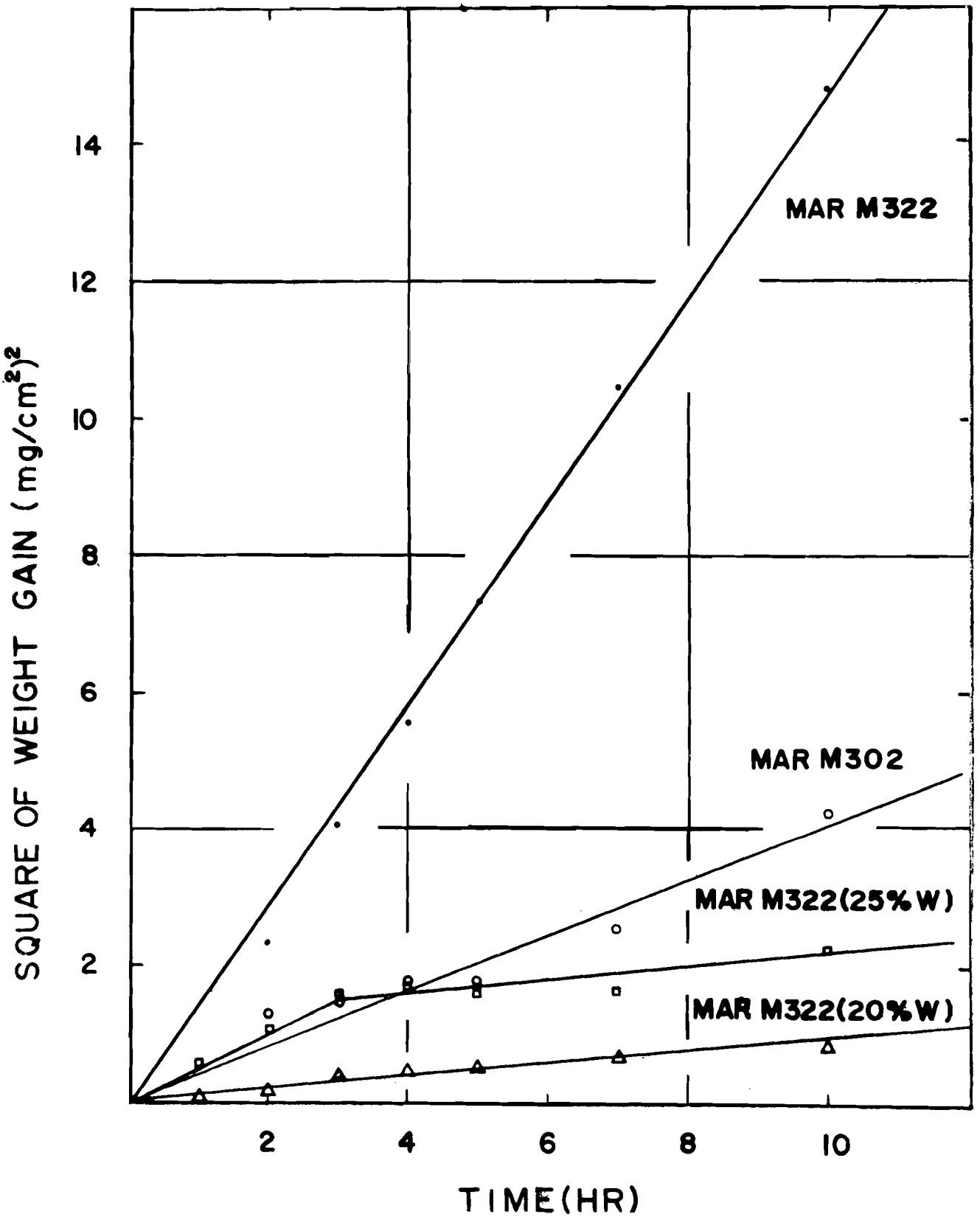


Figure 29. Weight gain vs. time in the initial stage of oxidation of various alloys shown in Figure 27.

