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Dispersion Strengthened Molybdenum and Molybdenum-Base Alloys

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Prepared for **BALLISTIC SYSTEMS AND SPACE SYSTEMS DIVISIONS**
AIR FORCE SYSTEMS COMMAND
LOS ANGELES AIR FORCE STATION
Los Angeles, California

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This technical documentary report has been reviewed and is approved for publication and dissemination. The conclusions and findings contained herein do not necessarily represent an official Air Force position.

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ABSTRACT

One of the problems associated with the use of molybdenum is the rapid decline in strength at low To/Tm ratios compared with some other structural materials and the increase in transition temperature accompanying recrystallization. A program was initiated to study the possibility of introducing a dispersoid capable of increasing the strength and recrystallization temperature and decreasing the grain growth characteristics of molybdenum. Candidate dispersoids were screened on the basis of physical properties, chemical inertness, and availability. The most promising candidate was found to be thoria.

The following materials were made by hot pressing:

Molybdenum
Mo + 2-1/2% ThO_2
Mo + 5% ThO_2
TZM
TZM + 2-1/2% ThO_2

The alloy charges were prepared by mechanical blending under purified argon. Elemental powders with particle sizes finer than 3 μ were used. Additions of ThO_2 were made by adding an aqueous or alcohol solution of $Th(NO_3)_4$ to the powders, then decomposing the compound by heating in dry hydrogen. Billets were hot-pressed in graphite dies lined with molybdenum foil. The as-pressed densities were in the order of 98% of theoretical. The hot-pressed billets were extruded and swaged to bar stock. The bar stock

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was evaluated in terms of recrystallization behavior, grain growth characteristics, and elevated temperature strength properties. The uniformity of the matrix and the composition of the dispersed phase were followed by electron probe analysis at various stages of the fabrication schedule.

Thoria was found to be quite effective in stabilizing the microstructure and increasing the strength of molybdenum. The TZM alloy with ThO_2 was found to have better workability than molybdenum with ThO_2. Due to an interaction between Ti, Zr, and ThO_2, the distribution of ThO_2 became quite coarse and no strength improvement was experienced. Out of several alloying elements only Hf showed promise for combined alloy and dispersion strengthening because of its compatibility with ThO_2.

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I. INTRODUCTION

The trend toward developing useful strength close to the melting point in many pure metal and alloy systems has focused attention on dispersion strengthening using an inert dispersant. Considerable success has been obtained in commercially available Al, Cu, Ni, and W base alloys while still others show promise in development stages. Relatively little work has been reported for Mo base materials in spite of the fact that use of these alloys depends largely upon attractive elevated temperature strength. A review of previous work on molybdenum containing a variety of oxide dispersions has been reported by Bruckart, et al.(1); however, properties were evaluated only up to 2000°F and no results were reported on materials which would exhibit both alloy and dispersion strengthening.

The purpose of this study was to evaluate the potential of dispersion strengthening in Mo as well as the possibility of combining it with the well established strengthening obtained from the combination of carbon and a strong carbide forming element (i.e., Ti, Zr, Cb, etc.). The temperature range of interest is from 2500° to 4000°F with particular attention to the area just above 3000°F where the current high strength alloys lose strength very rapidly.

Although many methods of incorporating the dispersant are available, nearly all involve consolidation by powder metallurgy. The powder approach used in this study does not necessarily represent a cost disadvantage since high grade Mo powder is priced only slightly above melting stock. By simple mechanical blending of elemental powders, alloys can actually be produced with homogeniety equally as high, in some cases, as cast materials (2).

After reviewing the stability of various oxide, nitride, and boride dispersants in Mo to 4000°F (3), the best candidate for stability, handling, and consolidation was found to be ThO_2. The ThO_2 dispersion was quite beneficial to both strength and stability of the Mo matrix; however, in the presence of many of the alloying elements a considerable degradation in both microstructural stability and strength was experienced. This reaction represents a serious deterrent to combining dispersion strengthening with the existing strength of such current alloys as TZM or TZC. The problem should not be insurmountable, however, and it is hoped that the results of this study will serve to lay the ground work for continued improvement in powder metallurgy molybdenum base alloys in the future.

II. MATERIALS AND PROCEDURE

All materials in this study were prepared entirely by powder metallurgy using blends of elemental powders for the alloys involved. The average particle size of the Mo, Ti, and Zr was 1 μ and for the Cb, Ta, and Hf, 5 μ. The Mo powder supplied by Climax was better than 99.5% pure with the major impurity oxygen at about 4000 ppm. The Ti and Zr were supplied by Metal Hydrides, Inc, Beverly, Mass. The Cb, Hf, and Ta were obtained from Wah Chang Corp, Albany, Oregon. The purity of each material was reported at better than 99.5% with oxygen again the major impurity on the order of 2000 ppm.

