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INVESTIGATION OF MECHANICAL PROPERTIES OF CHROMIUM, CHROMIUM-RHENIUM, AND DERIVED ALLOYS

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TABLE OF CONTENTS

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INTRODUCTION

It has been shown that alloys of Cr, Mo, and W containing high alloying additions of Re can have substantially improved ductility over that of unalloyed material.[1-3] However, while it is known that the ductility of the unalloyed material deteriorates rapidly as the amount of interstitial impurity increases, there has been no experimental documentation of the effect of a given impurity on the ductility of their rhenium alloys. In view of the fact that the beneficial effect of rhenium has been attributed to a modification of the interstitial distribution, it is desirable to investigate the effect of impurities on the ductility of a high-rhenium alloy. Furthermore, in order to try to understand the mechanism of any potential impurity-embrittling effect, it is desirable to investigate whether impurity in solution is a more potent embrittling agent than when present as a second phase, or vice versa.

In an extension of work on unalloyed chromium described previously, the present work was done on wires of Cr-35Re containing two different levels of nitrogen. The bend properties were determined for material of the two nitrogen levels in the quenched condition and also after two different aging treatments. Internal friction techniques were used to monitor the amount of nitrogen actually in solution.

EXPERIMENTAL WORK

Cr-35 atom percent Re ingots were prepared by arc-melting iodide chromium crystals with sintered rhenium pellets. The ingots were extruded and centerless ground to produce 0.2-inch-diameter rods from which 40-mil-diameter wires were drawn. Six-inch lengths of the fabricated wires were annealed in a quartz capsule containing argon for 1 hour at 1150 or 1200 C. This heat treatment resulted in complete recrystallization with a grain size of about 0.02 to 0.04 mm. Prior to nitrogen loading, the interstitial analysis was: 130 ppm oxygen, 1 ppm hydrogen, 10 ppm carbon, and 33 ppm nitrogen. The nitrogen concentration was increased to 117 ppm by annealing the recrystallized wires in a quartz tube containing ammonia for 48 hours at 1150 C. The recrystallized wires were quenched into water from 1150 C. Some of these wires were retained in this condition for subsequent mechanical property tests. The remaining wires were aged for 5 minutes at 500 C to nucleate nitride precipitates and then were held for 7 days at 600 C to allow the soluble nitrogen concentration to be reduced to its equilibrium value of about 3 ppm. It has been shown that a double aging treatment where the interstitial precipitate is seeded at one temperature and held at a higher temperature can increase the interstitial precipitation kinetics. The soluble nitrogen concentration in these wires was monitored by internal friction and electrical resistivity measurements as previously described.[4]

Additional wires were quenched from 1200 C and aged for 4 hours at 800 C. A summary of the conditions of the test wires and the batch numbers by which they will subsequently be described is given in Table 1.

Since only a limited amount of material was available from each batch, a testing technique had to be used which maximizes the number of test specimens obtainable. In earlier work bend tests on chromium wires had successfully been performed using a 3-point bend jig similar to that illustrated in Figure 1. Using such a jig, wires as short as 3/16 inch can be tested, which permits a determination to be made of the ductile-brittle bend transition temperature using as little as 2 inches of wire. Accordingly, this technique was used in the present tests.

As well as determining the relative ductility of the specimens over a temperature range, it is desirable to measure their respective yield stresses. Unfortunately, three-point bending is not well suited to the measurement of stress due to the stress-concentrating effect of the center loading point for which it is difficult to make allowance. In the present tests an additional complication existed in that the wires available varied in diameter (from batch to batch) over the range 20-40 mils so that it was not possible to make a simple comparison of the bend load at the yield. In order to take both these unknowns into consideration and get at least an estimate of the yield stresses, the bend jig was "calibrated" in the following way.

As-drawn 80-mil molybdenum wire was cut into lengths and each length was electropolished for a different time to produce wires of different diameters. Several specimens of each diameter were then tested at room temperature in the bend jig of Figure 1 and the load at the proportional limit was measured as a function of diameter. The results are presented in Figure 2 from which it can be seen that the proportional limit load varies as the cube of the diameter.

In order to normalize this curve in terms of stress rather than load, the load values were converted to stress by comparison to a tensile stress-strain curve obtained on the same wire. By comparing the tensile curve with the bend load-time history obtained on any diameter, the bend jig is calibrated for all diameters for which the inverse cube relationship holds. For the present apparatus the following relationship was obtained:

$$\text{Proportional Limit} = \frac{0.175\ ''L}{d^3}\ \text{psi}\ ,$$

where L is the load in pounds and d the diameter of the wire expressed in inches. The formula is only applicable up to the end of the elastic range and can therefore not be used to measure fracture stresses.

Bend tests were performed at 0.1 inch per minute crosshead speed in the temperature range -196 C to 200 C using liquid nitrogen or solid CO_2 and acetone baths at the lower temperature and oil baths at the higher temperatures.

After testing, the angle of bend prior to fracture was measured under a low power optical microscope, and the specimens were examined metallographically and fractographically.

