AD-753 340

Development of Superalloy Matrix-Refractory Metal Fiber Composites by Coextrusion of Blended Powders

Whittaker Corporation

prepared for

Army Materiel Command

SEPTEMBER 1972

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AMMRC TR 72-29

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DEVELOPMENT OF SUPERALLOY MATRIX-REFRACTORY METAL FIBER COMPOSITES BY COEXTRUSION OF BLENDED POWDERS

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PROCESS DEVELOPMENT DIVISION

September 1972

ARMY MATERIALS AND MECHANICS RESEARCH CENTER
Watertown, Massachusetts 02172

UNCLASSIFIED

Security Classification

DOCUMENT CONTROL DATA - R & D

(Security classification of title, body of abstract and indexing annotation must be entered when the overall report is classified)

1. ORIGINATING ACTIVITY (Corporate author)	2a. REPORT SECURITY CLASSIFICATION
Army Materials and Mechanics Research Center Watertown, Massachusetts 02172	Unclassified
	2b. GROUP

3. REPORT TITLE

DEVELOPMENT OF SUPERALLOY MATRIX-REFRACTORY METAL FIBER COMPOSITES BY COEXTRUSION OF BLENDED POWDERS

4. DESCRIPTIVE NOTES (Type of report and inclusive dates)

5. AUTHOR(S) (First name, middle initial, last name)

Jacob Greenspan and F. J. Rizzitano

6. REPORT DATE	7a. TOTAL NO. OF PAGES	7b. NO. OF REFS
September 1972	~~19~~ 22	0

8a. CONTRACT OR GRANT NO.	9a. ORIGINATOR'S REPORT NUMBER(S)
b. PROJECT NO. D/A 1T061101A91A	AMMRC TR 72-29
c. AMCMS Code 611101.11.844-X031462	9b. OTHER REPORT NO(S) (Any other numbers that may be assigned this report)
d. Agency Accession No. DA OD4790	

10. DISTRIBUTION STATEMENT

Approved for public release; distribution unlimited.

11. SUPPLEMENTARY NOTES	12. SPONSORING MILITARY ACTIVITY
	U. S. Army Materiel Command Washington, D. C. 20315

13. ABSTRACT

Fibers of molybdenum, TZM molybdenum, and tungsten were incorporated within a matrix of four different superalloys by extruding mixtures of spherical powders. Process feasibility, being a function of the flow characteristics of the coexisting materials, occurred only with certain materials, and at certain extrusion temperature. In these cases, fiber aspect ratios were sufficient, theoretically, to obtain fiber strengthening.

Fiber-matrix interdiffusion, as a major consideration in the development of this type composite, was observed to be negligible in the as-extruded condition, but increased in extent with further exposure to elevated temperature. In general, for the composites investigated here, extensive interdiffusion resulted in degradation of stress rupture properties when the fiber was tungsten, but in improved stress rupture properties when the fiber was molybdenum. (Authors)

DD FORM 1 NOV 68 1473 REPLACES DD FORM 1473, 1 JAN 64, WHICH IS OBSOLETE FOR ARMY USE.

UNCLASSIFIED

Security Classification

14 KEY WORDS	LINK A		LINK B		LINK C	
	ROLE	WT	ROLE	WT	ROLE	WT
Composite materials						
Superalloys						
Superalloy matrix						
Coextruding						
Refractory metal fibers						
Blended powders						
Creep rupture strength						

AMMRC TR 72-29

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Technical Report by
JACOB GREENSPAN and F. J. RIZZITANO

September 1972

D/A Project 1T061101A91A
AMCMS Code 611101.11.844-XO31462
In-House Laboratory Initiated R&D
Agency Accession Number DA OD4790

PROCESS DEVELOPMENT DIVISION
ARMY MATERIALS AND MECHANICS RESEARCH CENTER
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FOREWORD

The development described in this report is the result of a cooperative effort between the Army Materials and Mechanics Research Center and Nuclear Metals Division of the Whittaker Corporation under contract DAAG 46-71-C-0148. Particularly the materials concept, choice of materials, and evaluation were conducted cooperatively. The extrusion development was accomplished principally by the contractor, while collation and interpretation of results were principally by AMMRC. The contractor report references are NM-2400.1, August 1971, and NM-2400.4, October 1971.

CONTENTS

INTRODUCTION

In extrusion, the deformation consists essentially of reduction in area and unidirectional elongation and in this respect extrusion is a fibering process. Applied to a mass of powder comprised of two species of particles, the extruded structure may take the form of discontinuous fibers of one phase, unidirectionally aligned in a matrix of another. An important aspect therein is that the powder particles become both fibered and consolidated during the single and relatively brief period of flow through the die opening. Implications therefore are that the method is or can be relatively simple and direct, and thus economical for the purpose of composite synthesis. Further, there should be little or no diffusion reaction between fiber and matrix during this process, in view of the short dwell-time associated with flow through the die opening

In fiber-matrix composite material of this kind, fiber strengthening is realized only if the fiber material is inherently stronger and/or stiffer than the matrix material, if the fibers are not degraded by mechanical damage, if they are not degraded by diffusional reaction, and if the fibers have sufficient aspect ratio and interfacial bond to permit transfer of stress from matrix to fiber. Attainment of these conditions is a function primarily of the mechanical and metallurgical characteristics of the materials involved. One object of the present investigation was to determine whether in fact the coextrusion approach, as described, could feasibly apply to combinations of nickel or cobalt base superalloy and refractory metal to produce a fiber-strengthened superalloy, particularly for elevated temperature environment.

Particles in such mixtures are not necessarily reduced to fibers in accordance with the applied extrusion reduction ratio, but rather the extent of fibering depends upon the mutual flow characteristics inherent to the particular particle species. Thus, a stiff particle in a soft matrix elongates less than normal for the applied reduction ratio, whereas a soft particle in a stiff matrix deforms erratically and may not become fibered in the sense of the present composites concept. Fibering is optimum when flow characteristics of the coexisting materials are similar. Though this is seldom the case, there usually exists a temperature for which the flow mismatch is minimum, which is best for coextrusion. Some of the results of the present investigation do show variations in fibering that are so related.