The additions of ThO_2 were made by mixing a solution of $Th(NO_3)_4$ in distilled H_2O to the Mo powder. The mixture was then vacuum dried before heating in a retort for 10 hours at 600°C in dry H_2 to decompose the $Th(NO_3)_4 \rightarrow ThO_2$. The pure Mo control material was given a similar treatment in H_2 to remove as much of the adsorbed oxygen from the powder as possible. After the H_2 cleaning operation the powders were never exposed to atmospheric conditions since all handling was conducted in a vacuum glove box under purified argon.

Since all of the alloying elements considered in this study would readily form hydrides during the hydrogen cleaning operation the additions were made to either the pure Mo or the Mo + ThO_2 powders after cleaning. Blending was conducted dry in a Waring Blendor. Details of this process along with resulting homogeniety obtainable in the alloys have been reported earlier (2,4).

The powders were then hot-pressed in 1-1/2 in. I.D. graphite dies lined with Mo foil at 1600°C (~2900°F) and 5000 psi. Full pressure was maintained during heating and cooling with no holding time at temperature. Billets measured about 2-1/2 in. long and were all better than 98% of theoretical density. After hot pressing the billets were vacuum annealed for 3 hours at 1600°C.

The hot pressed billets were canned in TZM for extrusion at a ratio of 6:1. The extrusion temperature was 2200°F for the pure Mo, 2400°F for the Mo + 2.5% and 5.0% ThO_2, 2600°F for TZM, and 2800°F for the TZM + 2.5 ThO_2 alloy. After removing the can, swaging was attempted at 2200°F; however, the only alloys which could be swaged were the TZM and TZM + 2.5% ThO_2 alloys which underwent a 60% reduction.

Standard 3/16 in. diam by 3/4 in. long reduced section test specimens were machined directly from the swaged or extruded stock. Tensile tests were conducted in vacuo ($<10^{-4}$ torr) at a strain rate of 0.05 min^{-1}. Elongation measurements were made over a 1/2 in. gage length. Metallographic sample preparation was accomplished by mechanical polishing with SiC grit papers and a Linde-B Al_2O_3 on a Syntron vibratory polisher. Etching for grain structure and dispersed phase delineation was conducted electrolytically in a 2% NaOH solution. The second phase particles were extracted for x-ray identification by dissolving the matrix electrolytically in a 7% HCl 93% ethyl alcohol solution at about 12 V. Electron microprobe analysis was made on the polished and etched samples by continuous scanning at a rate of 100 μ/min. The electron beam excited a spot about 1 μ diam at 30 kV and 0.05 μ amp specimen current.

Hot hardness readings from 2000 to 3000°F were obtained by making three impressions at each temperature on an electropolished surface. A 5 Kg load was applied through a sapphire indenter ground to the Vickers Pyramid configuration. A purified argon atmosphere locally gettered with Ti sheet was utilized to prevent oxidation of the samples.

III. RESULTS AND DISCUSSION

A. FABRICATION

The results of extrusion helped to reveal the influence of alloy additions as well as consolidation methods on the performance of these materials. Although all of the alloys were given a hydrogen cleaning treatment prior to hot pressing under purified argon, there appeared to be a detrimental effect of residual impurities (probably oxygen) on the workability. Both the pure Mo and the Mo plus 2.5% and 5% ThO_2 alloys exhibited some cracking during extrusion and could not be swaged without rather severe cracking. The cracking was so severe during extrusion of the 5% ThO_2 material that sufficient stock could not be salvaged for testing. The TZM alloys with or without ThO_2, however, were extruded and swaged with very little difficulty.

Although the TZM and TZM + ThO_2 alloys were extruded at somewhat higher temperatures, the addition of Ti and Zr are believed to be resposible for the difference in workability. The effectiveness is believed to result from a gettering reaction whereby the Ti and Zr tie up the excess oxygen in the form of stable oxides. The annealed microstructures of these alloys reveal some randomly dispersed inclusion particles which have been identified by electron probe analysis as compounds of Ti and Zr. The increased workability of these same alloys prepared by vacuum arc melting or by sintering cold pressed compacts under hydrogen or vacuum where volatile interstitials are removed also supports this contention.

