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DEVELOPMENT AND FABRICATION OF HIGH STRENGTH ALLOY FIBERS FOR USE IN METAL-METAL MATRIX COMPOSITES

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SUMMARY

Metal fiber reinforced superalloys are being considered for construction of critical components in turbine engines that operate at high temperature. Two of the most promising fiber materials for use at temperatures to 1200° C are wires of alloys W-Hf-C and W-Re-Hf-C. However, because of their high strength, these alloys are difficult to fabricate and to date have been produced only under laboratory conditions. Another metal fiber being considered which is currently available on a near commercial basis is a high strength thoriated tungsten alloy (HSTW). The combination of alloy content and fabrication processing for this material was developed by the Westinghouse Electric Corporation Although this fiber has a lower strength advantage than W-Hf-C or W-Re-Hf-C, it still offers at lower cost a potential advantage of about 110° C in operating temperature over current turbine blade materials when used as the reinforcement in a superalloy composite. This temperature advantage may be achieved without the need of a protective oxidation resistant coating beyond that provided by the matrix.

This paper will discuss the problems involved in fabricating refractory metal alloys into wire form in such a manner as to maximize their strength properties without developing excessive structural defects. Also, the fundamental principles underlying the development of such alloy fibers will be briefly discussed. The progress made to date in developing tantalum and columbium base alloys for fiber reinforcement will also be reported and future prospects for alloy fiber development will be considered.

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INTRODUCTION

The development of more energy efficient gas turbine engines has been a research goal for a number of years. An increase in the turbine blade operating temperature from current values of 980° to 1010° C to temperatures of 1090° to 1200° C could result in a sizable increase in gas turbine engine performance. One of the most promising systems being considered to permit such a temperature increase is a composite of a nickel or iron superalloy matrix reinforced with refractory metal fibers. A system of this type potentially combines the good high temperature oxidation resistance of a superalloy matrix with the good high temperature strength of the refractory metal reinforcing fibers. Investigations were undertaken at a number of laboratories to evaluate composites made with high strength refractory metal fibers for use at elevated temperatures (refs. 1 to 5). Among commercially available refractory metal fibers evaluated it was found that W-1% ThO_2 wire incorporated in a superalloy matrix had a sufficient strength/density advantage over existing superalloy materials to permit a potential increase of about 60° C in turbine blade operating temperature (ref. 1). The strength/density advantage of other commercially available refractory metal fibers used in a superalloy matrix such as lamp filament grade tungsten or TZM (a molybdenum alloy) was found to be more moderate. Although an increase of 60° C in the turbine engine operating temperature would offer significant advantages, higher operating temperatures are needed to more fully exploit the potential of gas turbine engines. The attractive high strength potential of refractory fiber composites is largely based on the properties of the fiber. As such, there is a need for fibers with improved strength properties.

Investigations to produce higher strength fibers have been successful to a considerable degree. Work has been done to fabricate stronger refractory metal alloys into wire form (ref. 6). Two tungsten base alloys, W-Hf-C and W-Re-Hf-C were drawn into wire form and have high temperature strength properties sufficient to produce a composite material having the potential for an increase of about 220° C in the turbine blade material operating temperature (ref. 7). Wire of tungsten-1.5%

ThO_2 and tungsten-2% ThO_2, developed at the Westinghouse Lamp Division, potentially would permit an increase of about 110° C in the turbine blade material operating temperature if used as a reinforcement in a superalloy. In addition, a tantalum base alloy (ASTAR-811C) and a columbium base alloy (B-88) were developed at Westinghouse (refs. 8 and 9) and drawn into wire (ref. 6). The tantalum and columbium alloy wires have strength properties that are comparable to tungsten-2% ThO_2 wire on a strength/density basis.