It is inevitable that the fiber-matrix couple that is capable of being bonded metallurgically will undergo further diffusional reactivity on additional exposure to elevated temperature. Of concern is the possibility that mechanical properties may thereby become degraded, for example, by reaction products that are brittle, or by dissolution of matrix and/or fiber. But it is also possible that such reactions could lead to positive results. The materials of the present investigation were examined in this respect, and both positive and negative results were obtained.

Results here are given in two parts, (1) on composite synthesis by the powder coextrusion approach, and (2) on composite evaluation.

PROCEDURES AND RESULTS

Composite Synthesis by Coextrusion of Powders

Powders

Particles of spherical shape were employed as starting material for purposes of geometric uniformity. Thus, the extrusion reduction theoretically produces an ellipsoid of very long major axis, and the geometry approaches that of a fiber. For a reduction ratio of R, the calculated aspect ratio is $R^{3/2}$.

Consider a cylindrical element of which $d_1 = \ell_1$ is an approximation to a spherical particle, and which deforms homogeneously with the matrix.

$$\text{Reduction Ratio } R = \frac{D_1^2}{D_2^2} = \frac{d_1^2}{d_2^2} = \frac{\ell_2}{\ell_1} \ldots \ell_2 = R\ell_1 = Rd_1$$

$$\text{Aspect Ratio } AR = \frac{\ell_2}{d_2} = \frac{Rd_1}{d_2} = R \cdot R^{\frac{1}{2}} = R^{3/2}$$

Powders of this kind were produced by the rotating electrode process. The source material is an electrode in the form of a bar of about 2-1/2-inch diameter that spins rapidly on its axis as one end is maintained molten by an electric arc. Liquid particles thus are ejected by the centrifugal force, assume spherical shape in flight, and are rapidly quenched at the end of the flight path.

Materials converted in this way were molybdenum, TZM molybdenum, tungsten, René 41, René 95, Inco 625, and L-605. Compositions are given in Table I and mesh analyses in Table II. General appearance is illustrated in Figure 1. Powder particle diameters were generally of the order of 4 to 20 mils, as Table II indicates.

Table I. ALLOY COMPOSITIONS

Alloy	Element (wt percent)												
	Ni	Cr	Co	Mo	Ti	Fe	Al	Si	Mn	Nb	W	C	Zr
TZM Mo				99.6	0.5								0.08
René 41	55	18	11	10	3	2	1						
René 95	68	14	8	3.5	2.5		3.5	0.2	0.15			0.15	
Inco 625	61	22		9	0.2	3	0.3	0.3	0.2	4			
L-605	10	20	53					0.5	1.4		15	0.1	

Extrusion

Steel cans were filled with blended powders comprised of approximately 30 v/o refractory alloy and 70 v/o superalloy; the cans were capped, evacuated, sealed, and then preheated and extruded as given in Table III. The cans were initially 3" in diameter by 6" long, and the die opening was 1" in diameter, so that the reduction ratio was 9:1. All billets were successfully converted to rod this way. The rods were cropped and sectioned for further test and evaluation, as described in the following.

Table II. POWDER PARTICLE SIZE ANALYSES

Diameter (mils)*	Percent of Particles						
	20-14	14-10	10-7	7-5	5-3.5	3.5-2.5	<2.5
Mo	5.8	55.1	25.0	10.1	2.9	1.0	0.1
TZM Mo	6.2	53.3	25.2	11.1	3.0	1.1	0.1
Tungsten	6.5	37.3	34.0	14.4	4.8	1.4	0.46
Inco 625	8.5	18.8	30.2	20.0	15.2	7.6	1.7
René 41	6.8	6.8	22.9	35.8	17.1	5.7	11.6
René 95	14.4	27.0	33.1	15.7	12.6	3.5	3.7
L-605	14.0	15.0	25.5	20.0	8.0	3.5	15.0

*Thousandths of an inch

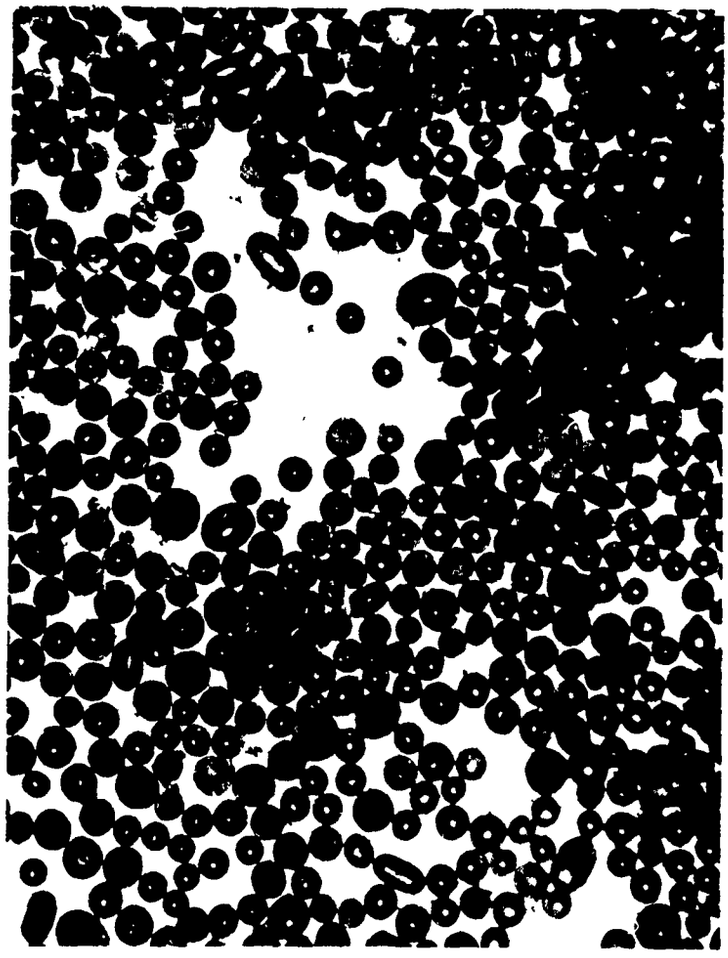


Figure 1. Spherical powder particles produced by rotating electrode meth... Mag 10X