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The microstructure of the alloys in the extruded condition shows that considerable stability is afforded by the presence of a ThO_2 dispersion. Complete simultaneous recrystallization was obtained during extrusion of the pure Mo and the TZM alloy. However, the Mo alloys containing 2.5% and 5% ThO_2 showed no evidence of recrystallization, grain growth, or ThO_2 instability. The TZM alloy containing 2.5% ThO_2 did not exhibit the same stability as the Mo - ThO_2 alloys during extrusion, in that considerable grain growth and ThO_2 agglomeration were observed. Although the TZM + ThO_2 material was extruded at a temperature 400°F higher than the Mo + ThO_2 alloys, the gross instability is attributed largely to an interaction between ThO_2 and the Ti and Zr alloying additions. The electron probe analysis of this alloy shown in Fig. 1 illustrates the extent of this reaction between the ThO_2 particles and the Ti and Zr in solution. Much higher concentrations of Ti and Zr are observed in the particles than in the matrix. Some Zr was always found in the ThO_2 particles, whereas Ti was somewhat less reactive. A similar reaction between Zr and ThO_2 has been observed in tungsten base alloys with equally detrimental results on ThO_2 stability. The reaction appears to be accelerated by higher temperatures and plastic deformation, the effects of which will be discussed in the following section.

B. ELEVATED TEMPERATURE PROPERTIES

Since the aim of this study was to develop materials with stability above 2000°F, the evaluation of all materials was restricted to this temperature range. The tensile properties of all materials studied are presented in Table 1. The strength of hot pressed and extruded pure Mo is in line with arc cast