The purpose of this paper is to describe the work conducted to fabricate 0.10 to 0.38 mm diameter high strength refractory metal alloy fibers. Only a moderate development effort has been conducted to fabricate wire of W-Hf-C and W-Re-Hf-C alloys (ref. 6), however, 10 000 meters of 0.38 mm diameter W-Hf-C wire have been produced for composite evaluation. Fabrication of wire from other alloys has required less development effort. It has been found that thoriated tungsten alloys in the 1 to 2% range can be fabricated into wire with only moderate changes in the techniques used for lamp filament grade tungsten wire production. The alloys B-88 and ASTAR-811C are reactive with the atmosphere at elevated temperatures and therefore require protection from contamination during working into wire form, otherwise, the fabrication techniques required are relatively simple.

FABRICATION OF ALLOYS

W-Hf-C and W-Re-Hf-C Alloys

The effort spent in developing fabrication techniques for the efficient production of W-Hf-C and W-Re-Hf-C alloys has been limited (ref. 6). The primary objective of fabrication studies to date has been to produce a quantity of wire suitable for evaluation. This objective was met satisfactorily with regard to the W-Hf-C alloy, but the success with fabrication of W-Re-Hf-C was more limited.

Both alloys were produced by vacuum arc melting of electrodes consisting of pressed tungsten powder wrapped with hafnium wire and carbon cloth in string form. The melt was vacuum cast into bars of a size suitable for extrusion with molybdenum cladding to rod dimensions of 16.5 to 25.4 mm diameter. The surface condition of the extruded rod after removal of the cladding is depicted in figure 1, and shows a rough corrugated surface which is detrimental to further mechanical working by swaging or wire drawing. Consequently, it was necessary to condition the surface after removal of the cladding to improve fabricability. The most efficient method was to immerse the rod in a molten solution of sodium nitrate-nitrite salts. An exothermic reaction occurs at temperatures above approximately 360° C which results in rapid removal of the rod surface layers. An example of the effect of this treatment on the surface condition of the rods is depicted in figure 2.

Another problem which very likely complicated the fabrication process was the presence of center cracks in a large percentage of the extrusions. The symmetry of the crack on opposite ends of bars suggests that in some instances the cracks extended throughout the entire extrusion length. Undoubtedly the most difficult problem to overcome was the high strength and brittleness of the extruded rods. The high strength of W-Hf-C and W-Re-Hf-C alloy rods necessitated the use of larger swagers than are normally used for rods of other alloys of comparable size. When this was not done, the rods fractured in the swager while attempting light reductions (10 to 15% reduction in area) at preheat temperatures as high as 1850° C. In addition to local heating of the rod to 1850° C in the region adjacent to the swaging die, the entire length of the rod was supported and heated to 400° C to prevent rod fracture as a result of vibrations imparted by the swager. However, once the rod had been swaged to a reduction in area of about 85%, it could be swaged on subsequent passes using only local heating at the die entrance to about 1300° C.

Wire drawing typically began at sizes of about 2.5 mm on a straight draw bench to avoid the stresses imposed by winding onto a capstan. However, after about 75% reduction in area on the straight draw bench the W-Hf-C alloy became sufficiently ductile to be drawn on a capstan by techniques typically employed for lamp filament grade tungsten. In fact, at sizes in the order of 0.48 mm the wire was ductile enough to be bent into a hairpin shape at room temperature.

The fabrication process outlined above was to a great extent dictated by precautionary measures since the amount of material and funds available for development work were limited. It can reasonably be expected that with greater experience and a larger development effort these alloys could be fabricated by a commercially competitive process.

W-ThO_2 Alloys

High strength thoriated tungsten alloys (HSTW) are produced by a proprietary powder metallurgy process. Unlike the extrusion bars from W-Hf-C alloys, the starting sintered ingots of HSTW are completely sound. The soundness and uniformity of the HSTW ingots greatly ease the fabrication processing. The main difficulty encountered in fabrication of HSTW resulted from a loss of ThO_2 which sometimes occurred at the surface of the swaged rod, probably through a reaction with the graphite lubricant. During subsequent intermediate anneals a coarse equi-axed grain structure formed at the rod surface which was susceptible to shear fracture during wire drawing. Local shear failure caused the formation of slivers on the wire surface which frequently bulged back in the drawing die leading to wire breaks. Removal of the thoria depleted surface layer before wire drawing began was accomplished by electropolishing, centerless grinding or fused salt bath etching. Once the surface conditioning step has been accomplished the W-ThO_2 alloys can be drawn in a manner typical of lamp filament grade tungsten, except that after large amounts of working (approximately 95% reduction in area), it may be necessary to decrease the reductions in area per pass to slightly less than normal because of work hardening.