Table III. COMPOSITE IDENTIFICATION GIVING FIBER ASPECT RATIOS

Extrusion*		Composition		Fiber Aspect Ratio
Example	Temperature, °F	Matrix	Fiber†	Approximated
1	2000	Inco 625	Mo	17-30
2	2000	René 41	Mo	16-25
3	2000	Inco 625	TZM Mo	3-10
4	2000	René 41	TZM Mo	3-17
5	2000	L-605	W	4-10
6	2200	L-605	W	1-2
7	2000	René 95	W	2-8
8	2200	René 95	W	1-2

*Billet Diameter 3" - Die Opening Diameter 1" - Reduction Ratio 9:1
†30 Volume Percent

Fibering

Fibering of the minor phase, as seen for examples 1 through 4 (see Table III), as illustrated in general by the photomicrographs in Figure 2. Best aspect ratios, and also the best geometric uniformity of the fibers, are exhibited in

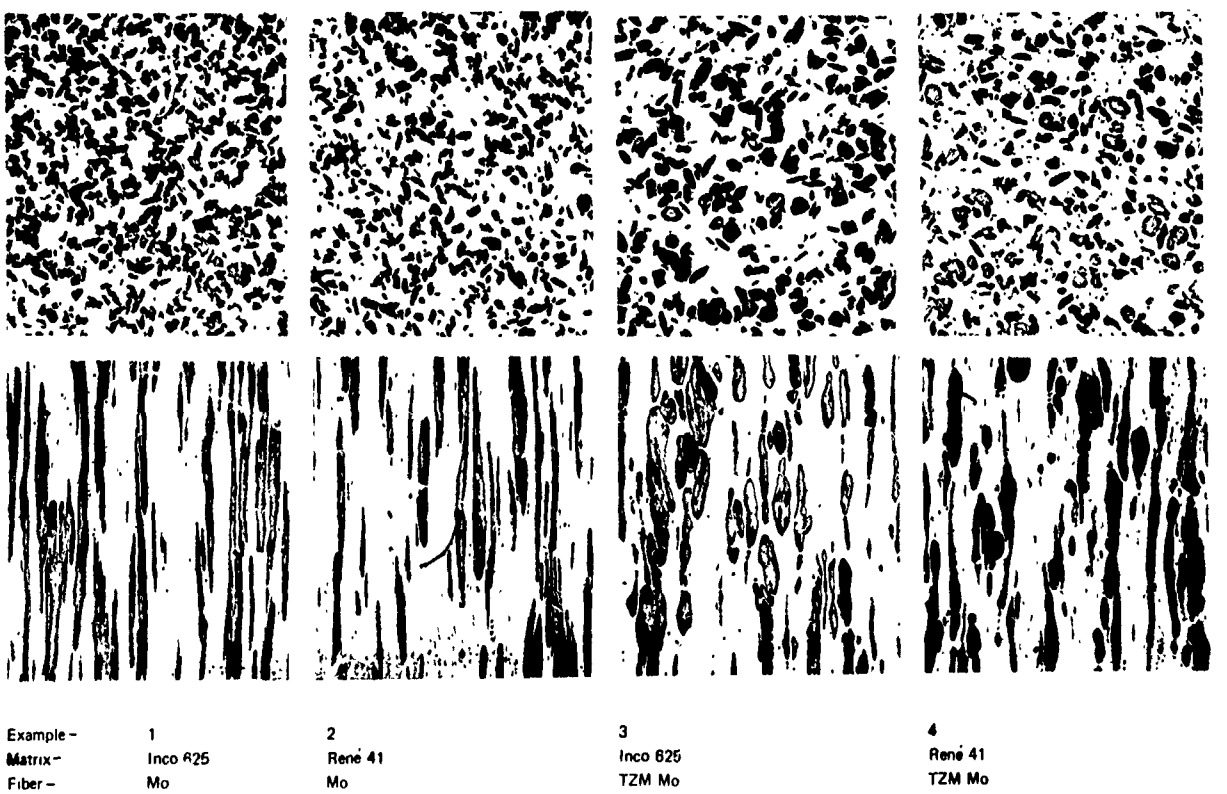


Figure 2. Composites produced by extrusion at 2000 F of blended spherical particles. Mag. 20X
Top - transverse section, bottom - longitudinal section

examples 1 and 2, which are comprised of unalloyed Mo fibers in matrices of Inco 625 and René 41. The respective aspect ratios of 17-30 and 16-25 that were measured from photomicrographs are seen to be a fair approximation of the ideal value of 27, given by $R^{3/2}$ for R (reduction ratio) of 9. However, when the fiber was TZM Mo, as given by examples 3 and 4, fibering was considerably inferior. Aspect ratios are less, and also fibers appear to have become fragmented. Extrusion temperature for these four examples was 2000 F. Greater detail of examples 1, 2, 3, and 4 is shown in Figure 3.

Since tungsten is more difficult to flow than Mo or TZM Mo, it was combined with the stiffer matrix materials L-605 and René 95 in examples 5, 6, 7, and 8. As shown in Figure 4, best fibering was obtained in example 5 of tungsten in L-605 matrix, extruded at 2000 F. Fibering was considerably less for tungsten in combination with René 95, as shown for example 7. Raising the extrusion temperature to 2200 F for both cases resulted in essentially no fibering, as given by examples 6 and 8. Thus, flow mismatch as related to matrix species is illustrated by examples 5 and 7, whereas flow mismatch as related to excessive softening of the matrix, regardless of matrix species, is illustrated by examples 6 and 8. The indication is that fibering could be improved by lowering extrusion temperatures to less than 2000 F, but this is limited by pressure capabilities of the extrusion equipment. Examples 5 and 6 are shown in greater detail in Figure 5.

Thus, various degrees of feasibility are demonstrated with respect to attainment of fibering of the reinforcing phase by the present approach. The fiber aspect ratios in examples 1 and 2 as observed in Figures 2, 3a, and 3b, appear sufficient for fiber strengthening, though the physical integrity of the fiber is unknown. On the other hand, it appears that fiber strengthening would be precluded in examples 3 and 4 in view of the fragmented condition of the fibers shown in Figures 2, 3c, and 3d. For examples 5 and 7, shown in Figure 4, aspect ratios appear to be insufficient for fiber strengthening.