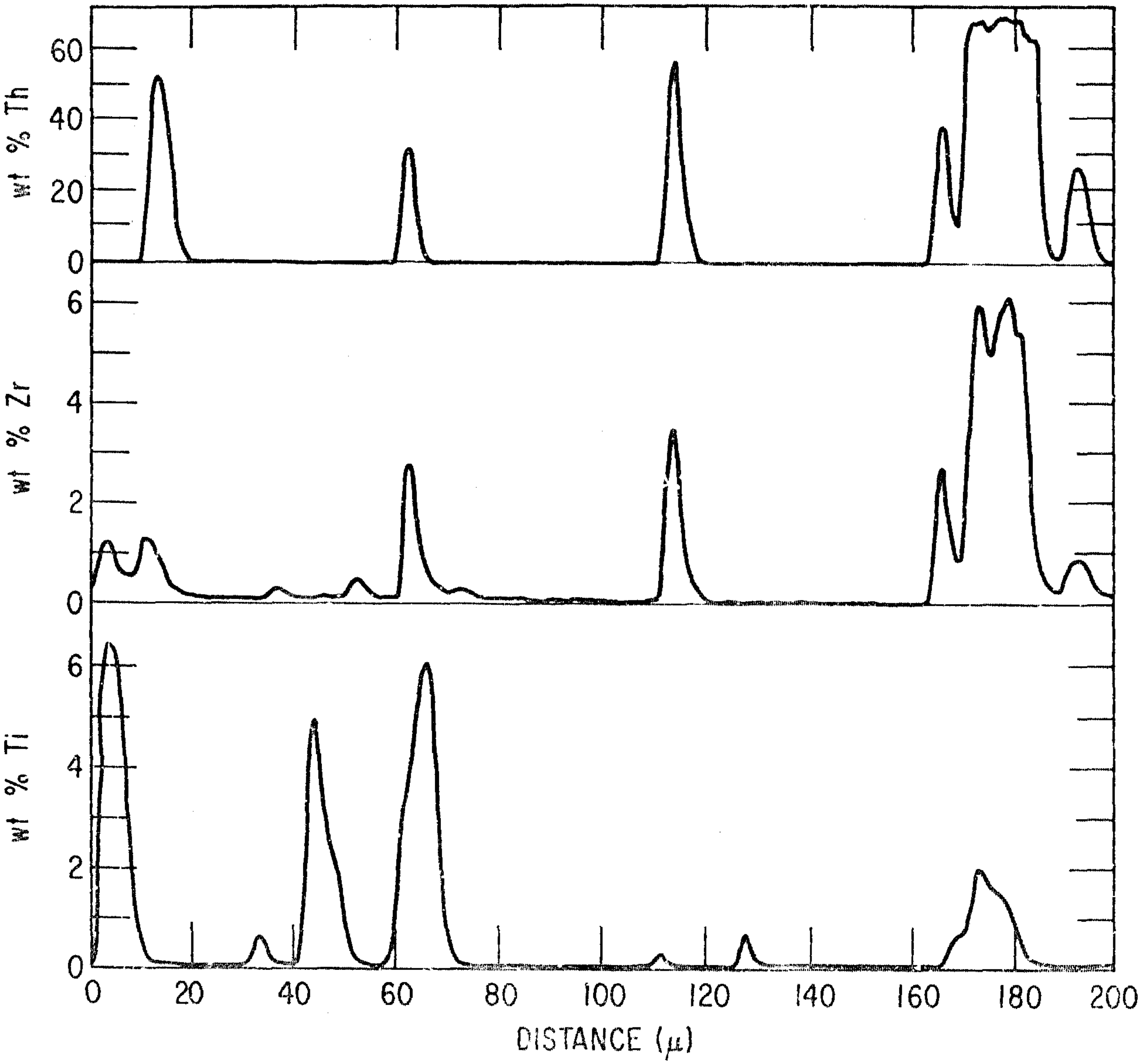


Figure 1. Chemical Composition vs Distance Across the TZM + 2.5% ThO_2 Alloy Swaged and Annealed 1 hr at 4000°F

material over the entire temperature range. The ductility, however, is much lower than reported for arc melted material (5). The factors which reduce both fabricability and ductility of these alloys apparently do not significantly alter the tensile strength at temperatures above 2000°F.

addition of 2.5% ThO_2 resulted in a remarkable increase in strength, as shown in Table 1. This strength improvement was also accompanied by very good microstructural stability over most of the temperature range. Partial recrystallization was obtained during testing at 3500°F, as shown in Fig. 2, where only about 60% of the reduced section retained the fine grained structure characteristic of the starting material. The hardness of the area which remained fine grained was considerably greater than the recrystallized area (Fig. 2). Although this material had not been swaged, the hardness of the fine grained area was nearly as high as the TZM alloys after swaging.

Elevated temperature grain growth and softening were promoted by strain since neither the extruded or the hot-pressed material exhibited such phenomena during unstressed exposure up to 3500°F. The areas which experienced recrystallization during testing at 3500°F had the same average ThO_2 interparticle spacing (~4 μ) as the areas which remained fine grained. This suggests that a difference in ThO_2 distribution was not responsible for the selected recrystallization nor did the recrystallization process promote any instability of the ThO_2 in these areas. The behavior of the dispersant is consistent with previous results (3), where ThO_2 was reported to be quite stable and effective in reducing grain growth below 4000°F. Even greater stability and strength may have been possible in this alloy if more stored

Table 1. Hardness and Elevated Tensile Properties of Molybdenum Base Alloys

Alloy	Temperature (°F)	Hardness $Knoop_{500}$	Tensile Strength (psi)	0.2% Offset Yield Strength (psi)	Elongation (%)	Reduction in Area (%)
Mo (0.004 C)	2000	-	21,300	19,900	3	1.6
	2500	-	4,400	2,900	3	2.4
	3000	-	2,400	1,100	0	0
	3500	-	570	-	4	1.6
Mo + 2.5 ThO_2 (0.005 C)	2500	-	19,600	14,300	1	1.7
	3000	-	10,200	-	3	1.7
	3500	-	7,800	4,900	3-1/2	1.2
TZM (Mo - 0.5 Ti - 0.1 Zr - 0.021 C)	As Swaged	273	-	-	-	-
	2000	-	29,100	28,600	43	95.1
	2500	-	9,700	-	80	98.4
	2500	230	8,700	6,400	101	98.6
	3000	211	4,800	2,900	125	98.9
	3500	192	1,500	-	136	97.4
TZM + 2-1/2% ThO_2 (Mo - 0.5 Ti - 0.1 Zr - 0.024 C)	As Swaged	280	-	-	-	-
	2000	-	29,400	29,100	48-1/2	97.1
	2500	218	7,800	5,900	111	98.7
	3000	220	4,600	2,200	104	99.2
	3500	195	1,000	-	88	98.0