TABLE 1. SUMMARY OF Cr-35Re TEST MATERIALS

Batch	Condition	Batch	Condition
1	Not N loaded (33 ppm N) Water quenched from 1150 C	6	N loaded (117 ppm N) Water quenched from 1150 C Aged 168 hours at 600 C (Repeat of Batch 5)
2	Not N loaded (33 ppm N) Water quenched from 1150 C Aged 168 hours at 600 C	7	N loaded (117 ppm) Water quenched from 1200 C Aged 4 hours at 800 C Contains some sigma phase
3	Not N loaded (33 ppm N) Water quenched from 1150 C Aged 168 hours at 600 C (Repeat of Batch 2)	8	N loaded (117 ppm) Water quenched from 1200 C Contains some sigma phase
4	N loaded (117 ppm N) Water quenched from 1150 C	9	N loaded (117 ppm) Water quenched from 1200 C
5	N loaded (117 ppm N) Water quenched from 1150 C Aged 168 hours at 600 C	10	N loaded (117 ppm) Furnace cooled from 1200 C to 800 C; aged 4 hours at 800 C

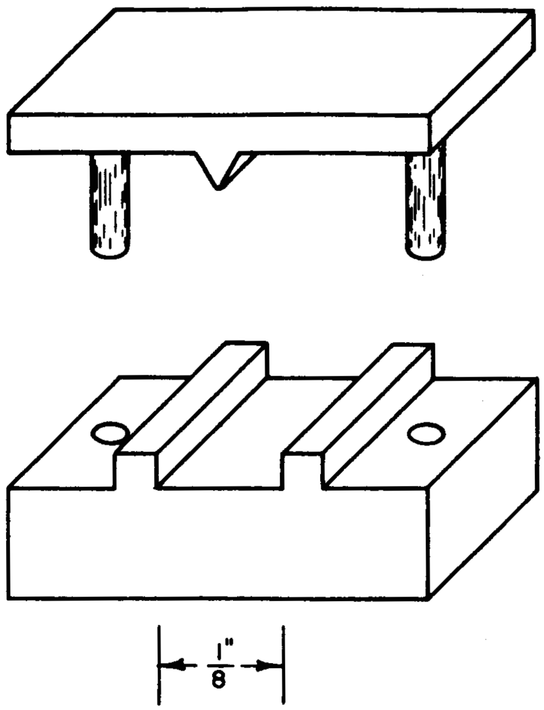


FIGURE 1. SCHEMATIC OF THE 3-POINT BEND JIG USED IN THESE TESTS

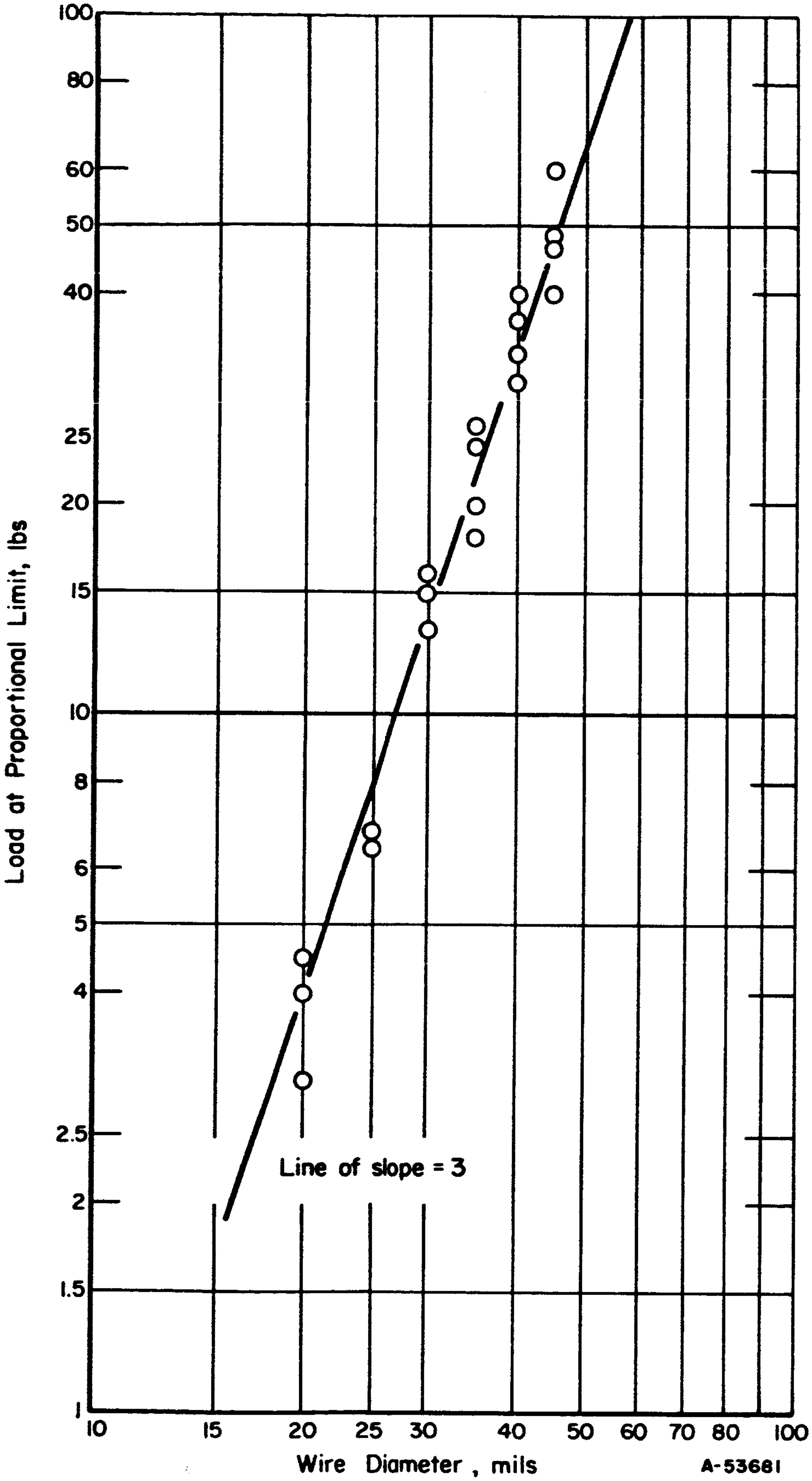


FIGURE 2. RELATIONSHIP BETWEEN DIAMETER AND LOAD AT THE PROPORTIONAL LIMIT FOR DRAWN Mo WIRE (USING THE BEND JIG OF FIGURE 1.)

EXPERIMENTAL RESULTS

Transition Temperatures

The bend data for Cr-35Re wire in various conditions is summarized in Table 2 and Figures 3 and 4. The important results are as follows:

(1) The nonnitrogen-loaded material is very much more ductile than the loaded (-150 C transition temperature compared to as high as +150 C for the loaded and quenched).

(2) Within the sensitivity of these experiments the transition temperature of the nonloaded material is not strongly dependent on heat treatment in that no distinction can be made between the transition temperature of the quenched and that of the quenched-plus-aged material.

(3) Nitrogen-loaded material is very sensitive to heat-treated condition. The quenched material is the most brittle, the heavily aged material is least brittle (of the nitrogen-loaded materials) and the lightly aged material (7 days at 600 C) lies in the middle.

(4) The presence of sigma phase at the grain boundaries is not detrimental to ductility (compare Batches 7 and 10, 8 and 9) in nitrogen-loaded material.

Twinning, Cracking, and Hardness

