PROPERTIES OF DISPERSION-STRENGTHENED CHROMIUM - 4-VOLUME-PERCENT-THORIA ALLOYS PRODUCED BY BALL MILLING IN HYDROGEN IODIDE

by Alan Arias

Lewis Research Center
Cleveland, Ohio 44135

1. Report No. NASA TN D-7512	2. Government Accession No.	3. Recipient's Catalog No.
4. Title and Subtitle PROPERTIES OF DISPERSION-STRENGTHENED CHROMIUM - 4-VOLUME-PERCENT-THORIA ALLOYS PRODUCED BY BALL MILLING IN HYDROGEN IODIDE		5. Report Date January 1974
		6. Performing Organization Code
7. Author(s) Alan Arias		8. Performing Organization Report No. E-7620
9. Performing Organization Name and Address Lewis Research Center National Aeronautics and Space Administration Cleveland, Ohio 44135		10. Work Unit No. 501-21
		11. Contract or Grant No.
12. Sponsoring Agency Name and Address National Aeronautics and Space Administration Washington, D.C. 20546		13. Type of Report and Period Covered Technical Note
		14. Sponsoring Agency Code

15. Supplementary Notes

16. Abstract

The effects of processing variables on the tensile properties and ductile-to-brittle transition temperature (DBTT) of Cr + 4 vol. % ThO_2 alloys and of pure Cr produced by ball milling in hydrogen iodide were investigated. Hot rolled Cr + ThO_2 was stronger than either hot pressed Cr + ThO_2 or pure Cr at temperatures up to 1537° C. Hot pressed Cr + ThO_2 had a DBTT of 501° C as compared with -8° to 24° C for the hot rolled Cr + ThO_2 and with 139° C for pure Cr. It is postulated that the dispersoid in the hot rolled alloys lowers the DBTT by inhibiting recovery and recrystallization of the strained structure.

17. Key Words (Suggested by Author(s)) Dispersion strengthening; Dispersion hardening; Oxide dispersion strengthening; Chromium; Chromium alloys; Thoria; Thoriated chromium; Ball milling; Powder metallurgy; Hydrogen iodide; Mechanical properties; Ductile-to-brittle transition temperature		18. Distribution Statement Unclassified - unlimited		
19. Security Classif. (of this report) Unclassified		20. Security Classif. (of this page) Unclassified	21. No. of Pages 29	22. Price* Domestic, $3.00 Foreign, $5.50

PROPERTIES OF DISPERSION-STRENGTHENED CHROMIUM - 4-VOLUME-PERCENT-THORIA ALLOYS PRODUCED BY BALL MILLING IN HYDROGEN IODIDE

by Alan Arias

Lewis Research Center

SUMMARY

This investigation was conducted to determine the effect of processing variables on the tensile properties and ductile-to-brittle transition temperature (DBTT) of chromium - 4 volume percent thoria (Cr-4 vol. % ThO_2) and pure chromium (Cr) prepared by ball milling in hydrogen iodide.

Densities of 98.6 to 99.8 percent of theoretical resulted from isostatic hot pressing the Cr and alloy powders either at 1093° C and 68.9 meganewtons per square meter (MN/m^2) or at 1204° C and 103.4 MN/m^2. The second conditions yielded alloys with better tensile properties.

Hot rolling canned Cr alloys at 871° C produced sound specimens with good tensile properties. Lower alloy DBTT resulted by hot rolling at 760° C, but the cans cracked. Roll consolidation of canned powders proved feasible, but the alloy produced had inferior tensile properties.

At 345°, 1093°, and 1316° C the ultimate tensile strengths (UTS) of hot pressed and hot rolled (HP and HR) alloys were 790, 103, and 46 MN/m^2, respectively; whereas the UTS of HP alloys were 615 (extrapolated) 45.4, and 6.9 MN/m^2, respectively. The UTS of pure Cr at 1093° C was 61 MN/m^2. The 0.2 percent offset yield strength (YS) of HP and HR alloys was 91 MN/m^2 at 1093° C as compared with 51 MN/m^2 for the HP alloy and 60.7 MN/m^2 for pure Cr. In the range below about 900° C both the HP and the HP and HR alloys have about twice the YS of pure Cr.

The DBTT of the HP and HR alloys was -8° to 24° C, as compared with 501° C for the as HP alloy and 139° C for pure Cr. The DBTT of the HP and HR alloys increased by heating at temperatures above 1316° C. It is theorized that the dispersoid lowers the DBTT by inhibiting the recovery and recrystallization of the strained structure.

INTRODUCTION

In recent years NASA and other organizations have shown considerable interest in chromium and chromium-base alloys. This interest stemmed from some of chromium's desirable properties: a relatively high melting point ($1893^{\circ}C$), a high elastic modulus ($282.7{\times}10^3$ MN/m^2), and low density (7.2 g/cm^3). In addition, when compared with other refractory metals (W, Mo, Ta, Cb, Re), chromium has good oxidation resistance and equivalent homologous temperature tensile strength (ref. 1). Unfortunately, chromium has a relatively high ductile-to-brittle transition temperature (DBTT). This DBTT is very sensitive to the impurity content (N and C, particularly) in chromium. The high re-activity of this metal aggravates the situation. For these reasons chromium must be processed with extreme care in order to minimize its contamination. Because of these difficulties, the development of chromium-base alloys of engineering significance has been hindered.

Arguments for and against the use of chromium and chromium-base alloys as engineering materials can be found in several review reports (refs. 2 to 4). These review reports show that a great deal of work has been done to improve the high-temperature strength and the DBTT of chromium by conventional alloying. However, relatively little has been done to improve the properties of chromium by dispersion strengthening. Yet, when considering its dramatic effects on nickel and nickel-chromium alloys, it was felt that dispersion strengthening may well offer a good approach for improving the high-temperature properties of chromium. In addition, there were indications that dispersion strengthening might also improve the DBTT of chromium (refs. 5 and 6).

Dispersion strengthening of metals can be accomplished by many methods (ref. 7). Among these methods, ball milling has shown promise of providing the required inter-particle spacings necessary for effective dispersion strengthening (ref. 8). In addition, ball milling offers the advantages of versatility, low cost, and scale up potential.

In a preliminary investigation (ref. 8) chromium-thoria mixtures were milled to sub-micron size powders with a minimum of contamination by using hydrogen iodide gas as the milling medium. Previous investigations by the author (refs. 8 and 9) have shown that comminution of ductile metals to submicron particle size requires reaction of these metals with the milling media. The main reason for using hydrogen iodide as a ball-milling medium is that the chromium iodide formed during ball-milling aids the milling, probably reduces oxygen and nitrogen contamination, and can be reduced by reaction with hydrogen at relatively low temperatures. The use of low temperatures in this so-called "hydrogen cleaning" process minimizes the chances of agglomerating the dispersoid.

Thus, the present investigation was undertaken to dispersion strengthen chromium by the hydrogen iodide ball-milling process and to determine the effectiveness of disper-sion strengthening in improving tensile properties and DBTT. Compositions of chromium with 4 volume percent thoria were prepared by ball milling in hydrogen iodide and

2

consolidated by isostatic hot pressing followed by hot rolling. Tensile properties were determined up to 1537° C, and the bend DBTT was evaluated. For comparison the properties of pure chromium processed by the same methods were determined. Attempts were also made to introduce elements (Y, Hf, Th) during the ball milling process that would scavenge embrittling interstitial elements such as nitrogen and carbon.

MATERIALS AND EQUIPMENT

Materials

The materials used in this investigation are given in table I. These materials were high-purity, powdered electrolytic chromium; yttrium, hafnium, and thorium powders; colloidal thorium dioxide (thoria); and hydrogen iodide. The chemical analysis (or manufacturer's specifications) and purities of the raw materials are also shown in table I.

Equipment

Apparatus and equipment used in this investigation included ball mills with pressure gages, chromium balls, a rig for evacuating the ball mills and pressurizing them with hydrogen iodide, a retort for hydrogen cleaning the ball milled powders, and a hydrogen cleaning rig.

Ball mills. - The type of ball mill used in this investigation has been described in reference 8. For all milling runs molybdenum lined mills were used.

Balls. - The balls used in all the milling runs were made from chromium. These chromium balls were 1 centimeter in diameter (nominal) and were made by powder metallurgy techniques. Approximately 3250 grams of these chromium balls were used in each milling run with the molybdenum lined mills.

Evacuating and pressurizing rig. - The ball mills were evacuated and then pressurized or repressurized with hydrogen iodide in the rig shown in figure 1. The purpose of the cryogenic trap (indicated in the figure) was to trap any residual hydrogen iodide that might remain in the ball mill from a previous run. Thus, the vacuum pump is protected from the corrosive effects of hydrogen iodide.

Retorts. - The retorts used in this investigation are larger versions of the retort used for the same purposes in the work described in reference 8. A retort used in the present investigation is shown in cross section as part of the hydrogen cleaning rig depicted in figure 2.

Hydrogen cleaning rig. - A schematic diagram of the hydrogen cleaning rig (with a retort in position) is shown in figure 2. The reduction process is monitored by means of a gas chromatograph. A four-way switch valve and a cryogenic trap allow the collection of any convenient size sample of condensables from the exhaust gases.

PROCEDURES

The procedures used in this investigation are described in the order shown in the flow diagram of figure 3. Unless otherwise noted, all operations involving the handling of powders were carried out in a helium filled glove box.

Loading ball mills. - In all runs with chromium and thoria, 141.7 grams of chromium and 8.247 grams of thoria were used. This is equivalent to 150 grams of Cr-ThO_2 mixture with 4 vol. % thoria. In one milling run with pure chromium, 150 grams of chromium powder were used.