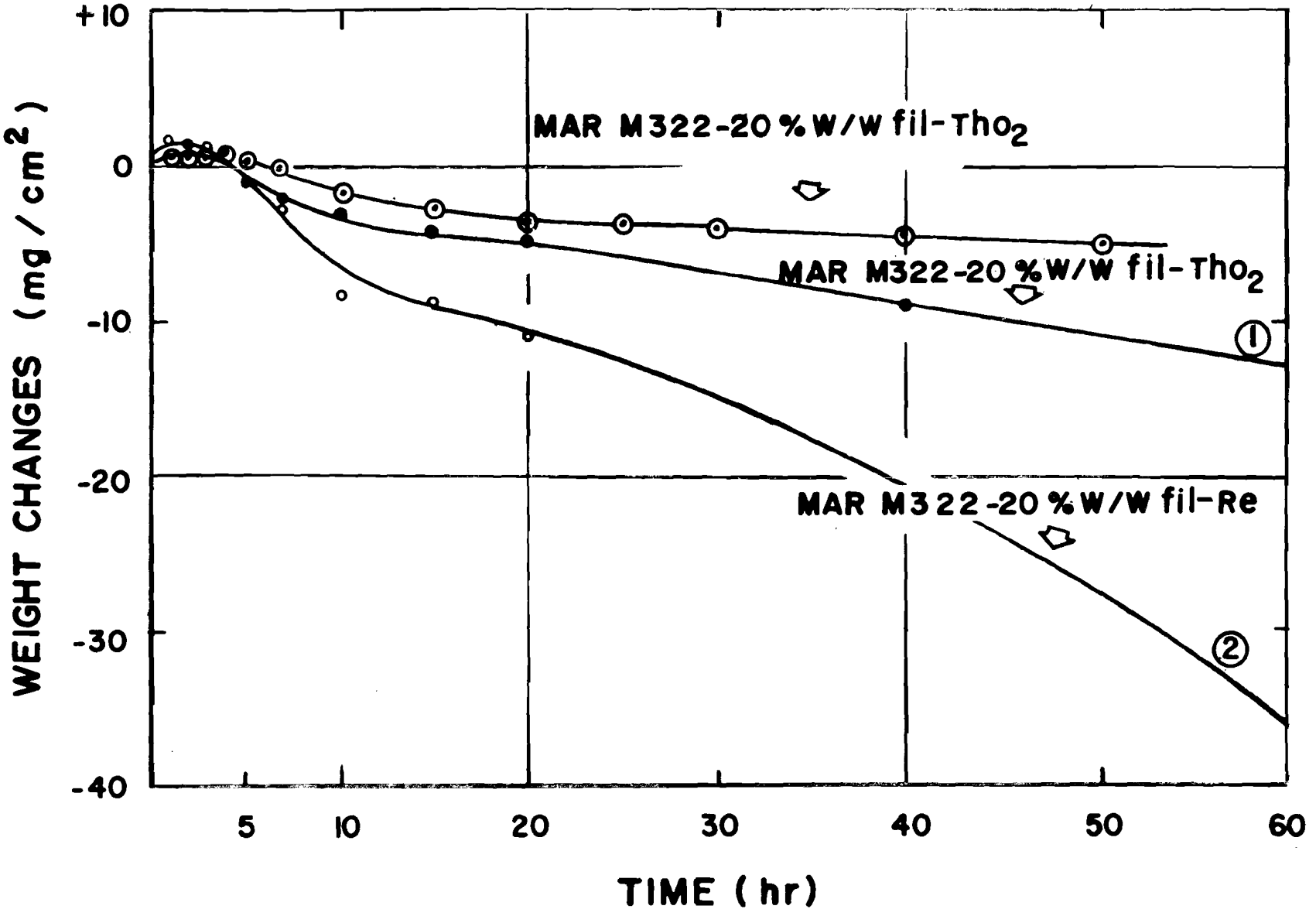


Figure 30. Oxidation behavior of composites.