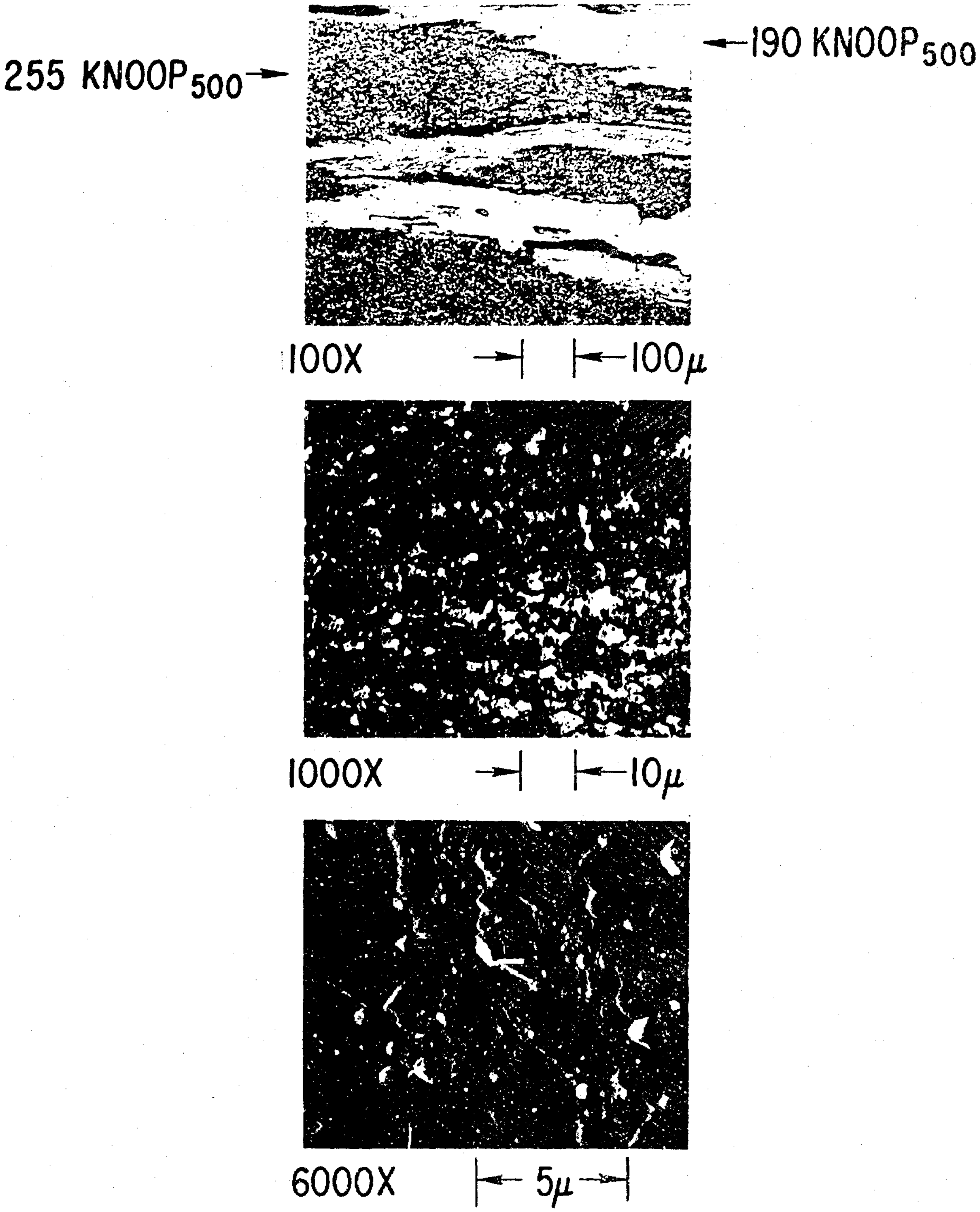


Figure 2. Mo + 2.5% ThO_2 Tested to Fracture at 3500°F

energy could have been incorporated into the material by a series of strain-anneal cycles. The importance of such processing in developing both optimum strength and resistance to recrystallization in dispersion strengthened alloys is well documented (6,7). The major deterrent to such processing here is the poor workability of the extruded stock which could not be swaged without cracking after extrusion. If workability could be increased without altering other characteristics of this alloy, the benefits of "stored energy" could be realized to further improve the properties at elevated temperatures.

The hot hardness values in Table 2 show that a considerable increase in hot hardness is realized by increasing the ThO_2 from 2.5 to 5%. This increment in elevated temperature stability may be difficult to realize in practice, however, due to the loss in workability and ductility which accompanies increased additions of ThO_2.