In view of the possible connection between the promotion of twinning and the enhanced ductility of the Cr-35Re alloy, metallographic examinations were made on specimens of each contamination level and heat treatment in order to establish the effect of these variables on the prevalence of twinning. The specimens were all tested at -196 C under the same conditions. Because of the localized strain produced by a bend test, twins were heterogeneously distributed both longitudinally (primarily close to the fracture) and across a diameter. Furthermore, some of the tested specimens had bent to a slight extent prior to failure while others had not. However, Table 3 lists the specimens examined and provides a quantitative description of the extent of twinning in each. The specimens are described in order of decreasing prevalence of twinning. Table 3 also lists the extent of grain boundary cracking and values of room temperature hardness. The following experimental conclusions can be drawn from Table 3.

(1) Nonloaded material twins more than loaded material of a similar grain size.* However this is due at least in part to greater bending in the former specimens.

(2) In the nonloaded specimens, quenched material twins more than aged after similar amounts of bending.

*It is generally found that coarse-grained material twins more readily, that is at lower stresses and/or higher temperatures, than does fine-grained material. Tests to be described in the final report show that this holds true for Cr-35Re.

TABLE 2. SUMMARY OF TEST DATA

Batch	Test	Test Temp, C	Angle Of Bend, degrees	Proportional Limit Load, lb	Wire Diameter, d, mils	$\frac{0.175''L}{d^3}$, psi
6	1	30	~ 5	---	37	---
3	2	30	75	---	26.5	---
4	3	30	~ 10	---	26.5	---
1	4	30	90	---	26.5	---
5	5	30	40	---	26.5	---
2	6	30	90	---	26.5	---
3	7	-196	15	---	26.5	---
1	8	-196	--	---	26.5	---
1	9	-196	~ 10	---	26.5	---
2	10	-196	~ 10	---	26.5	---
3	11	- 78	90	---	26.5	---
1	12	- 78	90	---	26.5	---
2	13	- 78	90	---	26.5	---
3	14	-196	~ 5	---	26.5	---
1	15	-196	20	---	26.5	---
2	16	-196	~ 10	---	26.5	---
4	17	108	45	---	26.5	---
6	18	100	25	---	26.5	---
5	19	108	60	---	26.5	---
4	20	156	80	---	26.5	---
4	21	128	35	---	26.5	---
5	22	111	70	---	26.5	---
7	23	30	60	7	24.3	85,000
7	24	30	105	---	24.3	---
7	25	- 78	40	---	24.3	---
7	26	- 78	45	4	24.3	49,000
7	27	-196	~ 5	6	24.3	73,000
7	28	-196	10	7	24.3	85,000
8	29	-196	< 5	10	24.3	122,000