Pressurizing ball mills with hydrogen iodide. - The loaded mills were placed in the pressurizing rig shown in figure 1. The mills were then evacuated. After evacuation, the ball mills were pressurized with hydrogen iodide gas to about 6.2×10^5 newtons per square meter (90 psi).

Ball milling. - The pressurized ball mills were placed in a ball milling rack adjusted to turn the mills at 100 rpm. Other steps in the milling process are shown in figure 3 and are also described in reference 8. The milling time was held constant at 320 hours. This time was determined by preliminary studies of the time required for the pressure drop in the mill to cease. The total amount of hydrogen iodide used for each batch of material was between 109 and 124 grams, as calculated from the pressure drop during ball milling.

The batches of material prepared for this investigation are listed in table II. Each batch of milled material is identified by a letter. The first numeral following the batch designation indicates some variations in processing steps.

The ball milled powders were separated from the balls by sieving. In a few instances the balls were removed from the mill and washed, dried, and weighed in order to determine the amount of material removed from the balls during ball milling.

Reduction or cleaning in hydrogen. - Each batch of milled powder was placed in a molybdenum boat and the boat was placed in a retort. The retort was then closed and transferred from the glove box to the hydrogen cleaning rig.

During the reduction or cleaning process, the hydrogen reacts with the chromium iodide formed during the ball milling operation to form hydrogen iodide and (solid) chromium (ref. 8). The reduction temperatures and times at temperature used for each run are listed in table II. The aim was to reduce the chromium iodide at 650° C. However, in some cases partial clogging of the stainless-steel filter due to its reaction with

4

hydrogen iodide decreased the hydrogen flow and caused a slight rise in the temperature of the retort, as indicated by the average retort temperatures shown in table II. Reduction times were determined by the results of exhaust gas analysis by gas chromatography. Reduction was regarded as completed when a sample collected during 10 minutes showed no hydrogen iodide. The reduction times required to reach completion varied mainly because of variations in hydrogen flow due to clogging of the stainless-steel filter.

Hot pressing and hot rolling. - In preparation for isostatic hot pressing, the clean powders were canned as shown in figure 4. About 30 grams of powder were loaded in the cans to be hot pressed only. About 70 grams of powder were loaded in the cans to be hot rolled. Details about the canning and the sealing of the cans by electron-beam welding are evident from figure 4.

The canned powders were isostatically hot pressed in a high-pressure, high-temperature autoclave. The temperature and pressure for each hot pressed batch is shown in table II. Time at temperature and pressure was 2 hours for all runs.

The hot rolling temperatures and reductions per pass are shown in table II. Total reduction of area was approximately 85 percent for all rolled materials.

After consolidation, the stainless-steel cans were removed by pickling in aqua regia. The thin tantalum thimble used as a can liner prevented the acid from attacking the chromium.

Densities. - The densities of the consolidated samples were determined by the water immersion method.

Tensile tests. - Dimensioned drawings of the tensile specimens used in this investigation are shown in figure 5. Button head specimens of circular cross section (fig. 5(a)) were used for testing some of the as hot-pressed materials. The thickness of the flat specimens (fig. 5(b)) after grinding was between 0.076 and 0.101 centimeter. All round and flat specimens were electropolished in a 5 percent sodium hydroxide solution before testing. Some of the tensile specimens were heat treated before testing (table III)[1] in an attempt to determine whether a strengthening effect similar to that observed in thoria dispersed nickel-chromium could be obtained (ref. 10). The 1316° C heat treating temperature was selected because previous work (ref. 8) showed only a slight thoria coarsening (after much longer heat treating time).

Tensile tests at temperatures of 1093° C and lower were carried out in vacuum. Above 1093° C the tests were carried out under argon. An Instron tensile tester run at a crosshead speed of 0.0508 centimeter per minute (0.020 in./min) was used for all tests. The load versus crosshead travel was recorded on a strip chart. The curve so obtained was used to determine the elongation of the specimen.

---

[1]In this table, the second number in the designation refers to a sample from a particular batch.

Ductile-to-brittle transition temperature tests. - Specimens for DBTT bend tests were made from the grip ends of the tensile test specimens after tensile tests. After cutting, the DBTT specimens were electropolished to a thickness of either 0.051 or 0.076 centimeter (0.020 or 0.030 in.).

The DBTT bend test were carried out by the three-point loading method. The specimens were tested on a 2.54-centimeter span, over 4T radius at 2.54 centimeters per minute. The DBTT was taken as the lowest temperature at which a specimen bent 90° without breaking.

The DBTT of one of the as-hot-pressed materials was determined by tensile tests. The specimen used was the same type used for tensile tests (fig. 5(a)). The specimen was heated and then stressed at constant temperature until it yielded slightly. The test was repeated at successively lower temperatures until the specimen broke in a brittle manner without yielding. The DBTT was taken as the average temperature between the last two tests.

RESULTS AND DISCUSSION

Mechanical Properties and Microstructure

Tensile properties. - Figures 6 to 8 show the effects of test temperature on the tensile properties of pure chromium (Cr) and of chromium dispersion strengthened with 4 volume percent thoria (Cr + 4 vol. % ThO_2). The ultimate tensile strengths of both as hot pressed (HP) and as hot pressed and hot rolled (HP and HR) samples are plotted in figure 6. The HP pure Cr (HP Cr) samples were made from batch A-0 (table II). The HP Cr + 4 vol. % ThO_2 samples were made from batches B-0 and C-0. The HP and HR Cr + 4 vol. % ThO_2 samples were made from batches D-2, E-2, and F-2. For comparison purposes the UTS of cast, extruded, and swaged pure Cr (CES Cr) from reference 1 was also plotted. Figure 7 shows the 0.2 percent offset yield strengths (YS) versus temperature plots for the same samples as in figure 6. Figure 8 indicates the corresponding elongations for the same samples and, in addition, for Cr + 4 vol. % ThO_2 hot rolled after hot pressing at 1093° C (instead of 1204° C).

As shown in figure 6, HP Cr is stronger than CES Cr at 620° C and both have about the same strength at 1093° C. The hot pressed Cr + 4 vol. % ThO_2 is stronger than HP Cr at 620° C and both have about the same strength at 1093° C. The hot pressed and hot rolled Cr + 4 vol. % ThO_2 is, in turn, stronger than HP Cr + 4 vol. % ThO_2 over the entire temperature range.

Figure 7 shows that HP Cr and CES Cr have about the same yield strength over the temperature range investigated. In turn, the yield strengths of HP Cr + 4 vol. % ThO_2 is higher than that of HP Cr at low temperature and they become equal at about 1093° C.

6

The hot pressed and hot rolled Cr + 4 vol. % ThO_2 has better yield strength than HP Cr + 4 vol. % ThO_2 below about 800° C and above about 1000° C; in the range from about 800° to 1000° C, the yield strengths are about equal.

The plots for both the ultimate tensile strength (fig. 6) and the yield strength (fig. 7) show that in the low temperature range (below about 1093° C) chromium is strengthened by thoria dispersions with or without the benefit of thermomechanical treatments. This is certainly true in the regime of 600° C where direct data comparisons are possible. On the other hand, in the high-temperature range (at and above about 1093° C), thermomechanical treatment is required to strengthen the Cr + 4 vol. % ThO_2 alloy.

Only one other investigation (ref. 6) dealing with the properties of unalloyed, dispersion strengthened Cr produced by a powder metallurgy method is known to the author. Both at low and high temperatures, the strength of the dispersion strengthened Cr + 4 vol. % ThO_2 alloys produced in the present investigation compare favorably with those reported in reference 6. Therein, dispersion strengthened Cr + 3 weight percent (nominal) ThO_2 alloys were found to have an ultimate tensile strength of 63.4 to 75.9 meganewtons per square meter and a 0.2 percent yield strength of 53.2 to 66.8 meganewtons per square meter at 1093° C; at 25° C the ultimate tensile strength and the 0.2 percent yield strength for the same alloy were reported to be 732 and 605 meganewtons per square meter, respectively.

It can be seen in figure 8 that CES Cr is more ductile than HP Cr, and this, in turn, is more ductile than HP Cr + 4 vol. % ThO_2, within the temperature range investigated (up to 1093° C). The ductility of HP Cr appears to decrease slightly with increasing temperature. The ductility of HP (at 1204° C) and HR Cr + 4 vol. % ThO_2 lies between that of HP Cr and HP Cr + 4 vol. % ThO_2 up to about 1000° C and shows a maximum in the elongation curve at about 900° C. In contrast, the HP and HR Cr + 4 vol. % ThO_2 produced by hot pressing at 1093° C has continuously increasing ductility with increasing temperature up to at least 1537° C. One of the reasons for the decrease in ductility with temperature for both the HP (at 1204° C) and HR Cr + 4 vol. % ThO_2 and for the HP Cr may be due to localized (as contrasted to uniform) elongation of the test specimens at high temperature. This localized elongation could be due to a nonuniform distribution of dispersoid, to large grain size (relative to the thickness of the specimen), or to porosity. Other explanations for this phenomenon are also possible. Properly heat treated TD-nickel chromium also shows a decrease in ductility with increasing test temperature. It appears reasonable to assume that, in the case of HP (at 1204° C) and HR Cr + 4 vol. % ThO_2, the decrease in ductility could have an origin similar to that in the TD-alloys. However, heat treating HP and HR Cr + 4 vol. % ThO_2 for 1/2 hour at 1316° C did not produce a great effect on strength and ductility (note samples D-2-1, D-2-2, E-2-3, and D-2-3, table III). It appears, however, that for as-hot-pressed Cr the main effect of heat treating at high temperature is to increase ductility, as can be seen by a comparison of the data for A-0-2 and A-0-3 in table III.