In all cases, the fiber is seen to be characterized by very irregular surface geometry and tapered ends. This could be an advantage from the point of view of (1) increased surface area for transfer of stress from matrix to fiber, and (2) improved stress field at fiber ends. These geometric characteristics could make possible the utilization of lesser aspect ratios than normally needed by smooth and regular fibers for provision of fiber strengthening.

Evaluation of Extruded Composites

The principal purpose of this evaluation was to determine whether fiber strengthening was in fact obtained. This appeared to be particularly relevant to examples 1 and 2, which exhibited best fiber aspect ratios, as shown in Figures 2, 3a, and 3b. Based on the known properties of the fiber and matrix materials alone, it was estimated that such strengthening should be most prevalent at temperatures above 1500 F (815 C), and would be best indicated by stress rupture test. It was recognized also, that some degree of fiber-matrix interdiffusion was inevitable, which could have additional influence on the strength characteristic. Therefore, stress rupture testing was conducted on materials of various degrees of fiber-matrix interdiffusion. More specifically, the present evaluation consisted of (1) metallographic examination of samples subjected to particular thermal exposure, and (2) determination of stress rupture life of sample materials of such thermal exposures.

Transverse a. Example 1; Matrix - Inco 625; Fiber - Mo Longitudinal

Transverse b. Example 2; Matrix - René 41; Fiber - Mo Longitudinal

Transverse c. Example 3; Matrix - Inco 625; Fiber - TZM Mo Longitudinal

Transverse d. Example 4; Matrix - René 41; Fiber - TZM Mo Longitudinal

Figure 3. Microstructures of various composites showing fibering
Extrusion temperature: 2000 F, extrusion reduction 9/1 Mag 65X

Fiber-Matrix Interdiffusion

Samples taken from the extruded composites, examples 1, 2, 3, 4, 5, and 7 were subjected to additional heating, such that various degrees of fiber-matrix interdiffusion would occur. The specific thermal history designations then were (a) as extruded, (b) 1280 F (695 C) in air for 24 hours, (c) 1780 F (974 C) in air for 24 hours, (d) 2180 F (1195 C) in air for 24 hours. The ensuing microstructures are shown in Figure 6.

For composites containing fibers of either Mo or TZM Mo, shown in Figures 6a through 6d, the extent of interdiffusion for conditions (a) and (b) appears relatively minor, and this extent increases in degree for condition (c) and further for condition (d). In this context, the following descriptive terms are employed, "minor" for (a) and (b), "intermediate" for (c), and "extensive" for (d). Similarly, for composites containing fibers of tungsten, Figures 6e and 6f, the terms are "minor" for (a), (b), and (c), and "extensive" for (d). These terms then apply conveniently to the ensuing stress rupture testing described in the remainder of the report.

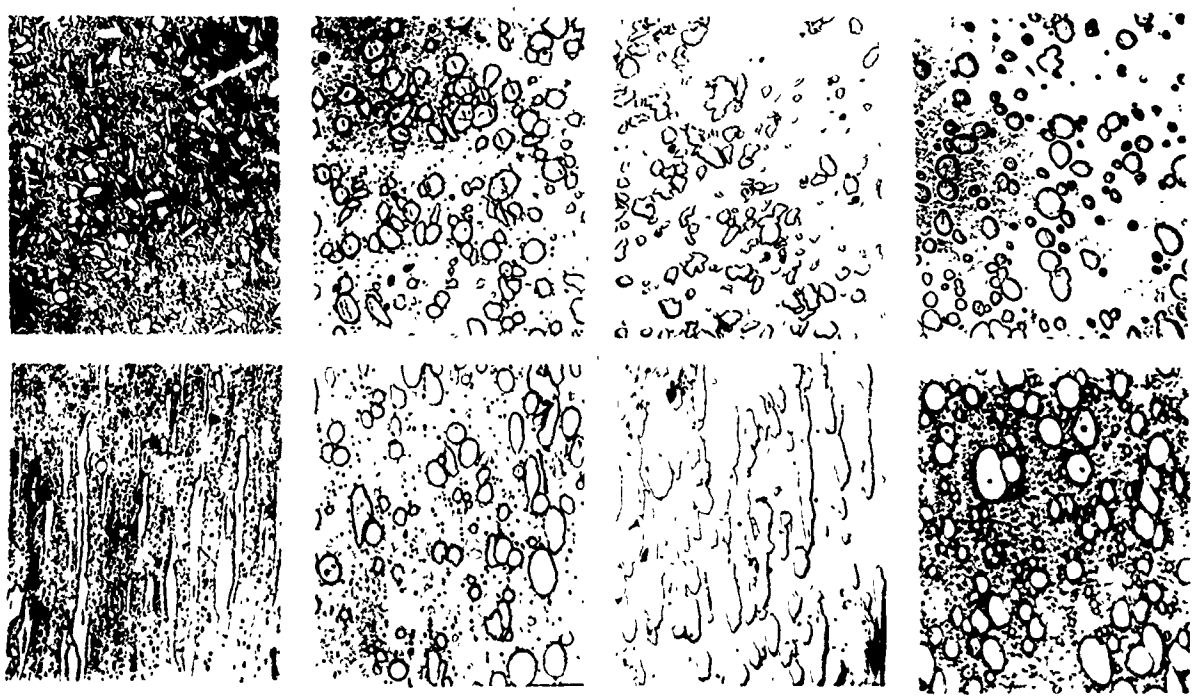
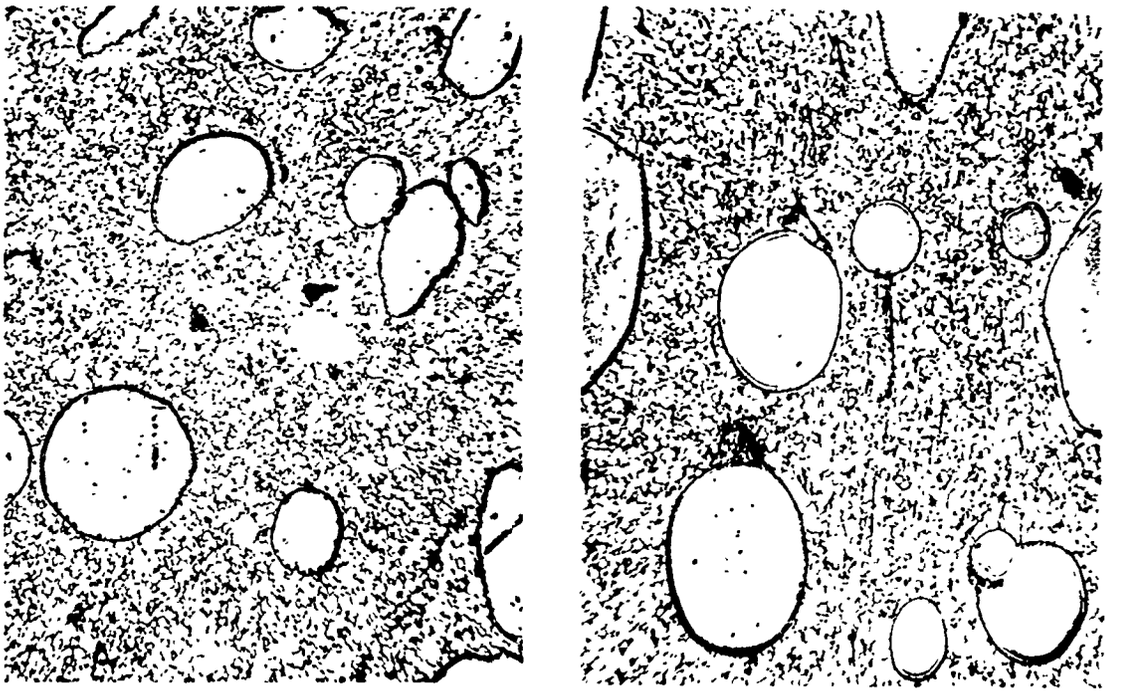