TABLE 2. (Continued)

Batch	Test	Test Temp, C	Angle Of Bend, degrees	Proportional Limit Load, lb	Wire Diameter, d, mils	$\frac{0.175"L}{d^3}$, psi
8	30	30	30	6	24.3	73,000
5	31	-196	~ 10	11	26.5	103,000
4	32	-196	~ 10	---	26.5	---
6	33	-196	~ 10	---	37.0	---
4	34	-196	~ 10	10	26.5	94,000
4	35	-196	~ 10	9	26.5	85,000
8	36	30	45	9	24.3	110,000
7	37	30	120	7	24.3	85,000
8	38	30	30	< 7	24.3	<85,000
7	39	30	110	6	24.3	73,000
8	40	125	110	7	24.3	85,000
8	41	85	30-35	6	24.3	73,000
7	42	- 78	60	6	24.3	73,000
7	43	- 78	50	8	24.3	95,000
10	44	30	80	20	37.0	69,000
9	45	30	~ 10	19	37.0	66,000
9	46	95	20	30	37.0	103,000
9	47	140	20	29	37.0	100,000
9	48	170	100	17	37.0	59,000
10	49	- 78	20	22	37.0	76,000
10	50	- 45	55	20	37.0	69,000
3	51	30	102	10.5	28.8	77,000
3	52	30	108	11	28.8	81,000
3	53	-196	15	14.5	29.0	104,000
3	54	-196	20	12	29.5	82,000
3	55	-196	15	16	29.5	109,000
3	56	-196	20	14	30.0	91,000
3	57	-196	25	14	30.0	91,000
3	58	- 78	110	13	30.5	80,000
3	59	- 78	120	13	30.0	85,000
3	60	110	90	11	30.2	71,000

TABLE 2. (Continued)

Batch	Test	Test Temp, C	Angle Of Bend, degrees	Proportional Limit Load, lb	Wire Diameter, d, mils	$\frac{0.175"L}{d^3}$, psi
3	61	130	65	11.5	30.0	75,000
3	62	130	125	11	30.2	71,000
-	63	---	---	---	----	---
8	64	30	35	6.5	25.5	69,000
8	65	30	25	6	25.8	61,000
7	66	30	122	6	25.0	67,000
9	67	30	10	20	38.0	64,000
10	68	30	120	21	37.8	68,000
10	69	30	60	24	37.8	78,000
10	70	- 78	25	21	37.0	73,000
9	71	- 78	10	21	37.5	70,000
9	74	-196	< 5	26.5	37.5	88,000
10	75	-196	< 5	24.5	37.5	81,500