Ductile-to-brittle transition temperature of Cr and Cr + 4 vol. % ThO$_2$. - As was mentioned in the PROCEDURE section, the DBTT tests carried out in this investigation were of two types: bend tests for flat specimens and tensile tests with round specimens. Since Cr changes from ductile to brittle within a very narrow temperature range, the data from the two types of test are believed to be directly comparable. As already stated, the bend DBTT were obtained on specimens cut from used tensile test specimens. It is estimated that during the tensile tests the specimens were held at temperature from 20 to 35 minutes (depending on the elongation of the specimen). This time at temperature must be added to any other heat treatments indicated in table III.

Although the DBTT of as-hot-pressed pure Cr was not determined experimentally, it is deduced that this DBTT is very close to 140° C. This DBTT value was arrived at by the following line of reasoning. Firstly, the bend DBTT of HP and HR pure Cr (specimen A-1-1, table III) is 139° C. Secondly, the tensile DBTT of HP and HR pure Cr was found to be 140° C in reference 6. Thirdly, it was also found in reference 6 that recrystallization of this Cr (by heat treating for 1 hr at temperatures above 800° C) did not change the DBTT. Finally, HP pure Cr and recrystallized HP and HR pure Cr have the same equiaxed grain structure. It follows that as HP Cr should have about the same DBTT as HP and HR Cr. By contrast, in the present investigation, the DBTT of HP Cr + 4 vol. % ThO$_2$ was found to be 501° C (sample C-0, table II). As explained in the PROCEDURES section, the specimen was slightly prestrained during each of the trials. Hence, since prestraining is known to lower the DBTT of chromium (ref. 11), the 501° C DBTT is probably close to a minimum value. Extrapolation of the elongation as a function of temperature plot for HP Cr + 4 vol. % ThO$_2$ in figure 8 further supports the validity of this DBTT. Hence, 4 vol. % ThO$_2$ raises the DBTT of pure Cr by about 360° C. It is surmised from this result that, in general, dispersoids in the absence of other counteracting mechanisms raise the DBTT of Cr.

The bend DBTT of HP and HR Cr + 4 vol. % ThO$_2$ are 16° to 24° C (D-2-1 and E-2-1, table III) as compared with a (tensile) DBTT of 501° C for the HP Cr + 4 vol. % ThO$_2$. Thus, hot working lowers the DBTT of HP Cr + 4 vol. % ThO$_2$ by about 480° C. Although both nitrogen and carbon are known to be detrimental to the DBTT of Cr (ref. 12), the relatively small differences in nitrogen and carbon contents for the samples in question (table IV) discount the possibility that this large DBTT difference is due to differences in chemical analysis. Hence, it can be concluded that hot working is beneficial to the DBTT of dispersion strengthened Cr.

After heat treating for 1/2 hour at 1316° C the DBTT of HP and HR Cr + 4 vol. % ThO$_2$ increases to 35° C (D-2-2, table III) and to 114° C after the 1537° C tensile test (E-1-3, table III). Hence, heat treating at high temperatures causes an increase in DBTT.

From these results and conclusions it is theorized that hot rolling lowers the DBTT of Cr + 4 vol. % ThO$_2$ because the dispersoid inhibits the recovery and

recrystallization of the strained structure. The well known facts that prestraining lowers the DBTT of Cr (refs. 11 and 13), that the DBTT of refractory metals is lowered by increasing their strain energy (ref. 14), and that recovery and recrystallization are inhibited by dispersoids (refs. 15 to 19) further support this theory. More pertinent, Cr dispersion strengthened with ThO_2 recovers and recrystallizes much more slowly than pure Cr on annealing (ref. 6, pp. 40 to 52). The fact that strain energy is retained by HP and HR Cr + 4 vol. % ThO_2 is also supported by the following additional results of the present investigation. First, even after annealing for 2 hours at 1150° C, the character-istic microstructure of heavily deformed metal is retained in the thoriated alloy but not in pure chromium, as a comparison of figures 10 and 11 shows. Second, lowering the hot rolling temperature lowers the DBTT of HP and HR Cr + 4 vol. % ThO_2, as a com-parison of samples D-2-1 (which was hot rolled at 871° C and has a DBTT of 16° C) and D-3 (which was hot rolled at 760° C and has a DBTT of -8° C) in table V shows. Finally, annealing at high temperatures raised the DBTT.

Comparison of properties of Cr + 4 vol. % ThO_2 with those of conventionally cast and wrought chromium base alloys. - Figure 9 shows the ultimate tensile strength as a func-tion of temperature for HP and HR Cr + 4 vol. % ThO_2 from this investigation superim-posed of the corresponding curves of cast and wrought Cr alloys from reference 20. The DBTT of all these alloys are also given in the figure. The cast and wrought Cr base al-loys reported in reference 20 have probably the best combination of tensile and DBTT properties of the cast chromium-base alloys reported in the literature. The Cr + 4 vol. % ThO_2 alloy is stronger than unalloyed Cr (Cr - 0.1 Y actually) over the entire tem-perature range investigated. Below about 750° C the Cr + 4 vol. % ThO_2 is stronger than any of the other alloys except Cr-35 Re. Between about 950° and 1300° C the Cr + 4 vol. % ThO_2 alloy is weaker than both the solid solution and the precipitation strength-ened alloys. At a temperature of approximately 1300° C the Cr + 4 vol. % ThO_2 alloy has strength equal to or better than that of some of the better precipitation strengthened alloys, but it is weaker than both the solid solutions and the solid solutions plus precip-itation strengthened alloys.

As regards the DBTT's, it should be noted that, in general (except for the Cr-35 Re alloy), the stronger the alloy the higher its DBTT. This appears to be a characteristic of Cr alloys (ref. 3), except for those ductilized by the rhenium effect. By comparison, the Cr + 4 vol. % ThO_2 has a DBTT practically as low as the lowest in the Cr base alloys (here again, excepting the Cr-35 Re alloy) despite its relatively high strength either be-low about 700° or above about 1300° C. These considerations suggest that the dispersion strengthening process used in this investigation should produce alloys with good high-temperature strength with a relatively low DBTT when this process is applied to a solid solution Cr base alloy (e.g., Cr-4 Mo).

Cr + 4 vol. % ThO_2 with scavenger additions. - Certain scavengers or gettering el-ements may be added to chromium to counteract the deleterious effects of impurities (N

and C, mainly) on its DBTT (ref. 21). Fruitless attempts to use the direct addition of scavengers to the mill feed led to the development of a novel method of incorporating them as hydrides into the Cr + 4 vol. % ThO_2 mixture. Although contamination during processing vitiated the results, this method is believed useful for incorporating some scavengers and alloying elements in powder metallurgy products, and for this reason it is described in the appendix.

Microstructures. - Figure 10 is an electron photomicrograph of the sample designated as E-1 (table II) after annealing for 2 hours at 1150° C and is typical of similar HP and HR Cr - 4 vol. % ThO_2 samples. The thoria particles are well distributed in the structure and range in size from about 0.02 to 0.2 micrometer. One interesting feature shown in this photomicrograph is that the thoria particles were flattened during rolling. These thoria particles tend to be stringered along the grain boundaries. The photomicrograph also shows very small grains elongated in the rolling direction. (These are believed to be grains because in order to observe subgrains it is usually necessary to resort to transmission electron microscopy). By contrast, HP Cr also annealed for 2 hours at 1150° C has much larger, equiaxed grains, and there is no evidence of hot rolling left (fig. 11). As already stated, these results show that the recrystallization of Cr is inhibited by the dispersoid.

Effect of Processing Variables and Chemistry on Properties

Ball milling. - During ball milling, some material is usually removed from balls and mill. This removed material contaminates and/or dilutes the milled mixture. In this investigation, the material removed from the mills is molybdenum, and the material removed from the balls is chromium. Molybdenum is reported to be slightly beneficial to the DBTT of chromium (ref. 22). However, the small amounts of molybdenum (700 to 2900 ppm, table IV) removed from the mill liner during milling are not expected to affect the properties of chromium appreciably. As determined by weight loss, the material removed from the chromium balls was between 2 and 3 grams per batch. Hence, contamination of the batches from this source is negligible.

Reduction or cleaning in hydrogen. - As shown by the chemical analysis in table IV, only a small amount of residual iodine (<100 to 500 ppm) remained in the samples used for tensile and DBTT tests. As shown in table I, the raw chromium powder contains 251 ppm carbon. Yet, all the samples listed in table IV (except HP Cr sample A-0) contain much smaller amounts of carbon than the raw chromium powder used for their preparation. This was to be expected in view of the results previously reported (ref. 8). The removal of carbon from chromium is very desirable because carbon is reported to be almost as detrimental as nitrogen to the DBTT of chromium (ref. 14). The reason for the relatively large carbon content of the HP Cr sample is not known. It is surmised,

10

however, that, since sample A-0 has no dispersoids, it sinters much faster than the other samples during cleaning thereby hindering the diffusion of carbon and its eventual removal.

Nitrogen does not appear to be affected by the reduction process. The variations in the nitrogen content of the samples listed in table IV may result from contamination of the powders during processing and/or from analytical inaccuracies.

As shown in a previous investigation (ref. 8) some ThO_2 is lost during the cleaning process. The ThO_2 was probably lost by formation of thorium iodide either during milling or during hydrogen reduction of the milled powders. From the results shown in table IV, it is calculated that the loss amounted to about 4 percent of the ThO_2 originally added. This calculation takes into account the dilution due to the chromium removed from the balls during ball milling.

The calculated amounts of oxygen in excess of that tied up in the ThO_2 are also shown in table IV. As a rule, the excess oxygen is only slightly above the oxygen content of the chromium powder originally used as mill feed.

The results of chemical analysis for nitrogen and oxygen show that the process used in this investigation is very good for preventing contamination of the powders with atmospheric gases. These results are better than those previously reported (ref. 8), mainly because of improvements in the equipment used.