B-88 Alloy

This columbium base alloy is produced by vacuum arc melting and subsequent mechanical working by extrusion in molybdenum cladding. The main difficulty in fabricating the alloy was the deleterious effect of atmospheric contamination at elevated temperatures on its ductility (ref. 6). Preheat temperatures between 1200° C (initial) and 650° C (final) were found to be necessary to avoid severe longitudinal cracks (splits) or transverse cracks during swaging. Molybdenum was used for vacuum cladding the rods when swaging at temperatures above approximately 1000° C, and mild steel was used for vacuum cladding at lower preheat temperatures. However, after a number of swaging passes the cladding ruptured locally and caused a brittle surface layer to form as a result of atmospheric contamination (fig. 3). This brittle surface layer made further working by swaging or wire drawing impossible until it was removed by chemical cleaning in a mixture of nitric and hydrofluoric acids. Removal of the brittle surface layer made the rod ductile enough to form a 180° hairpin bend at room temperature. Prior to drawing, the swaged rods were annealed in argon for 5 seconds at 1600° C.

Wire drawing was performed with unclad rods and the main problem became one of selecting a temperature that minimizes split formation (extended longitudinal surface cracks) without excessive embrittlement through atmospheric contamination. The temperature range found to be most suitable for this purpose was between 500° and 600° C. At temperatures of 400° C or less splitting increased rapidly, whereas at 650° to 700° C local embrittlement occurred. Removal of the oxide layer formed at the higher temperatures (650° to 700° C) was found to be very difficult.

ASTAR-811C Alloy

ASTAR-811C is a tantalum base alloy that is produced by vacuum arc melting followed by extrusion. The fabrication of this alloy proved to be very simple because of good low temperature ductility (ref. 6). During the initial breakdown swaging passes the unclad rods were preheated to about 550° C in air without detrimental effects. After a few swaging passes the preheat temperature was gradually reduced at room temperature. Swaging or drawing unclad metal at temperatures at or above 700° C led to embrittlement as the result of atmospheric contamination.

The wire was drawn at room temperature with dies heated to 400° C. Some experiments were made by drawing at preheat temperatures of 700° C in an attempt to reduce the number of splits found in wire drawn at room temperature. However, the wire drawn at 700° C preheat became so brittle after one or two passes that further drawing was not possible. When drawing at room temperature the oxide film, which is essential for good lubrication, was gradually lost as a result of die friction. Therefore it was necessary to periodically oxidize the wire lightly at about 500° C to provide a base for good lubrication so as to reduce wire breaks.

DISCUSSION OF RESULTS

It is desirable in the fabrication process to produce a defect-free wire with maximum strength and adequate ductility. In actual practice, a compromise among maximum strength properties, ductilitv, reducing macroscopic defects, and obtaining good material yields must be made. A few typical examples of the types of compromises required are given in the following sections.

W-Hf-C, W-Re-Hf-C and W-ThO_2 Alloys

Improved elevated temperature strength in these alloys depends predominantly on the presence of a stabilized substructure. The effectiveness of hafnium carbide precipitates in stabilizing the substructure of W-Hf-C is illustrated in figure 4 by a transmission electron micrograph (TEM) of a 1.78 mm diameter wire exposed to a 72 hour anneal at 1090° C. It can be seen that a substructure consisting of random dislocations and highly elongated subgrains about 0.5 micrometer in width is effectively pinned by the HfC precipitates. The effect of deformation on the development of the substructure is further illustrated in figure 5 by a TEM of a 0.38 mm diameter wire annealed for 50 hours at 1230° C which shows that the average width of the subgrains has decreased to about 0.25 micrometer.