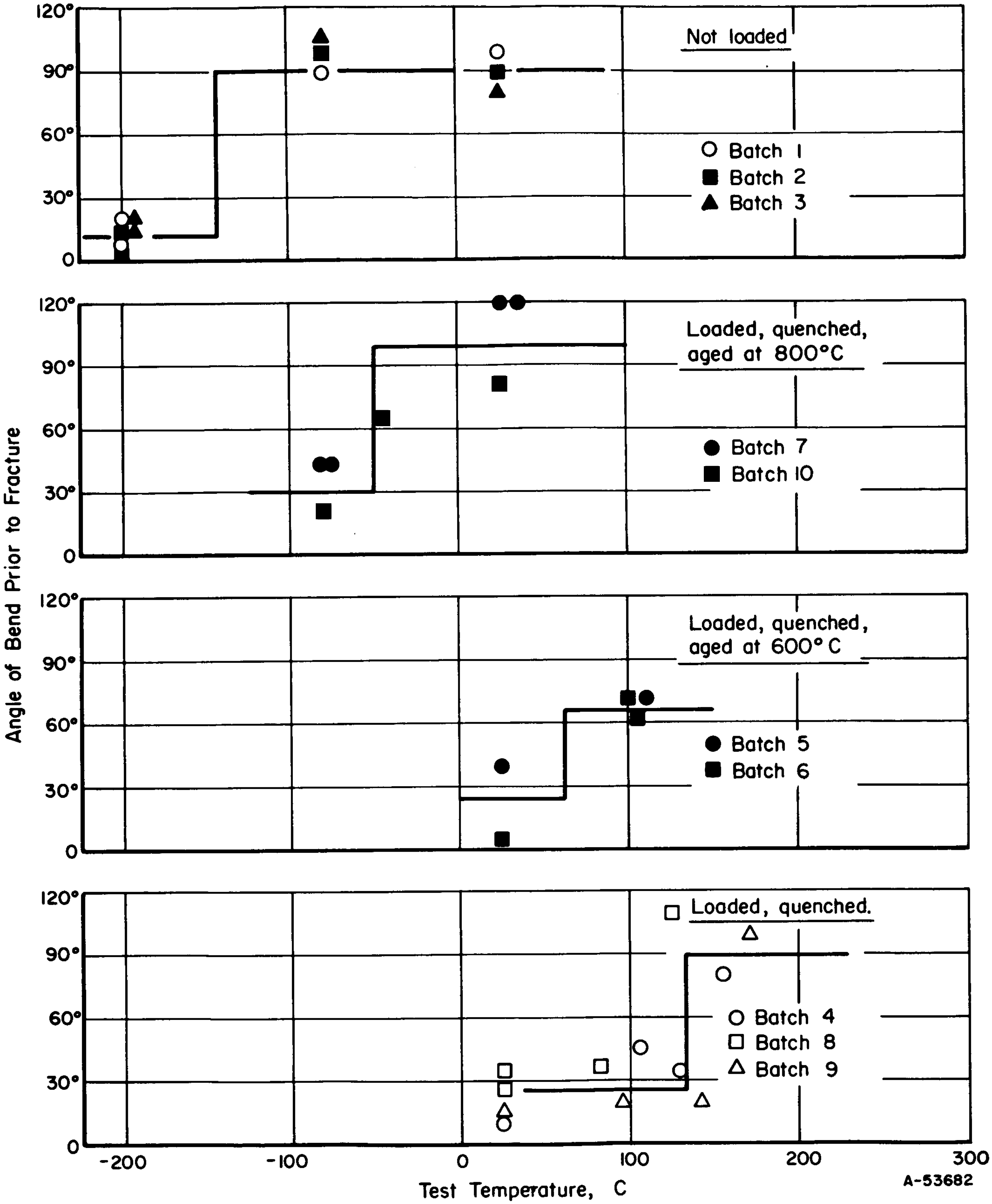


FIGURE 3. 60° BEND TRANSITION TEMPERATURES FOR Cr-35Re WIRES IN VARIOUS CONDITIONS, THREE-POINT BENDING

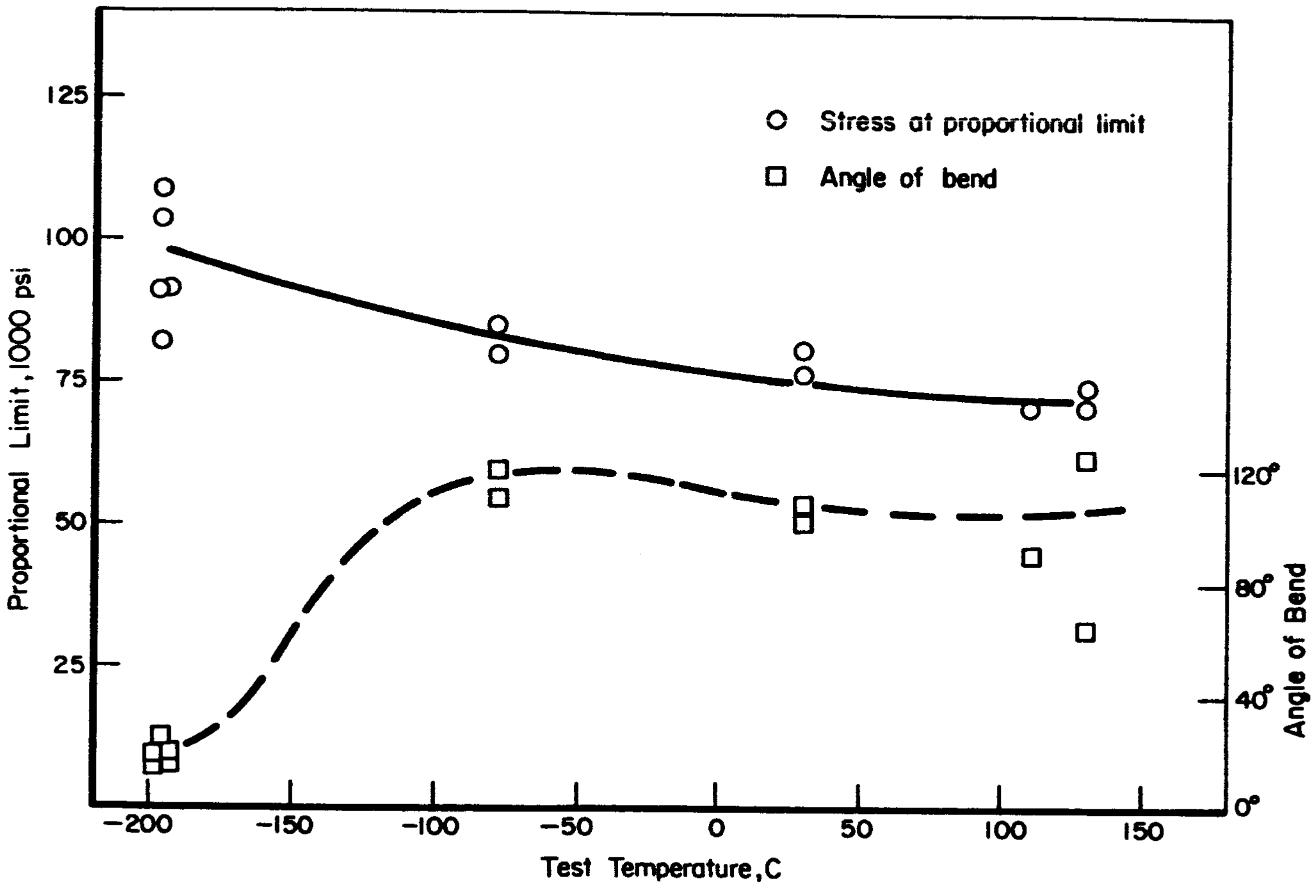


FIGURE 4. PROPORTIONAL-LIMIT AND ANGLE-OF-BEND DATA FOR BATCH 3 MATERIAL (Tests 51-62)