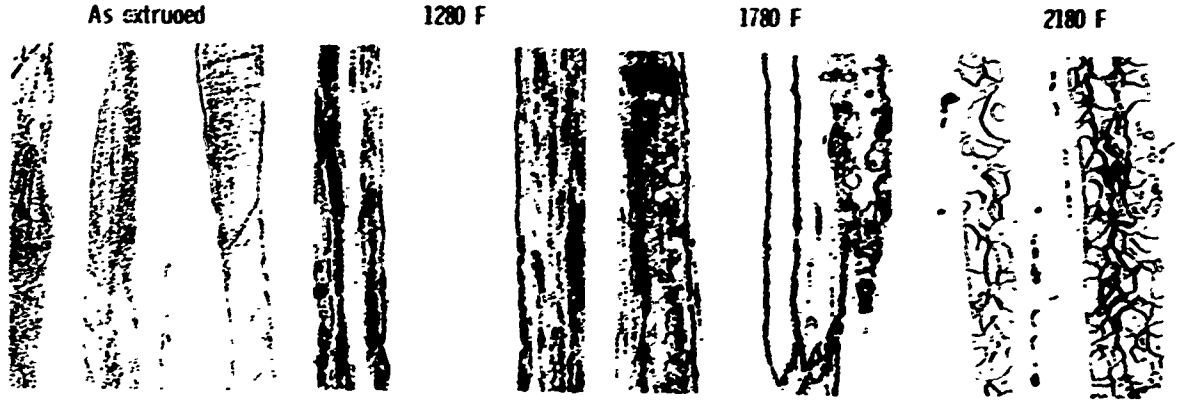
Figure 4. Composites produced by extrusion of blended spherical particles of tungsten Mag 12X
Top - transverse section, Bottom - longitudinal section.