Thoria in the form of a fine dispersion has a similar effect on stabilizing the substructure of high strength thoriated tungsten (HSTW) type alloys. This is depicted in figure 6 which shows a TEM of a 4.42 mm diameter, tungsten-2% ThO_2 (HSTW) alloy, rod after annealing for 1/2 hour at 2400° C. The alloy has not recrystallized as evidenced by the presence of about 1 to 2 micrometer subgrains. After working to fiber sizes (0.1 to 0.4 mm diam) the subgrain size decreases to less than 0.5 micrometer and remains stable at temperatures up to 2800° C for short periods of annealing. The effectiveness of the dispersion depends not only on the volume fraction but also on particle size and uniformity of its distribution. Figure 7 compares the 1040° C stress rupture properties of tungsten-1 and 1.5% ThO_2 (HSTW) alloy wire, 0.2 mm in diameter, with commercial grade W-1% ThO_2 wire of the same diameter. The tungsten-1 and 1.5% ThO_2 (HSTW) alloy wires contained smaller particle size thoria more uniformily distributed than the commercial grade wire. The properties of the HSTW wire are seen to be superior to the commercial grade wire. The effect of volume fraction thoria is also indicated in figure 7 with respect to stress rupture strength. The higher volume fraction thoria content (1.5%) HSTW wire is stronger than the lower volume fraction thoria content (1%) wire. The influence of the fabrication schedule on the strength properties of these alloys depends on the extent to which the substructure develops during working. This can be deduced from data obtained in reference 7 and shown in figure 8 which compares the stress rupture properties of W-Hf-C wire drawn without the use of intermediate anneals (hard drawn) with material annealed repeatedly at temperatures of about 2000° C in the early stages of fabrication. The hard drawn material has somewhat better rupture strength than the in-processed annealed wire, particularly at lower applied stresses. Another example of the importance of the substructure on strength properties is shown by the tensile data for a tungsten-2% ThO_2 (HSTW) alloy reported in reference 10 and shown in figure 9. In this instance it is seen that the effect of the retained substructure (occurring in the annealed material) on the yield strength of the alloy is considerably greater than the strengthening caused by direct Orowan type dislocation-particle interactions in the fully recrystallized condition.

In order to promote the formation of a dense substructure it is necessary that anneals at or near the recrystallization temperature be minimized, or better still, eliminated altogether. For the same reason it would be desirable to utilize low preheat temperatures throughout the working schedule. But the consequence of eliminating anneals or reducing fabrication temperatures would be to increase the frequency of wire breaks, and also to increase the number of splits in the fibers.

The presence of splits has not been found to have a direct detrimental effect on the tensile strength properties of the fibers. However, interface reactions in composites between the matrix and the fiber would be enhanced by the presence of splits to the detriment of composite strength. Thus, it is necessary to balance the desirable aspect of hard working against the negative effect of increasing defect level in the drawn wire and decreasing wire yield.

ASTAR-811C and B-88 Alloys

Both of these alloys developed their optimum creep properties in a recrystallized condition, however, recovery anneals led to softening (refs. 8 and 9). Since retention of the substructure introduced during working is not essential to good high temperature mechanical properties, anneals can be employed as needed to improve fabricability. Likewise, it would be desirable to work the material at as high a temperature as possible to prevent the formation of macroscopic splits. Unfortunately, the reactivity of the matrix with the atmosphere makes both of these approaches difficult to accomplish in a practical manner. During swaging, cladding can provide only a limited amount of atmospheric protection because of ruptures which develop in the clad wall after relatively small amounts of deformation (making the cost of maintaining cladding integrity prohibitive). In any event, the materials cannot be drawn with cladding in a practical way, and therefore require the use of low preheat temperatures (600° C) to prevent excessive contamination of unclad rod. One possible solution in avoiding splits would be to anneal periodically at high temperatures in an inert atmosphere together with drawing at relatively low temperatures. Whether or not the added cost would be justified depends on the extent to which splits in the wire reduce the effectiveness of the fibers as strengtheners of the composite matrix.