TABLE 3. SUMMARY OF METALLOGRAPHIC OBSERVATIONS MADE ON BEND SPECIMENS TESTED AT -196 C

Batch	Condition	No. of Twins Visible on Cross Section, N	No. of Grain-Boundary Cracks, n	$\frac{n}{N}$	Average Grain Size, mms(a)	Comments	Hardness at Room Temperature(b)	Average No. of Twins Surrounding Room-Temperature Hardness Impression(e)
1	Unloaded, quenched	1600	5	.003	.03	Bent ~10°	378.9	30
2	Unloaded, aged 600 C	1200	6	.005	.03	Bent ~10°	367.8	17
3	Unloaded, aged 600 C	1000	5	.005	.02	Bent ~10°	356.6	2
10	Loaded, aged 800 C	500	4	.008	.06	Bent ~ 5°	389.3	9
9	Loaded, quenched	150	5	.033	.06	No bending apparent	418.7	41
4	Loaded, quenched	150	12	.08	.04	No bending apparent	414.3	54
5	Loaded, aged 600 C	100	5	.05	.04	No bending apparent	392.4	3
6	Loaded, aged 600 C	100	6	.06	.04	No bending apparent	362.5	7

(a) Mean linear intercept.
(b) Knoop, 100-g load.
(c) Vickers 5-kg load.

(3) In the loaded specimens of .04-mm grain size, quenched material twins more than aged. (None of the specimens bent significantly.) In specimens of .06-mm grain size, this trend is reversed, but the sample from Batch 10 bent to a greater extent than did the one from Batch 9, which invalidates the comparison.

(4) Although the nonloaded specimens twinned to a much greater extent than the loaded, the extent of grain-boundary cracking was about the same as the loaded and aged, and less than the loaded and quenched.

(5) As can be seen from Table 4, the transition temperature of this material increases as the room-temperature hardness increases.

Temperature Variation of Proportional Limit

The measurements of the proportional limit stress summarized in Table 2 are not sufficiently reproducible that one determination at one temperature can be assumed to be meaningful. Thus, the hardness measurements given in Table 3 give a better measure of strength (due to a much greater statistical sample used to produce one hardness figure) than do the stress measurements. The major problem causing scatter in the stress determination was the imperfect surface of the test wires, even after electropolishing. However, sufficient material of Batch 3 was available to choose a number of test samples with a good surface for tests in bending over a range of temperatures. Accordingly, the temperature variation of the proportional limit was determined and the results are summarized in Figure 4, together with the bend data generated in these tests. It can be seen that the proportional limit is not strongly temperature dependent.

Metallography and Fractography

Under the optical microscope it was seen that all the fracture surfaces were made up of exposed grain boundaries showing twin traces. Specimens that failed at low temperatures contained many twin traces on each boundary, whereas those that failed at higher temperatures showed twins only occasionally.

There was no visible difference between the exposed grain boundaries of the quenched and aged conditions of the nonloaded material, nor between the loaded-quenched and that aged at 600 C. However, on aging the loaded and quenched material at 800 C, a pronounced grain-boundary precipitate was formed which was obvious on the exposed fracture surface. Figure 5 shows a comparison of electron replicas of the fracture surfaces with and without this boundary film, and a corresponding optical metallograph is shown in Figure 6. The grain-boundary film was identified by electron-diffraction patterns taken both from extraction replicas and transmission through thin films prepared from the material. It was shown to be Cr_2N.

An example of twin-induced grain boundary cracking is shown in Figure 7.

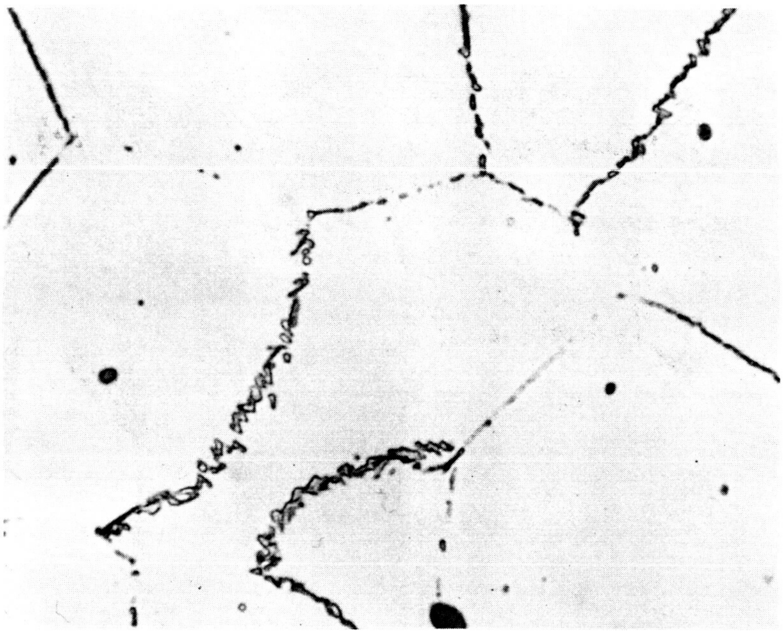
TABLE 4. COMPARISON OF ROOM-TEMPERATURE HARDNESS AND BEND-TRANSITION TEMPERATURE