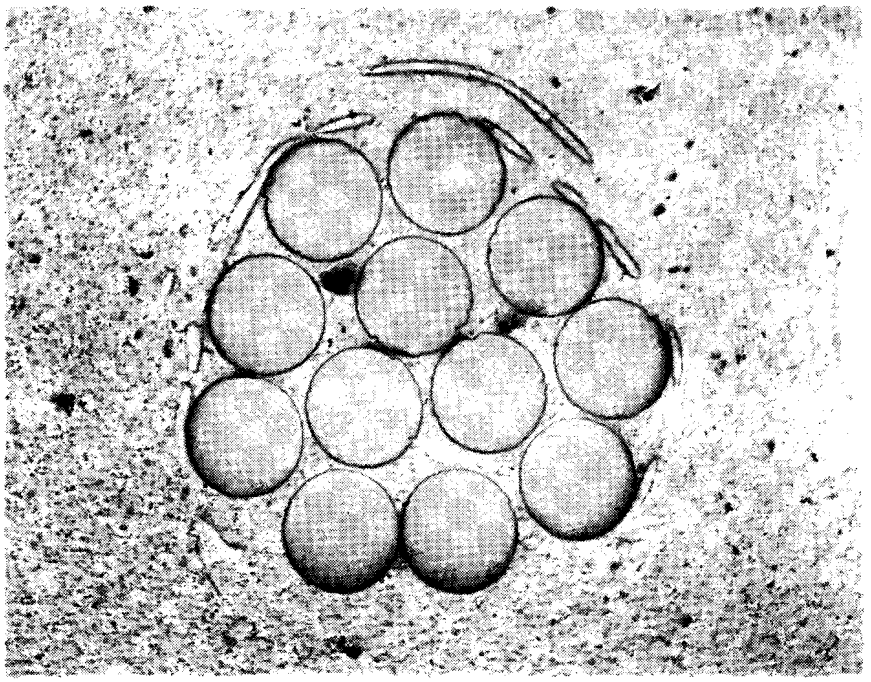


Figure 31. A sectional view of a composite specimen after cyclic oxidation showing absence of cracks due to thermal fatigue.

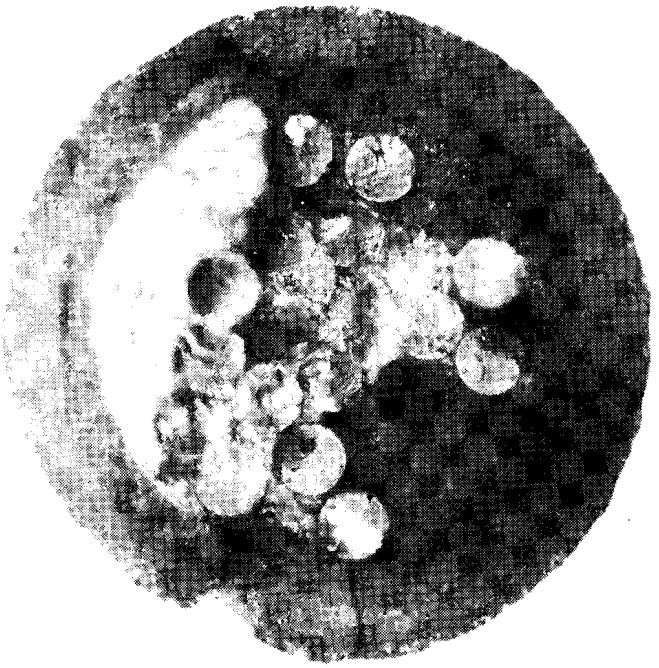


Figure 32. A view of the fracture surface of a composite after a 270-hour stress rupture test.