SUMMARY OF RESULTS

Metal fibers have been produced which have been shown to provide a potential of increasing the use temperature of critical parts in gas turbine engines by as much as 220° C. The biggest challenge at this point is to improve the techniques used to maintain or increase wire strength while decreasing its cost. Steps in this direction will undoubtedly require improvements in currently used techniques of wire production and fabrication. Also needed is the ability to tailor the composition of alloys to provide specific properties at a desired use temperature without impairing fabricability. The further development of light-weight-high strength fibers with good fabrication properties remains a desirable goal.

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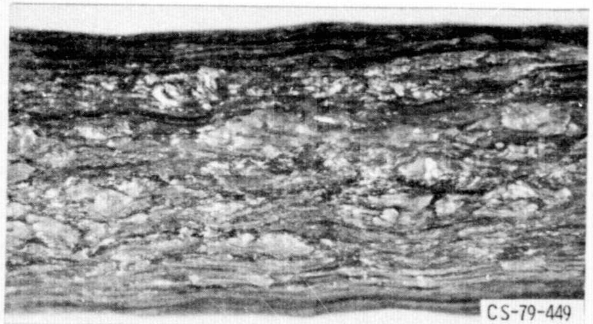
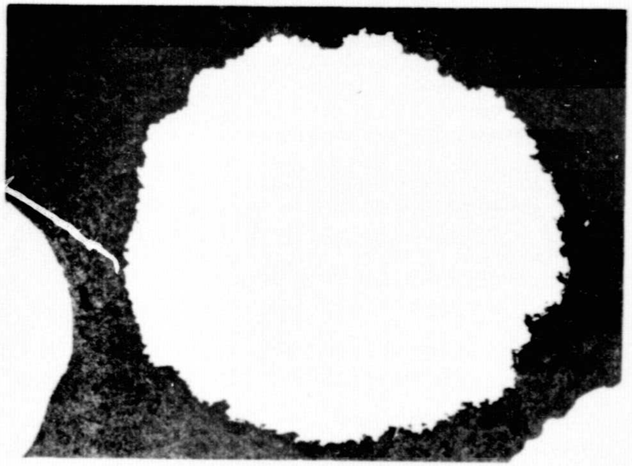
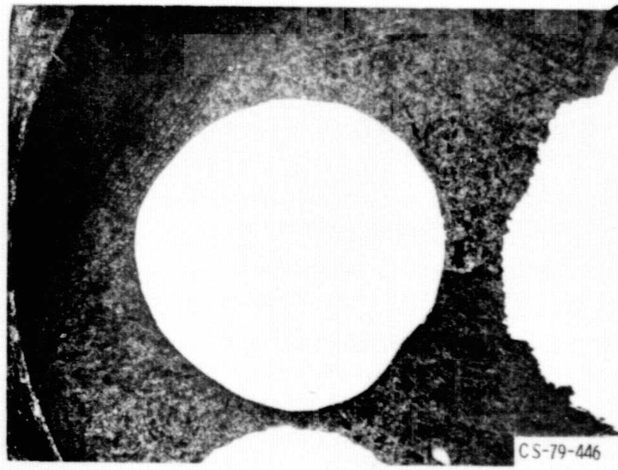


Figure 1. - Surface condition of W-Hf-C and W-Re-Hf-C extrusion bars after removal of cladding (ref. 6).



(a) BEFORE REMOVAL.



(b) AFTER REMOVAL OF SURFACE IN A FUSED SALT BATH (ref. 6); X8.5.

Figure 2. - Photomicrographs of a swaged rod of W-Hf-C.