Condition	Hardness	Transition Temperature, C	n/N
Unloaded, quenched	379 (Batch 1)	~ -140	.003
Unloaded, aged 600 C	368 (Batch 2) 357 (Batch 3)	~ -140	.005
Loaded, aged 800 C	389 (Batch 10)	~ - 50	.008
Loaded, aged 600 C	392 (Batch 5)	~ + 60	.05
Loaded, quenched	414 (Batch 4) 419 (Batch 9)	~ +130	.04 .03

a. Loaded-Quenched Wire (Batch 9)

b. Loaded-Aged Wire (Batch 10)

FIGURE 5. ELECTRON REPLICA FRACTOGRAPHS OF EXPOSED GRAIN BOUNDARIES



1500X 14979

Metallographic Section of Specimen in Figure 5b

FIGURE 6. GRAIN-BOUNDARY PRECIPITATES IN BATCH 10 WIRE

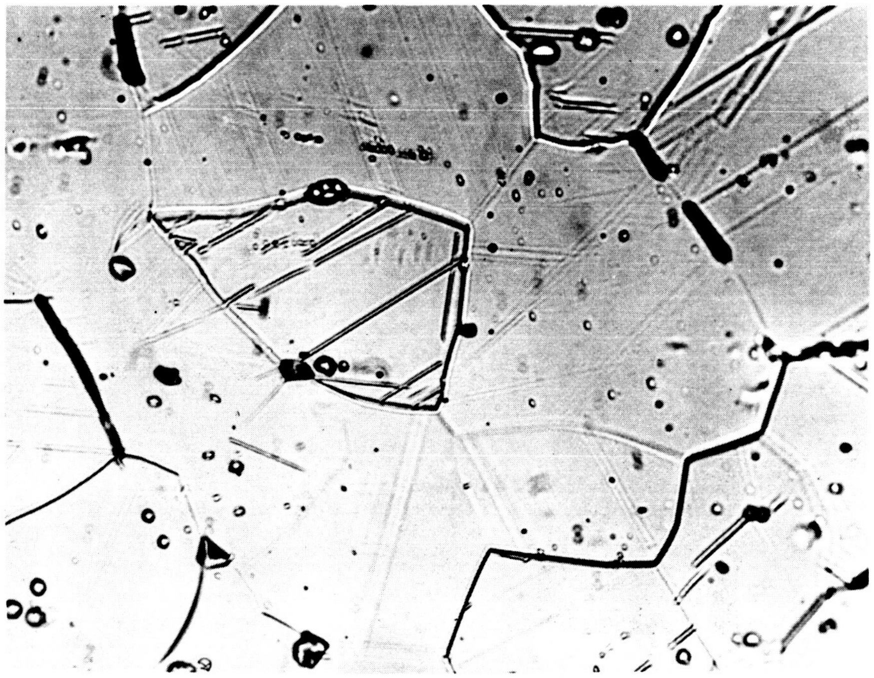


FIGURE 7. TWIN-INDUCED GRAIN-BOUNDARY CRACKS IN BATCH 4 MATERIAL TESTED AT −196 C

DISCUSSION

It is clear from Figure 3 that Cr-35Re is just as susceptible to embrittlement by nitrogen as is unalloyed chromium. There are, however, major differences in the two cases. Whereas chromium fails by cleavage, Cr-35Re fails by almost 100 percent grain-boundary parting. In addition, while the quenched chromium was more ductile than the aged, the reverse is true for the alloy.

The experimental results permit the following conclusions to be drawn concerning the mechanism of failure in Cr-35Re.

As in all fracture situations, the mechanism is best considered in two stages, initiation and propagation. However, in the present case where cracks are initiated at and propagate along grain boundaries, it may well be that similar considerations apply to both aspects. To summarize the pertinent fracture observations, the unloaded specimens were more ductile than the loaded and aged, which in turn were more ductile than the loaded and quenched. Metallography showed that in all the specimens tested at -196 C twin-induced grain-boundary cracks were present. The ratio n/N however in Table 3 shows that grain-boundary cracks are much less easily induced in the unloaded than in the loaded material. The implication of this last observation is that even at low temperatures, sufficient stress-relieving slip is possible in either one or both adjoining grains of the unloaded specimens such that the stress concentration produced as a twin hits the boundary can be relieved by plastic flow rather than cracking. Plastic flow is sufficiently difficult at -196 C, however, that enough cracks are generated in both loaded and unloaded specimens for failure to occur.