Transverse a. Example 5; Extrusion Temperature: 2000 F Longitudinal

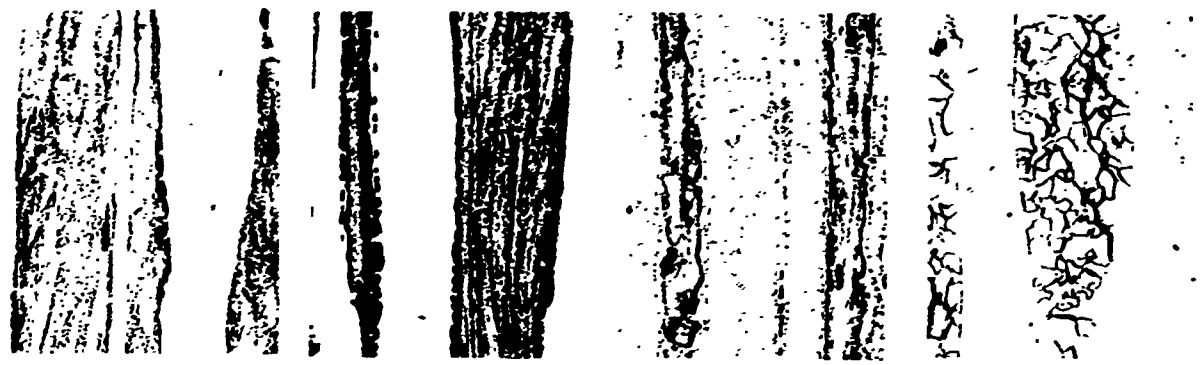


Transverse b. Example 6; Extrusion Temperature: 2200 F Longitudinal

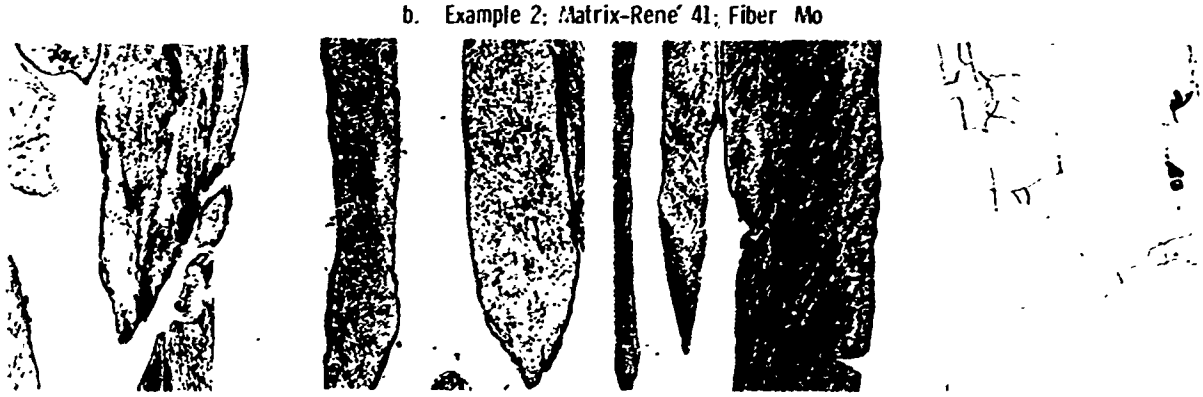
Figure 5. Microstructures of composites of tungsten with L605 matrix, showing fibering. Extrusion reduction: 9/1 Mag 78X



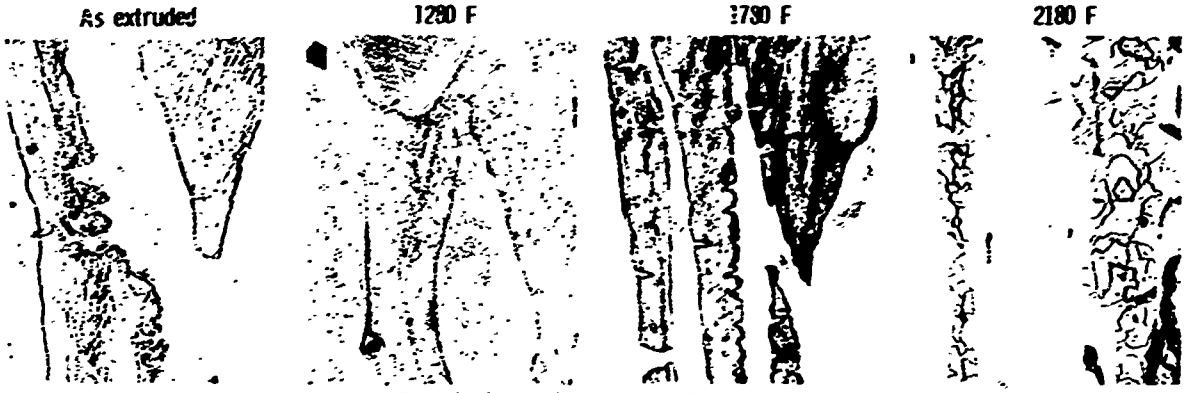
a. Example 1; Matrix–Inco 625; Fiber Mo



b. Example 2; Matrix–René 41; Fiber Mo



c. Example 3; Matrix–Inco 625; Fiber TZM Mo



d. Example 4; Matrix–Rene' 41; Fiber TZM Mo

e. Example 5; Matrix–L605; Fiber Tungsten

f. Example 6; Matrix–Rene' 95; Fiber Tungsten

Figure 6. Diffusion reactivity for examples heated in air at varying temperatures for 24 hours. Mag. 150X.

Stress Rupture Testing

Extruded bar stock of examples 1, 2, 3, 4, 5, and 7 was sectioned to provide blanks for stress rupture test samples. The blanks were heat treated in conformance with the previously described conditions for fiber-matrix interdiffusion, and later machined to the test bar configuration shown in Figure 7.

Stress rupture testing was done in air, using conventional equipment, properly instrumented for temperature control and for automatic recording of rupture time. In view of the limited number of test samples available, the choice of temperature and stress was based on relatively short time failure for the matrix materials, on the assumption that under these conditions, the strength contributions of the fibers would be most evident. This scope, together with the test data are summarized in Table IV.

The presence of fiber is seen to have had various degrees of influence on the rupture life, and also on the elongation and reduction in area. For those cases in which the fiber was Mo or TZM Mo, rupture life was generally increased, particularly in accordance with the history of diffusion pretreatment. The strengthened materials further are seen to have retained a significant degree of ductility. However, for those cases in which the fiber was tungsten, a negative influence by the tungsten is evident.

The influence of these fibers on stress rupture life is shown more clearly in Table V. Specifically in the case of example 1, the rupture life of the composite was about twice that of the matrix material when the diffusion pretreatment was minor, but was over twenty times greater when the extent of diffusion was increased. The trend of increasing rupture life with increasing diffusion is shown also for examples 2, 3, and 4 though to lesser extent. The very outstanding improvement in 1500 F rupture life for example 1 is shown graphically in Figure 8. Figure 9 shows this to be equivalent to a gain of the order of 110 F, for 100 hours of rupture life at stress of 20 ksi.

Based on the stress rupture data exhibited by example 1, Table V, and the related microstructures shown in Figures 2, 3, and 6, the increases in stress