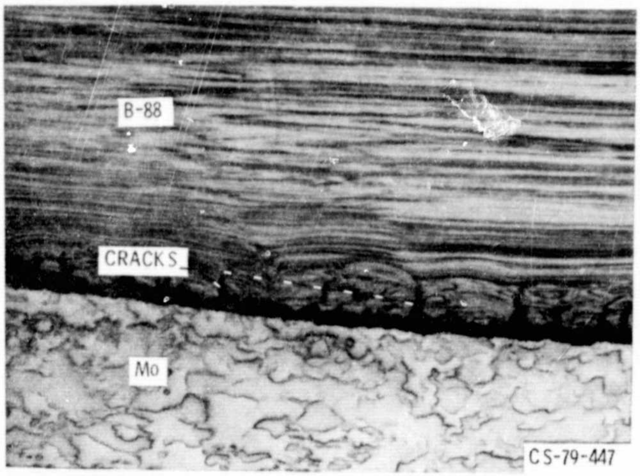


Figure 3. - Photomicrograph showing surface cracks in B-88 (Molybdenum clad) rod swaged to 3.66 mm diameter (ref. 6); X200.

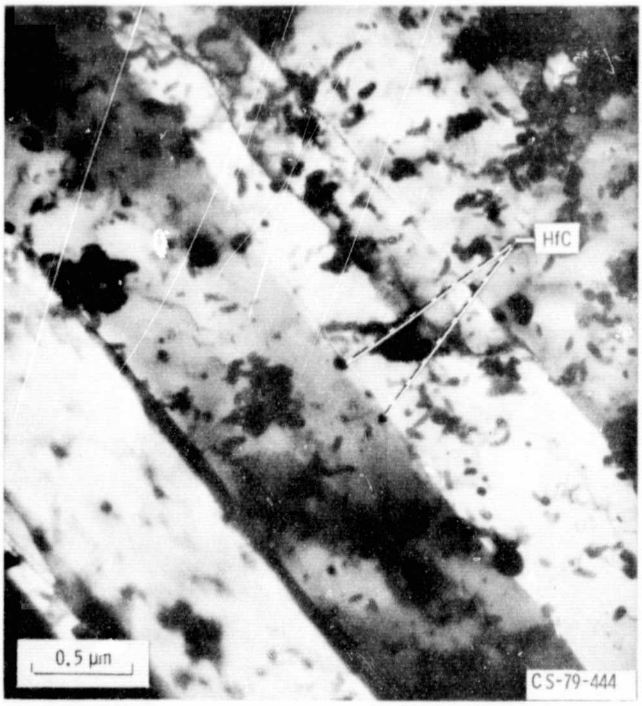


Figure 4. - Transmission electron micrograph of W-Hf-C 1.78 mm diameter swaged rod annealed 72 hours at 1093° C (ref. 6).

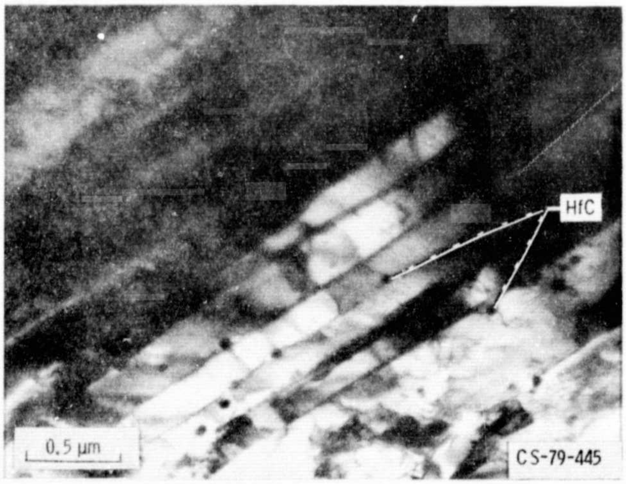


Figure 5. - Transmission electron micrograph of W-Hf-C 0.38 mm diameter wire annealed 50 hours at 1232° C (ref. 6).