Since similar considerations probably apply to the propagation of grain-boundary cracks as to initiation, the pronounced effect of impurity level and heat treatment can be explained purely in terms of the effect of these variables on the matrix strength, together with the rather small dependence of strength on temperature shown in Figure 4.

The proposed mechanism is shown schematically in Figure 8, where the mechanism has been simplified so that the fracture stress has been considered equivalent to the twinning stress, whereas in fact even in the presence of twinning considerable bending occurs until presumably the stress reaches a critical stress, or sufficient boundaries have cracked, to cause failure. The curves of Figure 8 have been drawn to the form shown experimentally to exist (See Figure 4). The upper curve represents loaded and quenched, the center curve loaded and aged, and the lower curve nonloaded material. The room-temperature hardness results summarized in Table 3 show that such differences in strength exist at room temperature. The transition temperature for material in a given condition is then considered to be that temperature above which slip occurs more easily than twinning, since below this temperature slip cannot easily occur to prevent the propagation of any grain-boundary cracks initiated by twins. These ideas receive support from two other experimental observations. First, as can be seen from Table 3, twinning produced round hardness impressions made at room temperature is very much heavier in the loaded and quenched than in either the loaded and aged or the nonloaded material. Thus twinning persists to higher temperatures in the stronger material. Second, the observation in loaded and quenched samples of twin traces crossing the grain boundary after fracture at temperatures >100 C again suggests that twin-induced grain-boundary cracking leads to failure where slip is difficult.

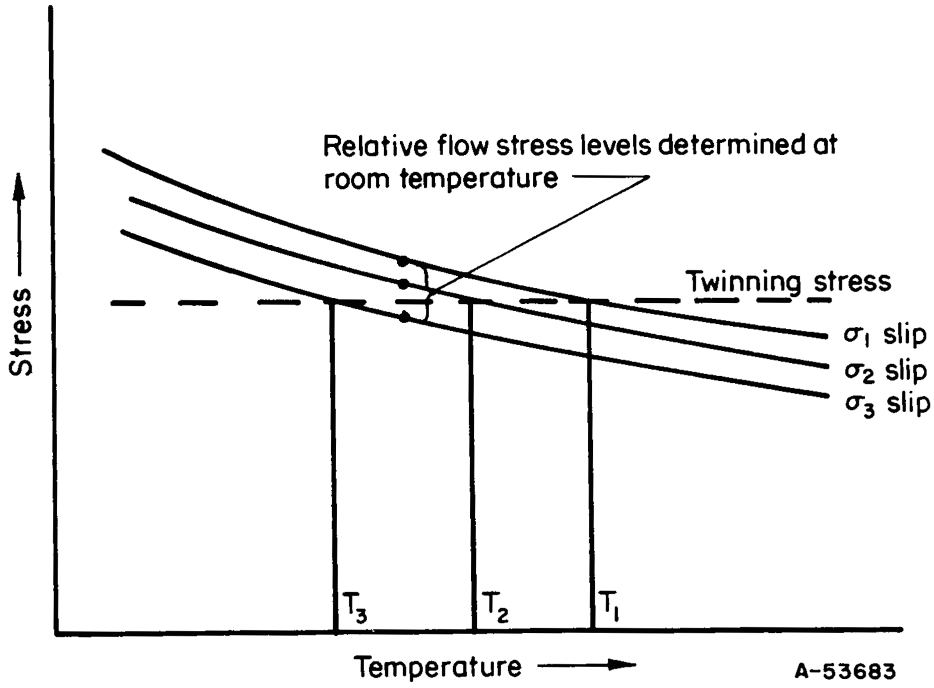


FIGURE 8. SCHEMATIC OF THE RELATIONSHIP BETWEEN SLIP, TWINNING, AND TRANSITION TEMPERATURE FOR TWIN-INDUCED FRACTURE

One other possible effect of impurity level and heat treatment is on the intrinsic "strength" of the grain boundary in terms of its resistance to cracking when impacted by a twin. One way in which this could change would be through the effect of quenching stresses. This is not likely to be important in the present case since, for the nonloaded material, the quenched and aged specimen had similar transition temperatures. The other way in which impurities and heat treatment could affect the grain boundaries is in terms of their chemical composition. In this respect, three observations are important. First, it was known from internal-friction measurements that, even in the loaded specimens, all the nitrogen was in solution after quenching. Thus the grain boundary composition should be the same as for the nonloaded specimen and yet the transition temperature was >250 C higher. Second, on aging the quenched material at 800 C a thick grain-boundary film of Cr_2N was formed, which would be expected to make the boundary more susceptible to brittle failure rather than less. From the present tests however, it does not appear that such a film greatly affects the properties of the grain boundary one way or the other. Finally, the sigma phase present at the boundaries in material from Batches 7 and 8 again did not seriouly affect the transition temperatures. It would thus seem that the properties of the matrix rather than the boundary control the transition temperature.

In summary it appears that the change in the bend-transition temperature of Cr-35Re wire produced by changes in impurity level and heat treatment reflect primarily the effect of these variables on the deformation response of the matrix.

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