Isostatic hot pressing. - Table V shows the effects of hot pressing conditions on the properties of subsequently hot rolled Cr + 4 vol. % ThO_2. The HP and HR Cr + 4 vol. % ThO_2 sample (sample D-2-1) has the best 1093° C strength and a low DBTT. For these reasons most of the samples used in this investigation were hot pressed at 1204° C and 103.4 meganewtons per square meter. It should be noted that the Cr and Cr + 4 vol. % ThO_2 specimens to be used in the as-hot-pressed condition samples (A-0, B-0, and C-0, table II) were hot pressed at 1093° C and 68.9 meganewtons per square meter. As shown in table II, despite the lower temperature and pressure used for these as-hot-pressed samples, their densities are very close to 100 percent of their theoretical densities.

It should be noted that sample E-4-1 was hot rolled but not hot pressed. Despite the slightly lower strength and higher DBTT of this sample, the direct roll consolidation of the powders is economically appealing.

Hot rolling. - Hot rolling experiments were carried out in order to determine the most suitable hot rolling parameters. Some other preliminary experiments, not included in this table, were carried out to determine the effects of hot rolling temperature on can and specimen conditions.

The main trouble encountered during hot rolling was edge cracking of the cans. This edge cracking was most severe at the lower hot rolling temperatures. To a lesser extent, high reduction per pass also causes edge cracking. Another source of trouble was cracking of the chromium samples during pickle decanning. This cracking is due to buckling of the sample after part of the supporting can is dissolved in the aqua regia. This

buckling occurred almost exclusively with the low-temperature rolled samples. For these reasons, most of the hot rolling for this investigation was carried out at 871° C and a 10-percent reduction per pass. However, it should, be noted, that hot-pressed sample D-3 which was hot rolled at 760° C has a DBTT of -8° C. This is the lowest DBTT of all the samples investigated.

As already mentioned, a tantalum liner was used with all the cans processed in this investigation. The purpose of the tantalum liner was to facilitate pickle decanning and to act as a diffusion barrier for interstitials from the stainless steel can. It would be expected that some tantalum would diffuse into the Cr during hot pressing and hot rolling. However, as shown by the analysis in table IV, the amount of tantalum that diffused into the Cr was less than 100 ppm. In addition, microprobe analysis of the chromium-tantalum interface showed no detectable diffusion of tantalum in Cr either after hot pressing or after hot rolling.

SUMMARY OF RESULTS

An investigation of the effects of processing variables on the tensile properties and the ductile-to-brittle transition temperature (DBTT) of chromium dispersion strengthened with 4 volume percent thoria (Cr + 4 vol. % ThO_2) and of pure chromium (Cr) made by ball milling in hydrogen iodide produced the following results.

1. The ultimate tensile strength of hot pressed and hot rolled (HP and HR) Cr + 4 vol. % ThO_2 was higher than that of HP Cr + 4 vol. % ThO_2 and of pure Cr over the temperature range investigated. At 345°, 1093°, and 1316° C the ultimate tensile strength of the HP and HR Cr + 4 vol. % ThO_2 were 790, 103, and 46 newtons per square meter, respectively, and the ultimate tensile strength of the HP Cr + 4 vol. % ThO_2 were 615 (extrapolated), 45.4, and 6.9 meganewtons per square meter, respectively. By comparison, the ultimate tensile strength of pure chromium was 61 meganewtons per square meter at 1093° C.

2. The 0.2 percent offset yield strength of HP and HR Cr + 4 vol. % ThO_2 was 91 meganewtons per square meter at 1093° C. The yield strength at 1093° C for the HP Cr + 4 vol. % ThO_2 was 51 meganewtons per square meter and for pure Cr 60.7 meganewtons per square meter. The HP and HR Cr + 4 vol. % ThO_2 has better yield strength than HP Cr + 4 vol. % ThO_2 below about 800° C and above about 1000° C; in the range form 800° to 1000° C the yield strengths were about equal. In the range below about 900° C both the HP and the HP and HR Cr + 4 vol. % ThO_2 alloys have about twice the yield strength of pure Cr.

3. The elongation of the HP and HR Cr + 4 vol. % ThO_2 exhibited a maximum at about 900° C. This maximum occurred with the alloys hot pressed at 1204° C before hot rolling. Despite this maximum, pure Cr was more ductile than the HP and HR

12

Cr + 4 vol. % ThO_2 alloys. These, in turn, were more ductile than the HP Cr + 4 vol. % ThO_2 alloys below about 1000° C.

4. The bend DBTT of HP and HR pure Cr was 139° C whereas that of HP and HR Cr + 4 vol. % ThO_2 ranged from -8° to 24° C. By contrast, the tensile DBTT of HP Cr + 4 vol. % ThO_2 was 501° C.

CONCLUSIONS

The results of the present investigation led to the following conclusions.

1. The hydrogen iodide milling process used in this investigation proved capable of producing Cr + 4 vol. % ThO_2 alloys having lower ductile-to-brittle transition temperatures (DBTT) than either pure Cr or than many solid solution and/or precipitation strengthened Cr base alloys reported in the literature. These Cr + 4 vol. % ThO_2 alloys also compare favorably in tensile strength up to 750° C and at 1300° C with some of the best cast and wrought chromium base alloys reported in the literature.

2. The dispersoid increases the ultimate tensile and the yield strengths of hot pressed and hot rolled (HP and HR) Cr + 4 vol. % ThO_2 over the entire temperature range investigated, as compared with that of as hot pressed (HP) pure Cr; however, the dispersoid increases the ultimate yield strengths of HP Cr + 4 vol. % ThO_2 only at temperatures below about 900° C.

3. In as-hot-pressed Cr the dispersoid, per se, raises the DBTT whereas the dispersoid combined with hot working lowers the DBTT. Dispersoids lower the DBTT of hot worked Cr by hindering the recovery and recrystallization of the strained structure. On this basis, the DBTT of dispersion strengthened Cr should be lowered by lowering the hot rolling temperature, increasing the total reduction and the reduction per pass, and optimizing the dispersoid particle size and interparticle spacing.

4. The improvement in mechanical properties brought about by thermomechanical processing is attributed to the relatively good distribution of dispersoid. This good distribution of the dispersoid results from the ability of the hydrogen iodide milling process to produce fine submicron powders. Other factors that help retain a good dispersion are that these powders can be hydrogen reduced at relatively low temperature and that the process minimizes their contamination by atmospheric gases.

Lewis Research Center,
    National Aeronautics and Space Administration,
        Cleveland, Ohio, August 24, 1973,
            501-21.

Chromium dispersion strengthened with thoria (Cr + 4 vol. % ThO_2) was ball milled in hydrogen iodide and then cleaned in hydrogen essentially as described in the PROCE-DURES section, except that the ball milling time was 960 hours. The scavenger mixture to be added to this Cr + 4 vol. % ThO_2 powder was prepared as follows.

A mixture of 60 weight percent yttrium, 20 weight percent hafnium, and 20 weight percent thorium coarse metal powder was first converted to the respective metal hydrides by heating the mixture in hydrogen. This scavenging composition was selected on the basis of work done in reference 23. After hydrogenation the brittle hydrides were ball milled with 4 vol. % ThO_2 for 114 hours in a ball mill pressurized with helium. The clean Cr + 4 vol. % ThO_2 powder was then mixed with 1 weight percent of the scavenger hydride-thoria mixture. After mixing for 24 hours by tumbling in a ball mill pressurized with helium, the powder mixture was dehydrogenated by gradual heating in vacuum to 870° C. The powder mixture was then hot pressed at 1204° C and 103.4 meganewtons per square meter for 2 hours followed by hot rolling at 871° C and at a 10-percent reduction per pass to a total reduction of 85 percent.

For comparison, a batch of the same Cr + 4 vol. % ThO_2 without scavengers was consolidated and hot rolled under the same conditions. Chemical analysis of the two batches of as-consolidated material gave the following results:

Cr + 4 vol. % ThO_2	Chemical analysis, ppm				
	N	C	O	Mo	Ta
With scavengers	370	68	6605	ND[a]	ND
Without scavengers	209	24	6130	700	<100

[a]Not determined.

Electron microscopy of the as-hot-rolled, scavenged alloy showed a microstructure similar to that in figure 9, except for the presence of yttrium chunks up to 15 micro-meters in diameter. The agglomeration of yttrium was to be expected on view of the very low solubility of this metal in chromium (ref. 24).

The two materials were tensile tested at 1093° C and the bend DBTT determined with the following results:

Cr + 4 vol. % ThO_2	Ultimate tensile strength		0.2 Percent yield strength		Elongation, percent	Bend DBTT, ^{o}C
	MN/m^2	ksi	MN/m^2	ksi		
Without scavengers	98.5	14.27	87.7	12.70	10.1	427
With scavengers	123.9	17.95	86.9	12.59	7.0	260

The scavenged alloy had the highest 1093° C ultimate tensile strength of all the materials reported in this investigation. The DBTT of both materials was too high when compared with those of materials consolidated under the same conditions (table III). The relatively high DBTT of these two materials is probably due to their relatively high nitrogen content. The high nitrogen content is probably due to accidental contamination during handling and to nitrogen in the scavenger metals. However, despite the fact that the scavenged alloy had higher nitrogen, it has a much lower DBTT than the alloy without the scavengers. Even though contamination with nitrogen vitiated the results, the method described is believed to be suitable for incorporating certain alloying and scavenging elements in alloys prepared by powder metallurgy methods.

REFERENCES

1. Pugh, J. W.: The Tensile and Stress-Rupture Properties of Chromium. Trans. of the ASM, Vol. 50, 1958, pp. 1072-1080.

2. Sims, Chester T.: The Case for Chromium. Jour. of Metals, Vol. 15, No. 2, Feb. 1963, pp. 127-132.

3. Maykuth, D. J.; and Gilbert, A.: Chromium and Chromium Alloys. DMIC Rept. 234, Battelle Memorial Institute (AD-810530), 1966.