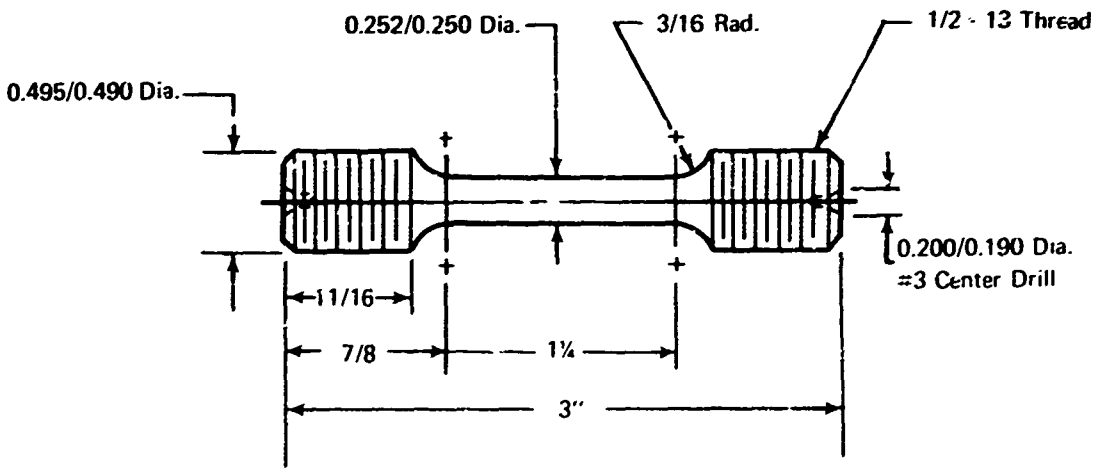


Figure 7. Stress rupture specimen

Table IV. SUMMARY OF STRESS RUPTURE TEST DATA

Example	Composite	Diffusion Pretreatment	Test Temperature (deg °F)	Rupture Stress (ksi)	Rupture Life (ksi)	Reduction in Area (%)	Elongation (%)
1	Matrix: Inco 625 Fiber: Mo	minor	1500	25	29.9	51.2	52.6
		minor	1500	25	27.9	36.3	35.4
		intermediate	1500	25	246.4	8.8	7.8
		intermediate	1500	25	226.6	8.0	8.4
		extensive	1700	15	25.5	9.4	10.2
		extensive	1700	15	23.5	9.4	10.7
	Matrix alone Inco 625	-	1500	25	12	-	-
		-	1500	18	100	-	-
		-	1500	15	100	-	-
		-	1700	15	41	-	-
		-	1700	6	25	-	-
2	Matrix: René 41 Fiber: Mo	minor	1700	15	22.7	24.4	26.5
		minor	1700	15	19.5	26.8	22.7
		intermediate	1700	15	96.8	2.6	1.5
		intermediate	1700	15	92.5	4.8	5.4
	Matrix alone René 41	-	1660	15	100	-	-
		-	1700	15	25	-	-
3	Matrix: Inco 625 Fiber: TZM Mo	minor	1500	25	10.1	22.2	15.4
		minor	1500	25	17.0	27.5	11.6
		intermediate	1500	25	34.8	6.2	4.6
		intermediate	1500	25	26.9	6.3	4.6
		extensive	1500	25	53.7	5.7	6.2
		extensive	1500	25	49.8	8.8	6.2
	Matrix alone Inco 625	-	1500	18	100	-	-
		-	1500	25	12	-	-
4	Matrix: René 41 Fiber: TZM Mo	minor	1700	15	18.4	13.8	16.2
		minor	1700	15	16.1	13.8	15.4
		intermediate	1700	15	----------	----------	---------- *
		intermediate	1700	15	55.4	2.0	3.5
	Matrix alone René 41		1660	15	50	-	-
		-	1700	15	25	-	-
5	Matrix: L-605 Fiber: Mo	extensive	1400	18	82	2.0	-
	Matrix alone L-605	-	1560	18	100	-	-
6	Matrix: René 95 Fiber: Mo	minor	1800	35	0.2	1.7	3.0
		minor	1800	35	0.1	2.7	4.6
		extensive	1800	35	0.1	-	1.5
		extensive	1800	35	0.2	-	1.5
	Matrix alone René 95	-	1750	35	100	-	-
		-	1800	25	100	-	-

*Controller malfunction

Table V. RUPTURE TIME OF THE COMPOSITE AND THE MATRIX

Example	Diffusion Pretreatment	Rupture Time, Hours		Stress Rupture Conditions	
		Composite	Matrix Alone	Temperature, °F	Stress, ksi
1	minor	27.9-29.9	12	1500	25
	intermediate	226.4-246.4	12	1500	25
	extensive	23.5-25.5	41	1700	15
2	minor	19.5-22.7	25	1700	15
	intermediate	92.5-96.8	25	1700	15
3	minor	10.1-17.0	12	1500	25
	intermediate	26.9-34.8	12	1500	25
	extensive	49.8-53.7	12	1500	25
4	minor	16.1-18.4	25	1700	15
	intermediate	55.4	25	1700	15
5	extensive	82	100	1600	18
6	minor	0.1-0.2	100	1800	25
	extensive	0.1-0.2	100	1800	25

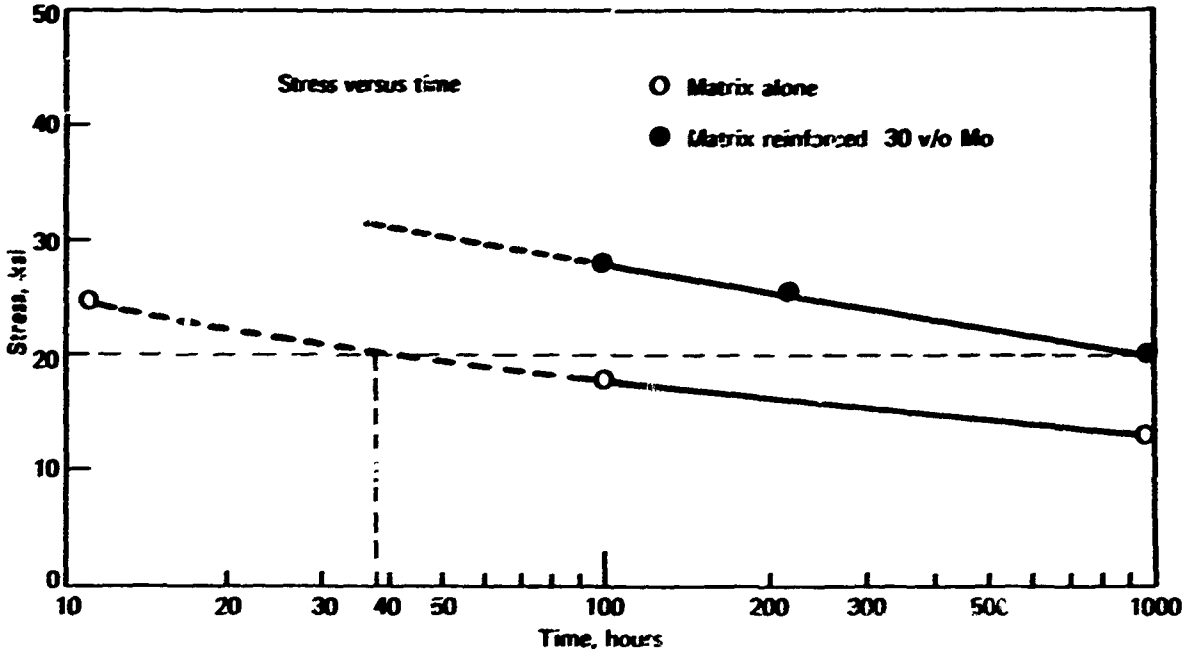


Figure 8. Influence of fiber reinforcement on 1500 F rupture life of Inco 625 alloy