In contrast to pure Mo, the properties of the TZM alloys reported in Tables 1 and 2 show that the elevated temperature, tensile strength, and hardness are insensitive to additions of ThO_2. The strengths are also on the low side of the band reported in the literature for high strength molybdenum base alloys (8,9,10). The ductility was much higher than the Mo or Mo + ThO_2 materials, which is consistent with the greater workability discussed previously. The contention that Ti and Zr have increased the ductility by removing oxygen from solution in the form of an oxide suggests that much of the Ti and Zr may have also been removed from solution. The rather low strengths of these alloys may then reflect a smaller capacity for the necessary carbide

Table 2. Hot Hardness Values of Mo Base Materials

Material and Composition	Diamond Pyramid Hardness		
	2000°F	2500°F	3000°F
Mo	45.8	23.8	15.3
Mo + 2.5 ThO_2	41.4	32.3	24.0
Mo + 5 ThO_2	84.9	56.4	32.2
TZM	37.7	25.9	17.1
TZM + 2.5 ThO_2	37.9	24.5	15.6
Mo + 2 Ta + 0.1 C + 2.5 ThO_2	48.9	30.8	16.4
Mo + 1 Cb + 0.1 C + 2.5 ThO_2	58.8	37.4	21.7
Mo + 2 Hf + 1 Ti + 1 Zr + 0.1 C + 2.5 ThO_2	--	26.0	11.2

strengthening. Powder metallurgy TZM alloys have been produced commercially with reported properties as high as any obtained on cast material (11). The solution to the problem of low strength here appears to hinge on more complete removal of oxygen from the elemental powders or greater additions of Ti and Zr to allow for depletion due to oxide formation.

The fact that an addition of 2.5% ThO_2 had very little influence on the strength or hardness of the TZM alloy stems largely from the reaction observed between Ti, Zr, and ThO_2 mentioned earlier. The adsorption of Ti and Zr into the ThO_2 particles (Fig. 1) not only further reduces the effective solution level of Ti and Zr but also results in considerable degradation of the ThO_2 stability. This behavior is probably the result of Ti and Zr entering into solid solution with ThO_2, since x-ray identification of extraction residues shows a shift in the ThO_2 lattice parameter but no evidence of additional phases containing Th. The size and distribution of ThO_2 in the presence of Ti and Zr after annealing (Fig. 3) is obviously inferior to that in the Mo - 2.5 ThO_2 alloy (Fig. 2); however, a rather significant resistance to grain growth was still retained during annealing as high as 4000°F relative to the straight TZM alloy (Figs. 3 and 4). To attain maximum strength, however, the ThO_2 must remain more finely dispersed.