4. Klopp, W. D.: Recent Developments in Chromium and Chromium Alloys. Jour. of Metals, Vol. 21, No. 11, Nov. 1969, pp. 23-32.

5. Conrad, H.: Guilding Principles for Lowering the Ductile-to-Brittle Transition Temperature in the BCC Metals. In High Temperature Refractory Metals, Part 2. R. W. Fountain, Joseph Maltz, and L. S. Richardson, eds., Gordon and Breach Science Publ. Inc., 1966, pp. 113-128.

6. Veigel, N. D.; Wilcox, B. A.; Blocher, J. M., Jr.; Clauer, A. H.; Seifert, D. A.; Meiners, K. E.; Browning, M. F.; and Pfeifer, W. H.: Development of a Chromium-Thoria Alloy. Battelle Memorial Inst. (NASA CR-72901), 1971.

7. Bunshah, R. F.; and Goetzel, C. G.: A Survey of Dispersion Strengthening of Metals and Alloys. New York Univ. (WADD TR 59-414), Mar. 1960.

8. Arias, Alan: Feasibility of Producing Dispersion Strengthened Chromium by Ball-Milling in Hydrogen Halides. NASA TN D-4912, 1968.

9. Arias, Alan: The Role of Chemical Reactions in the Mechanism of Communition of Ductile Metals into Ultrafine Powders by Grinding. NASA TN D-4862, 1968.

10. Wilcox, B. A.; Clauer, A. H.; and Hutchinson, W. B.: Structural Stability and Mechanical Behaviour of Thermomechanically Processed Dispersion Strengthened Nickel Alloys. Battelle Memorial Inst. (NASA CR-72832), 1971.

11. Wain, H. L.; Henderson, F.; and Johnstone, S. T. M.: A Study of the Room-Temperature Ductility of Chromium. Jour. of the Institute of Metals. Vol. 83, 1954-55, pp. 133-142.

12. Cairns, Raymond E., Jr.; and Grant, Nicholas J.: The Effects of Carbon, Nitrogen, Oxygen, and Sulfer on the Ductile-Brittle Fracture Temperature of Chromium. Trans of the Metal Soc. of AIME, Vol. 230, Aug. 1964, pp. 1150-1159.

13. Hook, Rollin E.; and Adair, Attwell M.: On the Recrystallization Embrittlement of Chromium. Trans of the Metal Soc. of AIME, Vol. 227, Feb. 1963, pp. 151-159.

16

14. Seigle, L. L.; and Dickinson, C. D.: Effect of Mechanical and Structural Variables on the Ductile-Brittle Transition in Refractory Metals. In Refractory Metals and Alloys II, M. Semchyshen and I. Perlmutter, eds., Interscience Publishers, 1963, pp. 65-116.

15. Gregory, E.; and Smith, G. C.: The Effects of Internal Oxidation on the Tensile Properties of Some Silver Alloys at Room and Elevated Temperstures. Jour. of the Institute of Metals, Vol. 85, Pt. 3, 1956-57, pp. 81-87.

16. Adachi, Masao; and Grant, Nicholas J.: The Effects of Stored Energy and Recrystallization on the Creep Rupture Properties of Internally Oxidized Copper-Alumina and Copper-Silica Alloys. Trans. of the Metal. Soc. of AIME, Vol. 218, Oct. 1960, pp. 881-887.

17. Westerman, E. J.; and Lenel, F. V.: Recrystallization of Cold-Drawn Sintered Aluminum Powder. Trans, of the Metal. Soc. of AIME, Vol. 218, Dec. 1960, pp. 1010-1014.

18. Walter, J. L.: Growth and Preferred Orientations of Large Elongated Grains in Doped Tungsten Sheet. Trans. of the Metal. Soc. of AIME, Vol. 239, Feb. 1967, pp. 272-286.

19. Preston, Oliver; and Grant, Nicholas J.: Dispersion Strengthening of Copper by Internal Oxidation. Trans of the Metal. Soc. of AIME, Vol. 221, Feb. 1961, pp. 164-173.

20. Clark, J. W.: Development of High-Temperature Chromiom Alloys, Final Report. General Electric Co., (NASA CR-72731), 1970.

21. Ryan, N. E.: An Appraisal of Possible Scavenger Elements for Chromium and Chromium Alloys. Jour. Less-Common Metals, Vol. 6, 1964, pp. 21-35.

22. Carlson, O. N.; Sherwood, L. L.; and Schmidt, F. A.: The Effect of Low Percentage Alloying Additions on the Ductility of Iodide Chromium. Jour. Less-Commom Metals, Vol. 6, 1964, pp. 439-450.

23. Wukusick, Carl S.: Research on Chromium-Base Alloys Exhibiting High-Temperature Strength, Low-Temperature Ductility, and Oxidation Resistance. ASD-TDR-63-493, General Electric Co., June 1963.

24. Taylor, A.; Hickman, W. M.; and Doyle, N. J.: Solid Solubility Limits of Y and Sc in the Elements W, Ta, Mo, Nb, and Cr. Jour. Less-Common Metals. Vol. 9, 1965, pp. 214-232.

TABLE I. - CHARACTERIZATION OF RAW MATERIALS

Material	Form	Supplier	Grade	Purity, percent	Manufacturer's specification or chemical analysis
Cr	Electrolytic flake crushed to -20 mesh	Union Carbide Corp.	High purity	99.5 (min)	Oxygen, 134 ppm (a); nitrogen, 85 ppm; carbon, 251 ppm; iron, 3 ppm
Y	Powder, -40 mesh	Alfa Products	m2N5	99.5	Tantalum, 3000 ppm; calcium, 700 ppm; nickel, 700 ppm; iron, 500 ppm; aluminum, 300 ppm; other metals, 500 ppm (b)
Hf	Powder, -80 mesh	Carborundum Co	(c)	96.5	Hafnium, 96.5%; zirconium, 3.5%; oxygen, 800 ppm; nitrogen, 26 ppm; carbon, 86 ppm
Th	Powder, -80 mesh	UMC	High purity	99.95	(c)
ThO_2	Colloidal powder, 0.0050 to 0.0150 μm	Thorium Ltd.	High purity	99.9 (min)	Sulfur, 100 ppm; calcium, 350 ppm (max); iron, 10 ppm (max); silicon, 60 ppm (max); sodium, 100 ppm (max); all other elements, · 50 ppm total
HI	Liquid under pressure in steel tanks	The Matheson Co.	(c)	96 (min)	Minimum liquid purity of 96 percent. Impurities consist of iodine in the liquid phase and hydrogen in the gaseous phase.

[a] In house analysis.
[b] Analysis for nonmetallic impurities not available.
[c] Not available.

TABLE II. - PROCESSING CONDITIONS OF POWDER SAMPLES BALL MILLED 320 HOURS.

Sample identification	Nominal composition	Cleaning		Hot pressing[a]			Hot rolling		Density of solid sample, % of theoretical
		Temperature, °C	Time, hr	Temperature, °C	Pressure		Temperature, °C	Reduction in area per pass, %	
					MN/m^2	ksi			
A-0	Pure Cr	660	281	1093	68.9	10	(b)	(b)	99.3
A-1	Pure Cr	660	281	1093	68.9	10	871	10	99.7
B-0	Cr + 4 vol. % ThO_2	650	399	1093	68.9	10	(b)	(b)	99.8
C-0		650	228	1093	68.9	10	(b)	(b)	99.8
D-2		680	352	1204	103.4	15	871	10	99.3
D-3		680	352	1204	103.4	15	760		99.2
E-1		675	290	1093	68.9	10	871		98.6
E-2		675	290	1204	103.4	15			99.5
E-4		675	290	(c)	(c)	(c)		20	99.5
F-2		670	212	1204	103.4	15		10	99.8

[a] Hot pressing time, 2 hr.
[b] Not hot rolled.
[c] Not hot pressed.

PROPERTIES AND DBTT OF Cr AND Cr + 4 VOL. % ThO_2.

Sample identification	Heat treatment			Tensile properties					Elongation, %	Bend ductile-to-brittle transition temperature, °C
	Temperature, °C	Time, hr	Atmosphere	Temperature, °C	Ultimate tensile strength		0.2-Percent yield strength			
					MN/m^2	ksi	MN/m^2	ksi		
A-0-1	----	---	-----	621	439.0	63.7	222.0	32.2	21	(a)
A-0-2	----	---	-----	1093	65.1	9.44	60.8	8.82	17.1	(a)
A-0-3	1316	2	Argon	1093	72.8	10.55	48.5	7.04	35.0	(a)
A-1-1	----	---	-----	1093	74.5	10.80	49.8	7.22	42.1	139
B-0-1	----	---	-----	1093	45.4	6.58	42.6	6.18	10.0	(a)
B-0-2	----	---	-----	1316	6.88	.996	5.49	.796	48.0	↓
C-0-1	----	---	-----	558	567.0	82.2	511.0	74.0	1.2	
C-0-2	----	---	-----	780	389.5	56.5	379.0	55.0	4.1	↓
D-2-1	----	---	-----	1093	103.0	14.93	91.3	13.22	1.8	16
D-2-2	1316	1/2	Argon	1093	101.7	14.75	87.4	12.67	1.3	35
D-2-3	1316	1/2	Argon	1316	66.3	9.60	66.3	9.60	0.2	(a)
E-1-1	----	---	-----	1093	102.8	14.93	68.3	10.04	13.2	24
E-1-2	----	---	-----	1316	35.0	5.08	23.7	3.44	14.4	16
E-1-3	----	---	-----	1537	8.1	1.18	5.9	.90	32.0	114
E-2-3	----	---	-----	1316	32.35	4.69	31.9	4.63	.64	(a)
E-2-4	----	---	-----	1537	18.4	2.67	17.8	2.59	.40	
F-2-1	----	---	-----	345	790.0	114.5	631.5	91.5	6.9	↓
F-2-2	----	---	-----	653	631.5	91.5	526.0	76.3	11.6	
F-2-3	----	---	-----	871	295.0	42.8	263.0	38.1	17.9	↓

[a]Not available.