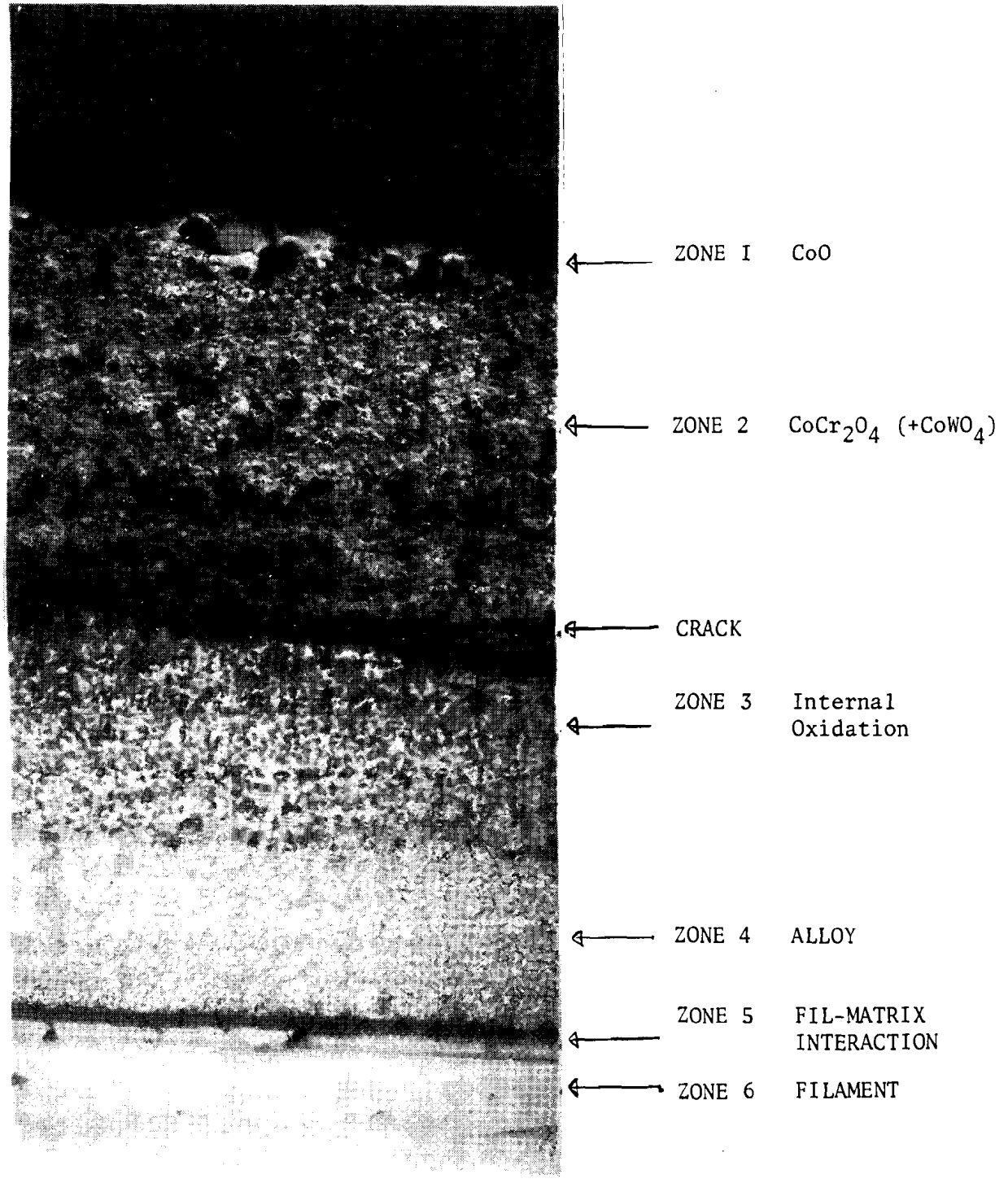


Figure 33. An enlarged view of the structure of the oxide layer on the specimen shown in Figure 32.