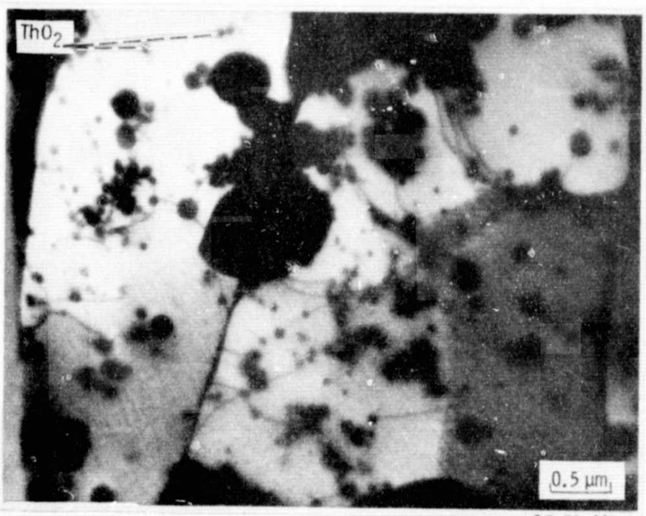


Figure 6. - A typical electron transmission micograph of W-3.8 vol pct ThO_2 annealed 1/2 hr at 2400° C (ref. 10).

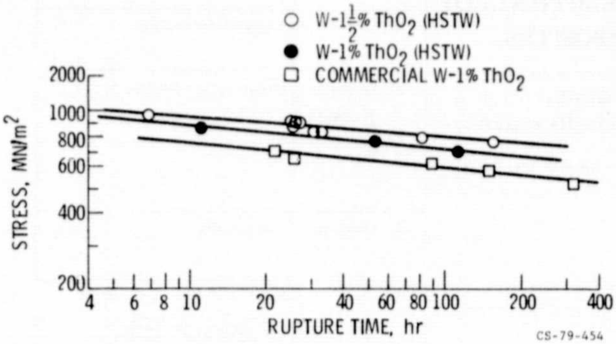


Figure 7. - Stress rupture properties of 0.2 mm diameter W-ThO_2 wire at 1040° C.

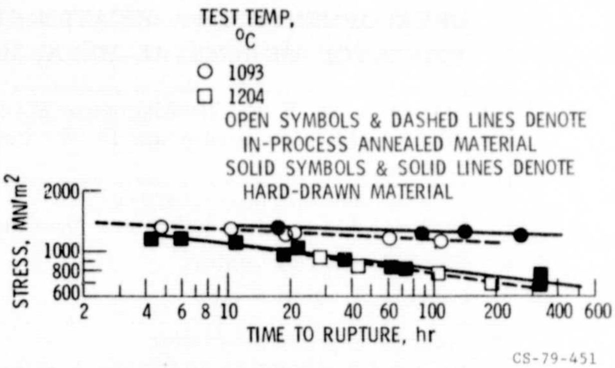


Figure 8. - Time to rupture as function of stress for W-Hf-C wire (ref. 7).

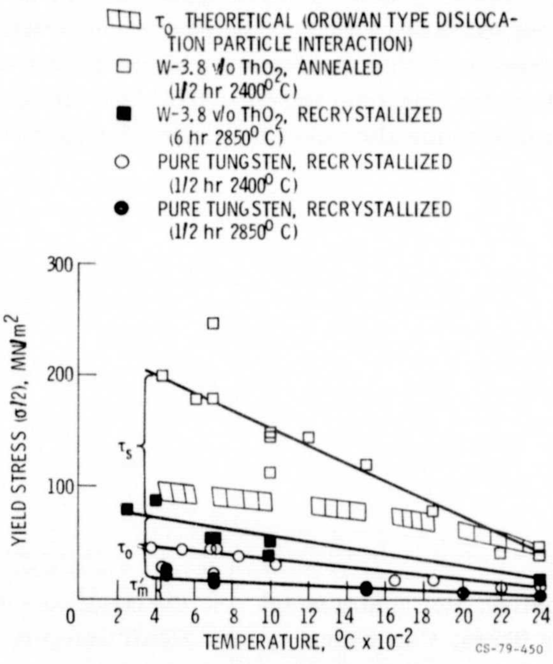


Figure 9. - Yield stress (σ/2) of pure tungsten and W-3.8 v/o ThO_2, variously annealed, as a function test temperature (ref. 10).