TABLE IV. - CHEMICAL ANALYSIS OF SOME CONSOLIDATED SAMPLES

Sample identification	Iodine, ppm (b)	Nitrogen, ppm	Carbon, ppm	Oxygen, ppm	Thoria, %	Calculated excess oxygen, ppm	Molybdenum, ppm	Tantalum, ppm
A-0	(a)	78	240	310	0	310	2900	(a)
A-1	<100	44	(a)	324	0	324	(a)	(a)
C-0	(a)	93	94	6440	5.13	220	700	↓
D-2	500	105	26	6270	5.09	120	1000	
E-1	(a)	66	33	6980	(a)	(a)	600	
E-2	500	83	13	6285	(a)	(a)	(a)	<100
F-2	(a)	143	31	6600	5.10	420	800	(a)

[a]Not determined.
[b]Estimated.

TABLE V. - EFFECT OF HOT PRESSING AND HOT ROLLING CONDITIONS ON 1093° C TENSILE PROPERTIES

AND ON DBTT OF Cr + 4 vol. % ThO_2.

Sample identification	Hot pressing			Hot rolling			Tensile properties					Ductile-to-brittle transition temperature, DBTT, °C
	Temperature, °C	Pressure		Temperature, °C	Reduction per pass, %	Condition of rolled material	Ultimate tensile strength,		0.2-Percent yield strength		Elongation, %	
		MN/m^2	ksi				MN/m^2	ksi	MN/m^2	ksi		
E-1-1	1093	68.9	10	871	10	No cracks	102.8	14.93	68.3	10.04	13.2	24
D-2-1	1204	103.4	15	871	10	No cracks	103.0	14.94	91.3	13.22	1.8	16
D-3	1204	103.4	15	760	10	Five cracks in can	83.4	12.08	64.6	9.36	5.0	-8
E-4	(a)	(a)	(a)	871	20	Cracks in can	99.6	14.45	85.6	12.40	6.1	118

[a]Not hot pressed.
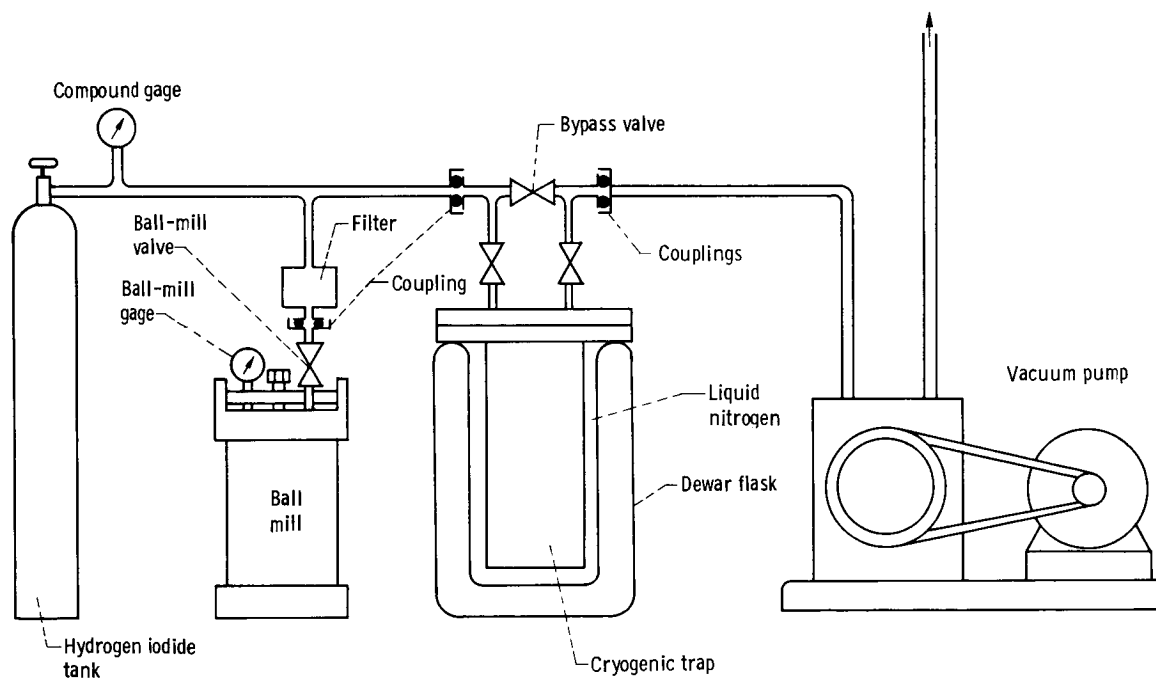
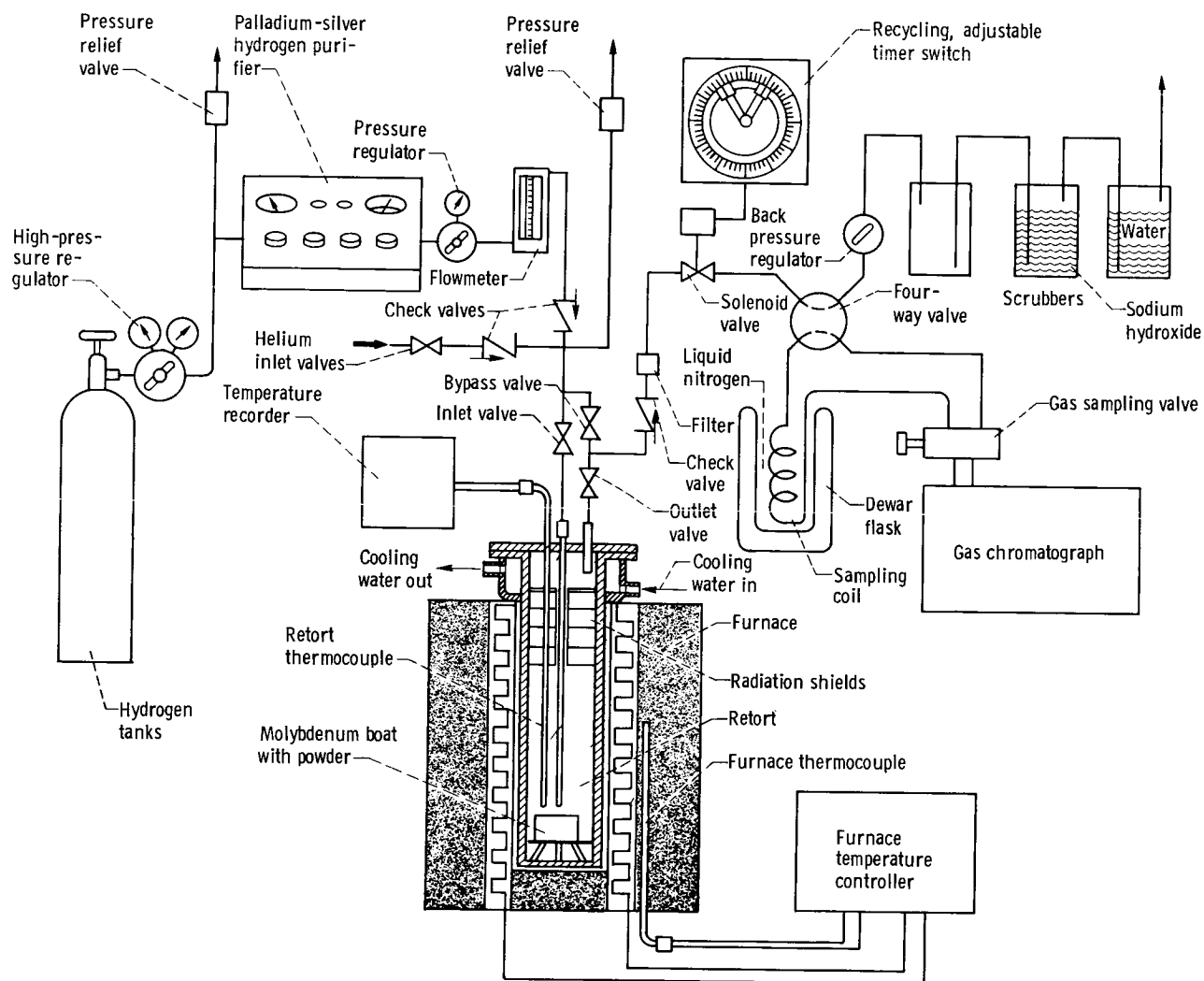Figure 1. - System for pressurizing ball mills with hydrogen iodide.
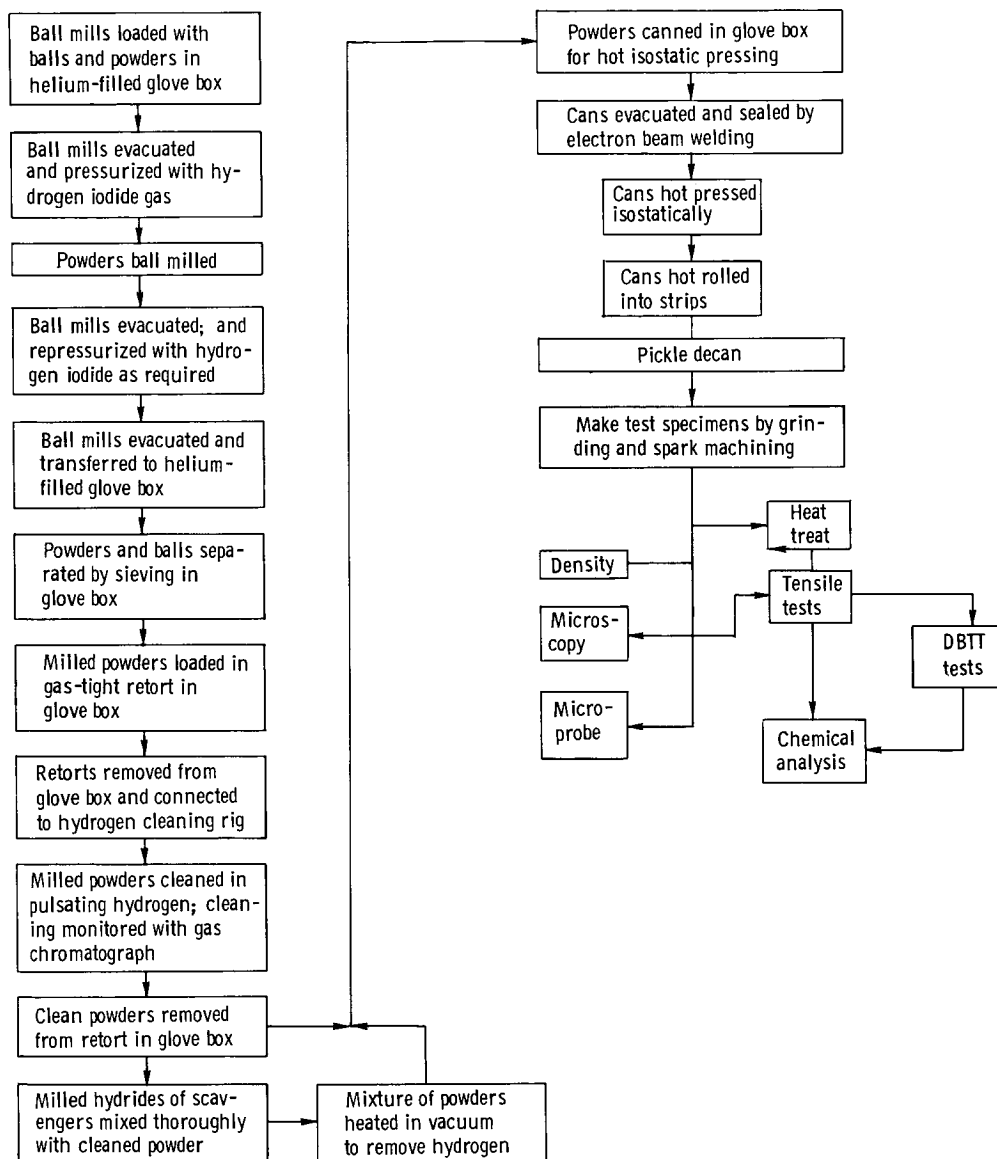
Figure 2. - Hydrogen cleaning rig.