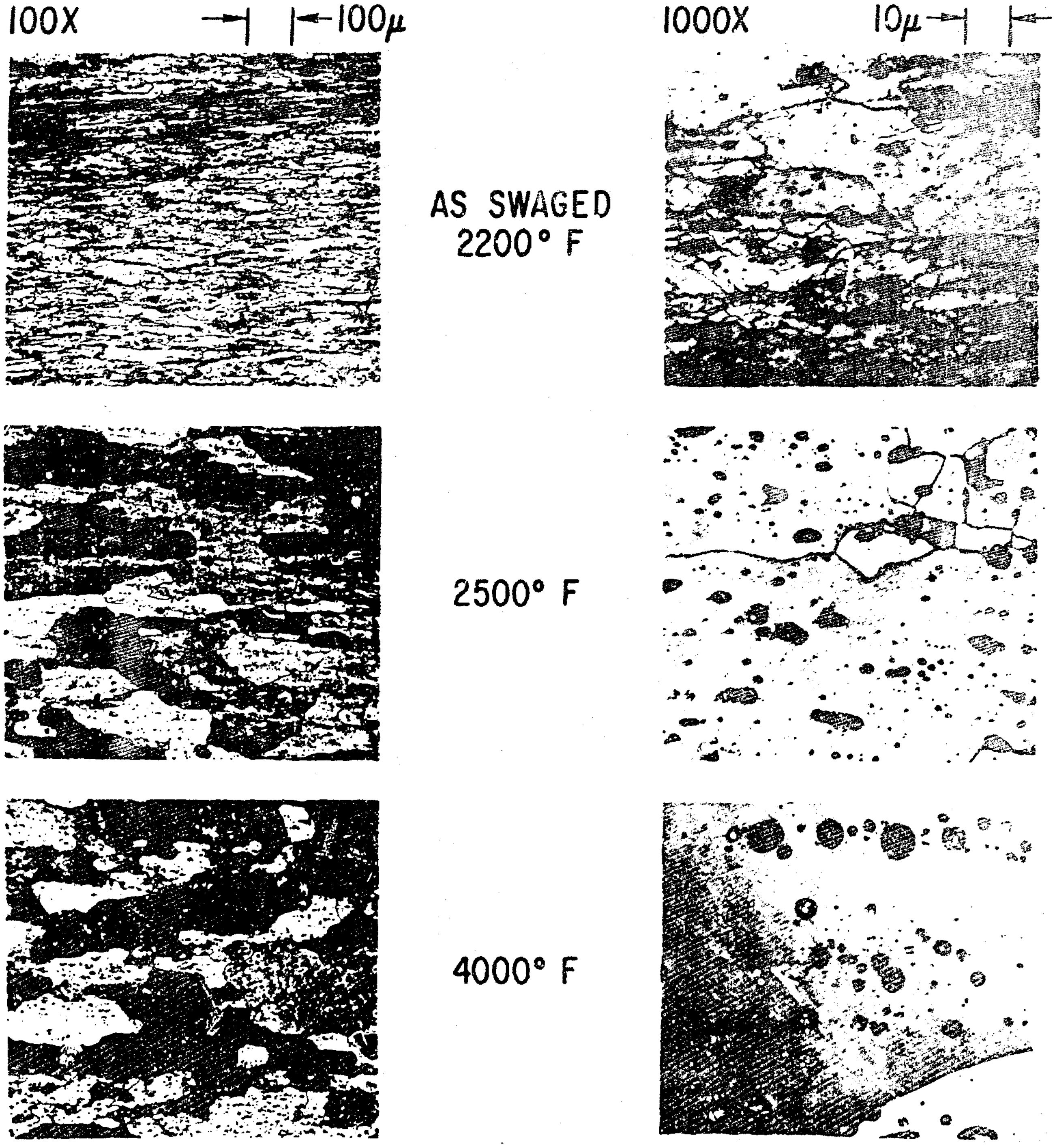
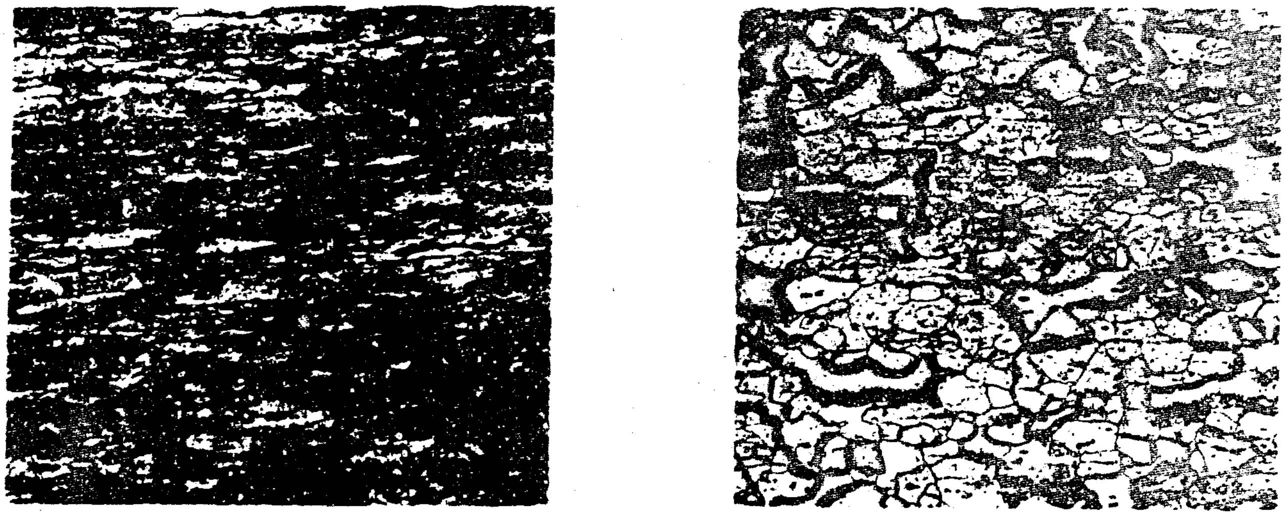
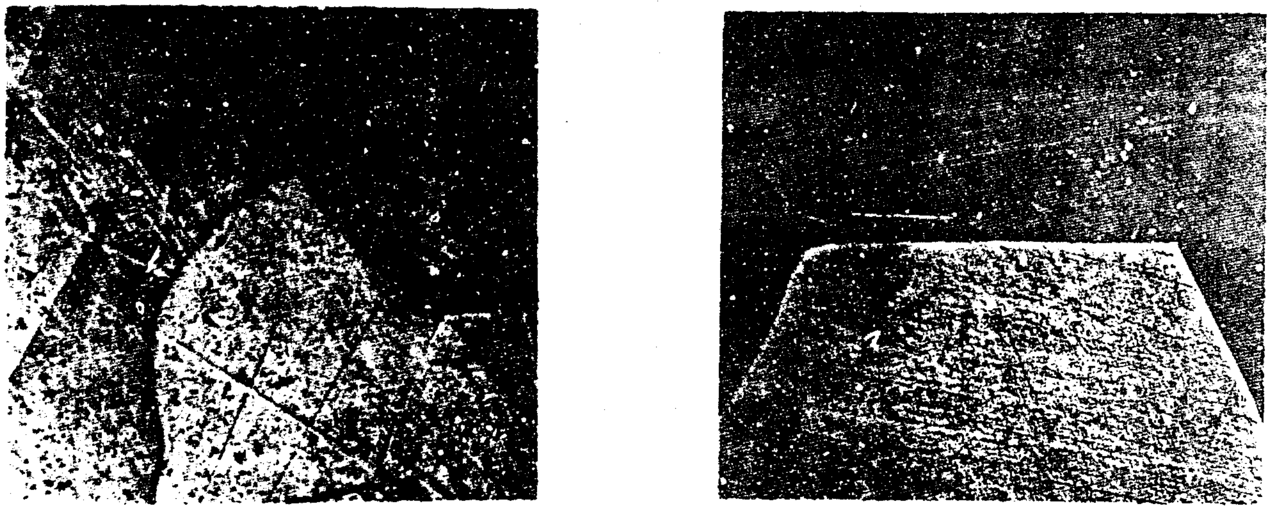