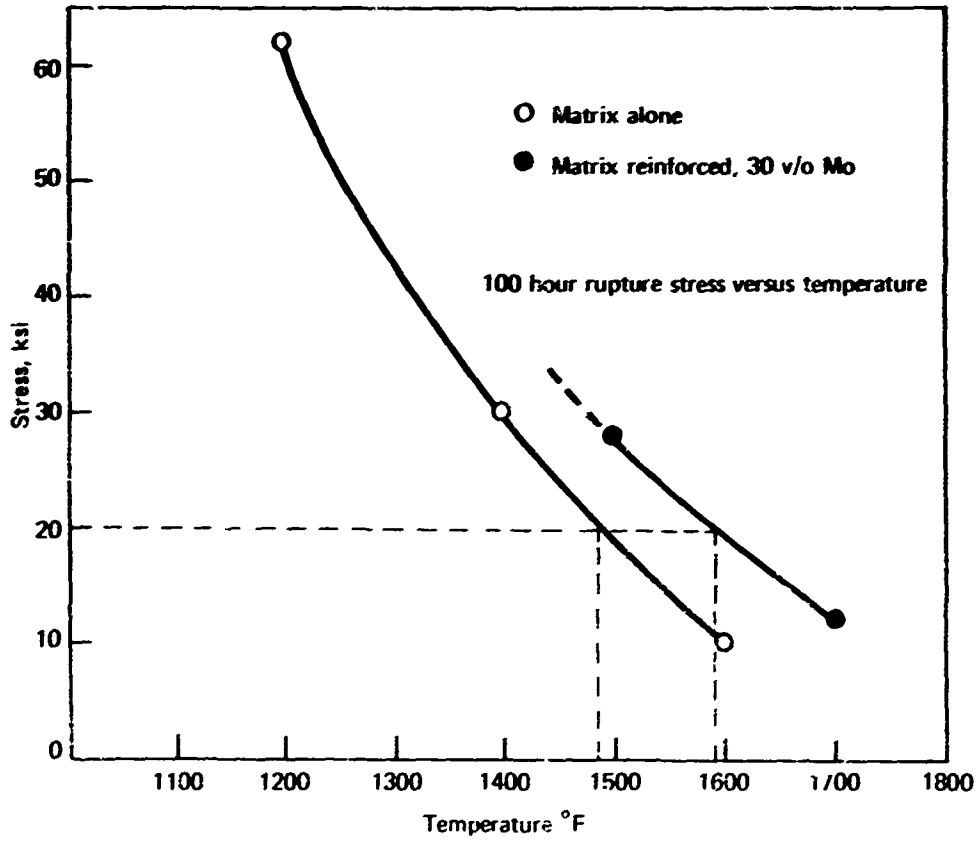


Figure 9. Influence of 30 volume percent fiber reinforcement on rupture life of Inco 625 alloy

rupture life appear to have been effected by (1) fiber strengthening alone, demonstrated by the case of minor diffusion, and (2) this plus an increment derived from the fiber-matrix diffusion, demonstrated by the cases of more extensive diffusion. Examples 2, 3, and 4, which exhibited inferior fibering, exhibited no fiber strengthening as demonstrated by cases of minor diffusion, but did exhibit diffusion strengthening as demonstrated by cases of more extensive diffusion.

SUMMARY AND CONCLUSIONS

Extrusion basically is a fibering process which can be applied to a mass of blended powders to obtain structure of fibers of one phase contained in a matrix of another. The present work pertains to combinations of refractory metal fiber incorporated in a superalloy matrix. The present determinations were with respect to (a) feasibility of the extrusion process to obtain such composites and (b) evaluation on possible utility of this type composite.

The process was found to be entirely feasible in the sense that all of the blended powder billets were integrally reduced to rod within the limits of the extrusion parameters employed. However, feasibility with regard to attainment of fibering of the reinforcing phase is viewed arbitrarily within the range of variations encountered. A range for further possible optimization through parameter control is indicated.

More specifically, fiber aspect ratios obtained here varied from about 30:1 to less than 2:1. The present composites in this order of merit were: Mo fiber in Inco 625 matrix; Mo fiber in René 41 matrix; TZM Mo fiber in Inco 625 matrix; TZM Mo fiber in René 41 matrix; W fiber in L-605 matrix; W fiber in René 95 matrix. In microstructural examination, Mo fibers appeared intact, but TZM Mo fibers appeared fragmented. In all cases fibers were of irregular surface geometry and fiber ends were tapered. This geometry is interpreted as beneficial with respect to fiber strengthening.

In the as-extruded condition, fiber-matrix interdiffusion was minor or essentially undetected by ordinary optical metallography. The extent of interdiffusion was then deliberately increased by additional exposure to elevated temperature to explore the influence of such microstructural changes on the material integrity.

Samples so characterized were then tested in stress rupture, in air, at temperatures of 1500 F (815 C) and 1700 F (925 C). In general, increases in stress rupture life were obtained in materials in which fibers were Mo or TZM Mo, but not in materials in which fibers were W.

Increases in stress rupture life were greatest in materials in which fibering appeared to be best and in which fiber-matrix interdiffusion was greatest. This was exemplified best by Mo fiber in Inco 625 matrix.

It is concluded that increases in stress rupture life were effected by (1) fiber strengthening alone, demonstrated by cases where interdiffusion was minor, and (2) this plus an increment derived from the interdiffusion, demonstrated by cases where interdiffusion was more extensive. Further details on the latter are as yet undetermined.