| Ball mills loaded with balls and powders in helium-filled glove box |
| Ball mills evacuated and pressurized with hydrogen iodide gas |
| Powders ball milled |
| Ball mills evacuated; and repressurized with hydrogen iodide as required |
| Ball mills evacuated and transferred to helium-filled glove box |
| Powders and balls separated by sieving in glove box |
| Milled powders loaded in gas-tight retort in glove box |
| Retorts removed from glove box and connected to hydrogen cleaning rig |
| Milled powders cleaned in pulsating hydrogen; cleaning monitored with gas chromatograph |
| Clean powders removed from retort in glove box |
| Milled hydrides of scavengers mixed thoroughly with cleaned powder |

| Mixture of powders heated in vacuum to remove hydrogen |

| Powders canned in glove box for hot isostatic pressing |
| Cans evacuated and sealed by electron beam welding |
| Cans hot pressed isostatically |
| Cans hot rolled into strips |
| Pickle decan |
| Make test specimens by grinding and spark machining |

| Density |
| Microscopy |
| Microprobe |

| Heat treat |
| Tensile tests |
| DBTT tests |
| Chemical analysis |

Figure 3. - Flow chart for preparation and testing of chromium and chromium + 4 vol.% thoria specimens.

22

1. 27- or 1. 90-
cm o. d.
stainless
steel can

Tantalum
thimble

(a) Insert tantalum
liner in can.

Powder

(b) Fill tantalum
thimble with
powder.

Plunger

(c) Press powder
in thimble.

Can

Plug

Tantalum
thimble

(d) Cap with
plug.

To vacuum pump

Vacuum valve

Vacuum coupling

Flatten in hydraulic
press after evacuation

Can

(e) Connect can to
vacuum coupling,
evacuate, and
flatten can as shown.

E B gun

Can

E B welder
electrode and clamp

(f) Cut off can across flattened section
in electron beam (E B) welder.

E B welder electrode-clamp

E B gun
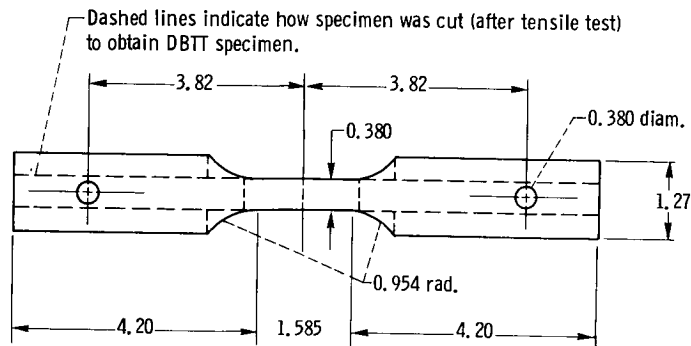
(g) Weld lips of flat
section of can in
E B welder.

Figure 4. – Canning of powders for isostatic hot pressing.
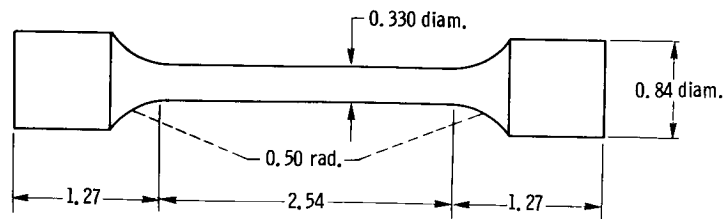
(a) Hot pressed specimen.

(b) Hot rolled specimens. Thickness, 0.076 to 0.101 centimeter.

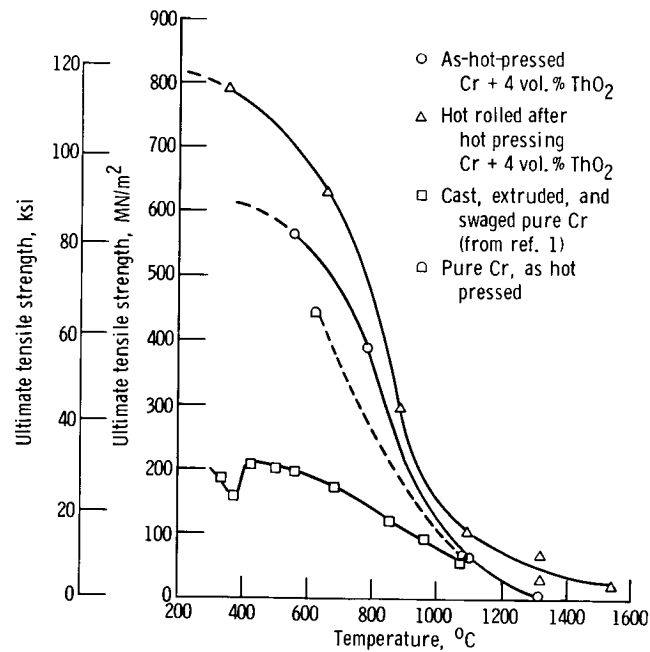Figure 5. - Tensile specimens. (All dimensions in cm.)

○ As-hot-pressed
   Cr + 4 vol.% ThO$_2$

△ Hot rolled after
   hot pressing
   Cr + 4 vol.% ThO$_2$

□ Cast, extruded, and
   swaged pure Cr
   (from ref. 1)

○ Pure Cr, as hot
   pressed

Figure 6. - Effect of temperature on ultimate tensile strength of
chromium with 4 vol.% thoria.