Figure 3. Microstructures of the Mo, 0.5 Ti, 0.1 Zr, 0.025 C + 2.5% ThO_2 (TZM + ThO_2) Alloy Vacuum Annealed for 1 hr after Swaging



AS SWAGED-2200° F

2500° F



3500° F

4000° F

Figure 4. Microstructures of the TZM Alloy Vacuum Annealed 1 hr After Swaging. 100 X

IV. FUTURE POSSIBILITIES

Although the attempt to combine alloy strengthening with dispersion strengthening in a TZM base alloy was not successful, the principle is basically sound, and preliminary studies have been made on other molybdenum base alloys. Success, of course, hinges upon finding an alloying element which will provide the necessary carbide strengthening without adversely reacting with the dispersant. This requires finding an alloying element compatible with ThO_2 or replacing ThO_2 with another dispersant such as ZrO_2 or HfN (see Ref. 3). Since ThO_2 could be obtained in the desired distribution by methods used in this study, further evaluation was limited to additions of Cb, Ta, or Hf to alloys containing 2.5% ThO_2.

The alloys containing 1% Cb or 2% Ta both exhibited the same general type of reaction with ThO_2 that was observed for Ti and Zr in the TZM alloys (Fig. 1). The penetration of both Cb and Ta was also accompanied by rather extensive particle agglomeration and grain growth during vacuum annealing at 3500°F. Although some improvement in hot hardness was exhibited by the Cb containing alloy up to 3000°F (Table 2), the instability observed at higher temperatures suggests that no better strength would be possible using either of these alloying elements in place of Ti or Zr.

Hafnium additions to a 2.5% ThO_2 alloy containing 2% Hf, 1% Ti, and 1% Zr were also evaluated. Electron probe analyses of this alloy showed equally as much reaction between ThO_2 and all three of the alloying elements

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as experienced for the TZM - 2.5% ThO_2 alloy in Fig. 1. The rather low hot hardness of this alloy in Table 2 also reflects poor elevated temperature stability. In light of the detrimental effects of the Zr - ThO_2 interaction, Hf additions have been made to alloys without Zr. Preliminary structural evaluation after annealing to 3500°F looks encouraging; however, much additional work must be done on each of these alloy systems to properly evaluate the potential for combined alloy and dispersion strengthening.

V. CONCLUSIONS

Although this study has been essentially exploratory in nature, the following conclusions should provide some criteria for future powder metallurgy development.

A. An addition of 2.5% ThO_2 markedly improves the elevated temperature tensile strength of molybdenum from 2500 to 3500°F. In addition, a very pronounced resistance to recrystallization and grain growth in this temperature range is also afforded.

B. Additions of less than 1% elemental Ti and Zr powders to molybdenum billets hot-pressed under an argon atmosphere provide a marked improvement in both fabricability and elevated temperature tensile elongation. This is apparently the result of Ti and Zr removing oxygen by forming stable oxide inclusions.

C. Ti and Zr additions to Mo alloys containing a ThO_2 dispersion result in considerable degradation of the ThO_2 distribution due to a solid state reaction occuring primarily between Zr and ThO_2. The resulting dispersed phase distribution then affords no improvement in elevated temperature mechanical properties relative to TZM alloys of the same matrix composition.

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