24
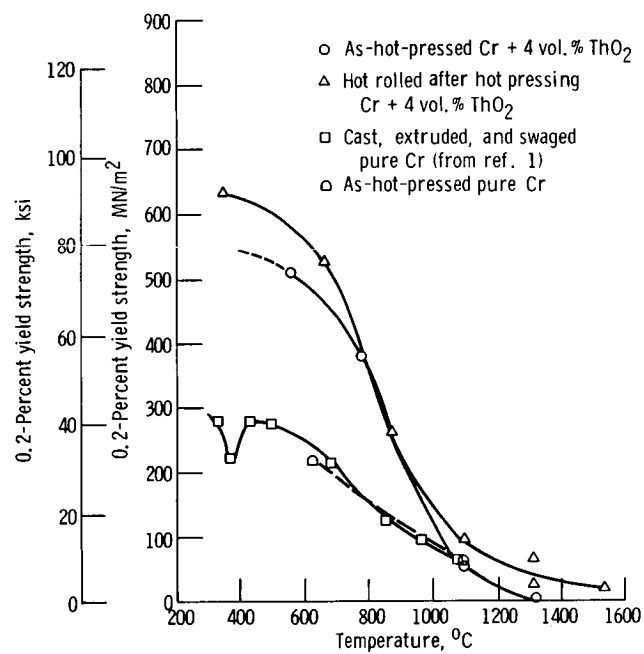
Figure 7. - Effect of temperature on 0.2-percent yield strength of chromium with 4 vol. % thoria.
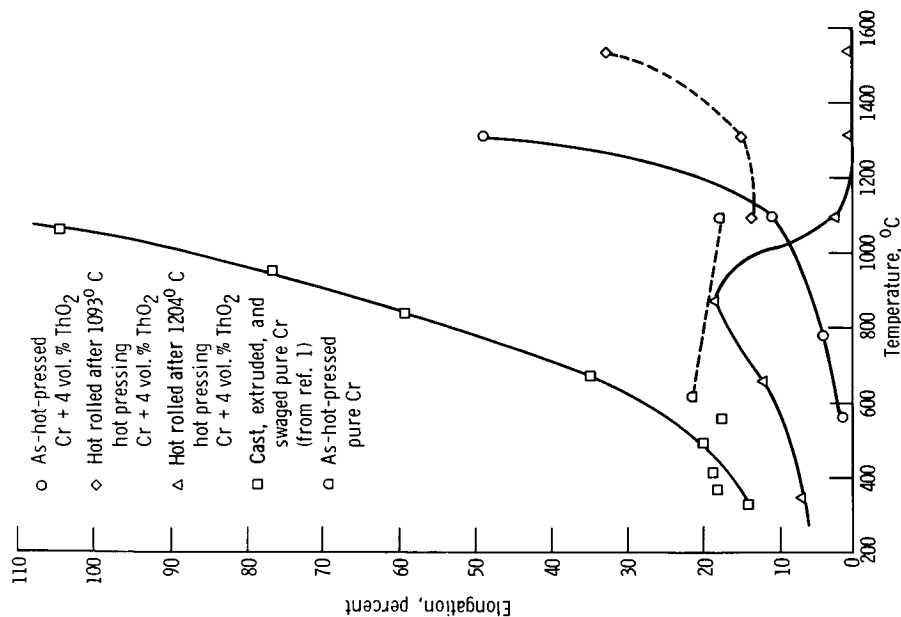
□ Cr-4 ThO$_2$, this work
△ Cr-35Re
□ Cr-4Mo-0.05Y-0.4Zr-0.2Ti-0.4C
○ Cr-4Mo-0.1Y
◇ Cr-0.05Y-0.4Zr-0.2Ti-0.4B
▽ Cr-0.05Y-0.4Zr-0.2Ti-0.4C
◁ Cr-0.1Y

To 1065 MN/m^2 at 24° C

Ductile-to-brittle transition temperature, °C

−129
232
149
10
−8 to 24
−4
38

Ultimate tensile strength, MN/m^2
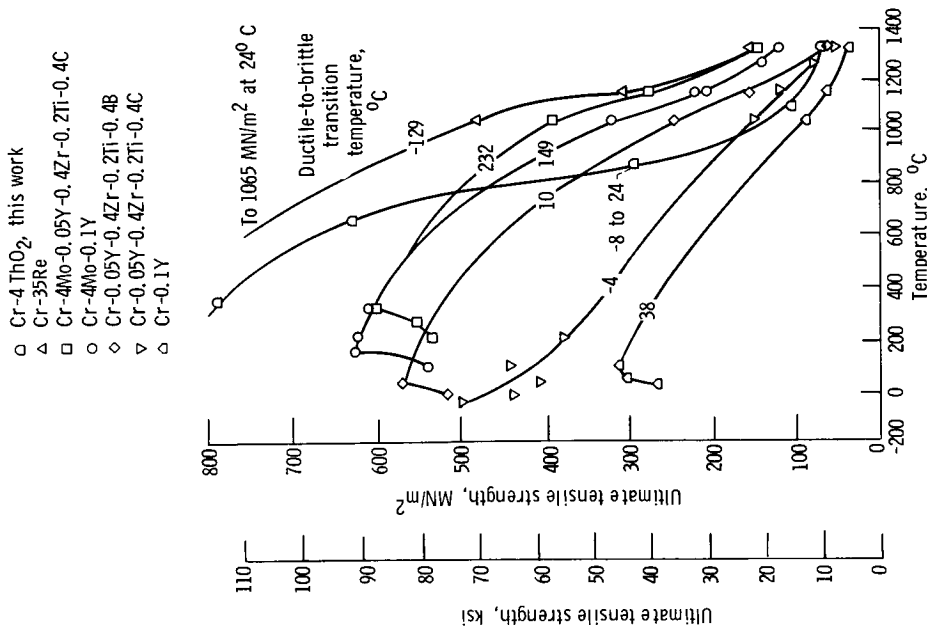
Ultimate tensile strength, ksi

Temperature, °C

Figure 9. - Effect of temperature on ultimate tensile strength of cast and wrought chromium base alloys from reference 20 and chromium with 4 vol. % thoria from this investigation.
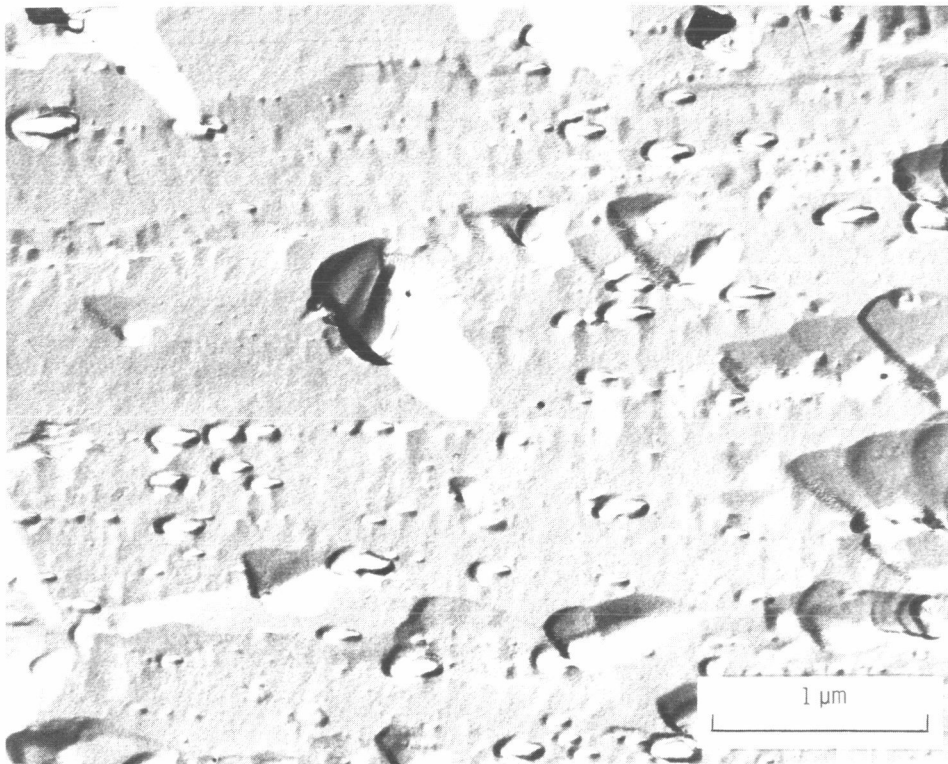

○ As-hot-pressed Cr + 4 vol. % ThO$_2$
◇ Hot rolled after 1093° C hot pressing Cr + 4 vol. % ThO$_2$
△ Hot rolled after 1204° C hot pressing Cr + 4 vol. % ThO$_2$
□ Cast, extruded, and swaged pure Cr (from ref. 1)
○ As-hot-pressed pure Cr

Elongation, percent

Temperature, °C

Figure 8. - Effect of temperature on elongation of chromium with 4 vol. % thoria.

26

Figure 10. - Electron photomicrograph of hot rolled chromium with 4 vol. % thoria (sample E-1, table II) after annealing for 2 hours at 1150° C.
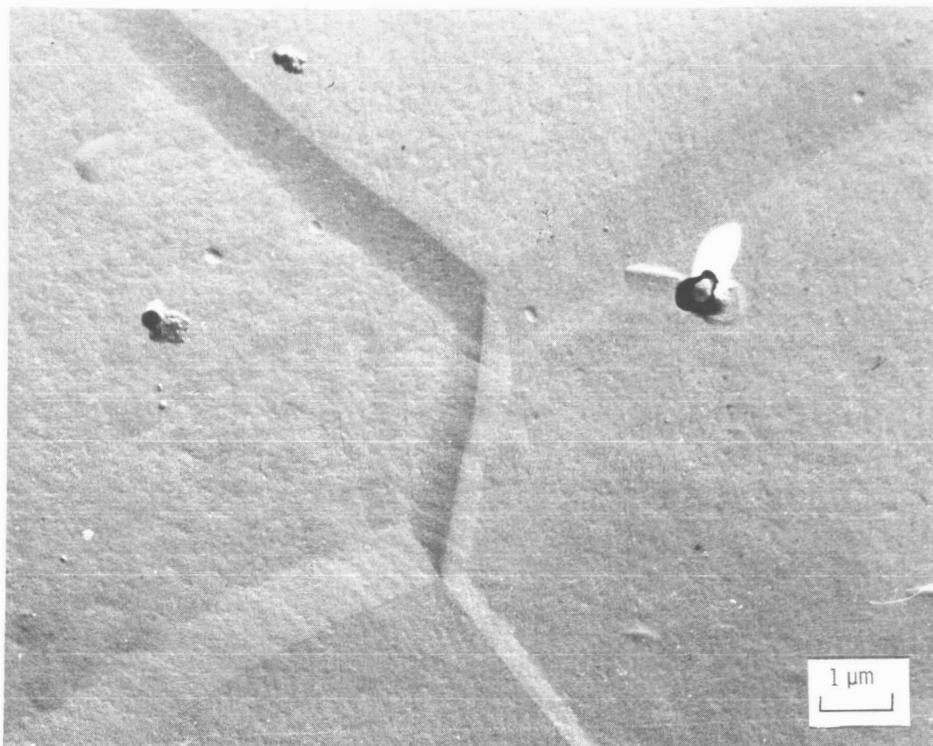
Figure 11. - Electron photomicrograph of hot rolled pure chromium (sample A-1, table II) after annealing for 2 hrs. at 1150° C.