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FINAL REPORT

on

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

to

NATIONAL AERONAUTICS
AND SPACE ADMINISTRATION

August 31, 1966

by

A. Gilbert, M. J. Klein, and J. W. Edington
Metal Science Group

BATTELLE MEMORIAL INSTITUTE
Columbus Laboratories
505 King Avenue
Columbus, Ohio 43201

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by

A. Gilbert, M. J. Klein, and J. W. Edington

GENERAL INTRODUCTION

During the past year of this research program, further experimental work has been carried out to delineate certain aspects of the rhenium alloying effect as an aid to interpreting the mechanisms by which rhenium additions promote ductility in chromium. As has been the procedure in previous yearly reports, individual segments of work will be described in separate sections.

A general discussion of the results and their implications as to the mechanisms of the rhenium alloying effect will be given in a final section. Since this is a final report on the contract, that section will also discuss pertinent experimental results described in previous yearly reports or in the literature the better to summarize the present status of our understanding of the effect.

The report will consist of the following sections:

Section I. The Effect of Quenching on the Ductile-Brittle Bend-Transition Temperature of Chromium Wire

Section II. The Effect of Quenching on the Ductile-Brittle Bend-Transition Temperature of Cr-35Re Wire

Section III. The Effect of Temperature on the Hardness of Cr-Re Alloys in the Range 0-40 At. % Re

Section IV. Activation Volume Analysis for Cr and Cr-35Re

Section V. The Effect of Rhenium on the Strain-Rate Sensitivity of Chromium at Room Temperature

Section VI. General Discussion – The Rhenium Alloying Effect.

In addition one other piece of research was begun but, because of the demands on time and funding made by other phases of the program, was not completed. In view of the noncompletion of this work, it will not be included as a section in the main body of this report. Several interesting observations were made, however, which will be described in the Appendix, Quenched-In Defects in Mo-35Re.

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N67-15834

SECTION I. THE EFFECT OF QUENCHING ON THE DUCTILE-BRITTLE BEND-TRANSITION TEMPERATURE OF CHROMIUM WIRE

by

A. Gilbert and M. J. Klein

Introduction

Although it is known that, in general, the ductile-brittle transition temperature of the Group VI-A refractory metals increases as the interstitial content increases(1)*, it is difficult to distinguish effects due to interstitials in solution from those due to the presence of second-phase interstitial compounds. The problem of making this distinction has proved to be particularly difficult for Cr, which has very low equilibrium solubilities for the common interstitials(1) and, in the case of nitrogen, very rapid precipitation kinetics due to high interstitial diffusivities(2). In view of these difficulties, it is not safe to assume that a "quenched" specimen of Cr contains a significantly greater fraction of its total impurities in solution than does a "slow-cooled" specimen.

In order to make a meaningful comparison of the mechanical properties of quenched and slow-cooled material, some sensitive measure is needed of the amount of interstitial retained in solution compared to that present as second phase. The purpose of these experiments was to make such a comparison on Cr that had been quenched at a very high rate, using internal friction as an indicator of the amount of nitrogen in solution. Nitrogen has been considered to be the interstitial primarily responsible for the brittleness of Cr.

Experimental Work

Crystals of iodide chromium were compacted, hot-extruded, swaged, and then centerless ground to produce a rod of 1/10-inch diameter. The rod was then warm-drawn to wire .017 inch in diameter, the material on which the experiments were conducted. A 10-inch length was annealed in a quartz capsule containing argon for 1 hour at 1150 C, and was directly quenched into water (breaking the capsule) from 1000 C. Previously, a Cr wire .037 inch in diameter had been used in experiments to determine the actual cooling rate under these conditions.(3) From the output of a thermocouple spot-welded to the specimen surface (recorded using a cathode-ray oscilloscope), the surface-cooling rate was found to be ~9000 C/second. It is, therefore, reasonable to expect that the cooling rate for the present thinner wire was at least this high, and probably higher. The heat treatment produced a recrystallized structure containing approximately 40 grains in a cross-section area, and chemical analysis showed the wire to contain 50 ppm oxygen, 2 ppm hydrogen, 15 ppm carbon, and nitrogen in the range 10-15 ppm.

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*References are given on page 60.

A 152 C aging curve was obtained in one-half of the quenched wire, taking intermittent internal-friction readings (0.7 cycles per second). After 3000 minutes, the internal-friction peak was found to have decreased to the background level, indicating that the nitrogen retained in supersaturated solid solution by the high quenching rate(3) had fully aged out. Specimens were cut from the half of the wire still in the quenched state, and also from the fully aged material, for comparative bend tests. Because of the relatively small length of wire available, a 3-point bend jig was constructed, which was capable of testing specimens greater in length than 5/16 inch. The specimens were electropolished and tested at 0.1 inch/minute crosshead speed on a table-model Instron, elevated temperatures being obtained in an electrically heated silicone oil bath.

Experimental Results

The aging curve for the Cr wire, represented by the decreasing height of the internal-friction peak with increased aging time, is presented in Figure 1. The conversion to ppm nitrogen is obtained using Reference 3.

Bend-test results for quenched and for quenched and aged Cr wire, corresponding to the beginning and end, respectively, of the curve of Figure 1 are listed in Table 1. As has been seen previously for Cr(4), it was found that the transition from ductile to brittle behavior was extremely sharp, in that a specimen either failed in a completely brittle manner (described as brittle in Table 1) or bent to the maximum extent permitted by the jig (ductile in Table 1). The lowest temperature at which a quenched specimen was ductile was 74 C below the lowest temperature at which an aged specimen was ductile, and the highest temperature at which a quenched specimen was brittle was 97 C below the equivalent temperature for aged material. Thus, regardless of how the ductile-to-brittle transition is defined, the quenched material has a transition temperature between 74 and 98 C below that for aged material. Ductile specimens exhibited yield drops on the load-time curve that were more pronounced for quenched than for aged specimens to the extent shown in Table 1.

Discussion

Previous investigations(5-7) into the effect of cooling rate on the ductile-brittle transition temperature of Cr have shown "quenched" material to be more brittle than "furnace-cooled" material, in contrast to the present results. Recent experimental results, however, suggest that the quenching rates used in previous work have been insufficient to maintain <u>all</u> the nitrogen in solution. This conclusion is based on the data quoted in Table 2(8) which shows that quenching rates greater than 1000 C/second are necessary to retain even 20-30 ppm in solution. The larger specimens used in previous investigations(5-7) together with use of oil as a quenching medium(5, 7) could not have permitted such a high cooling rate. Furthermore, previous work has been performed on Cr containing higher nitrogen concentrations which, aging studies have shown(3, 9), increases the kinetics of nitride precipitation, and correspondingly increases the critical cooling rate necessary to maintain the nitrogen in solution. In the light of these considerations, it seems likely that the quenching rates used previously served primarily to modify the morphology and distribution of the nitride phase rather than to maintain all the nitrogen in solution. This certainly seemed to be the case in earlier work by one

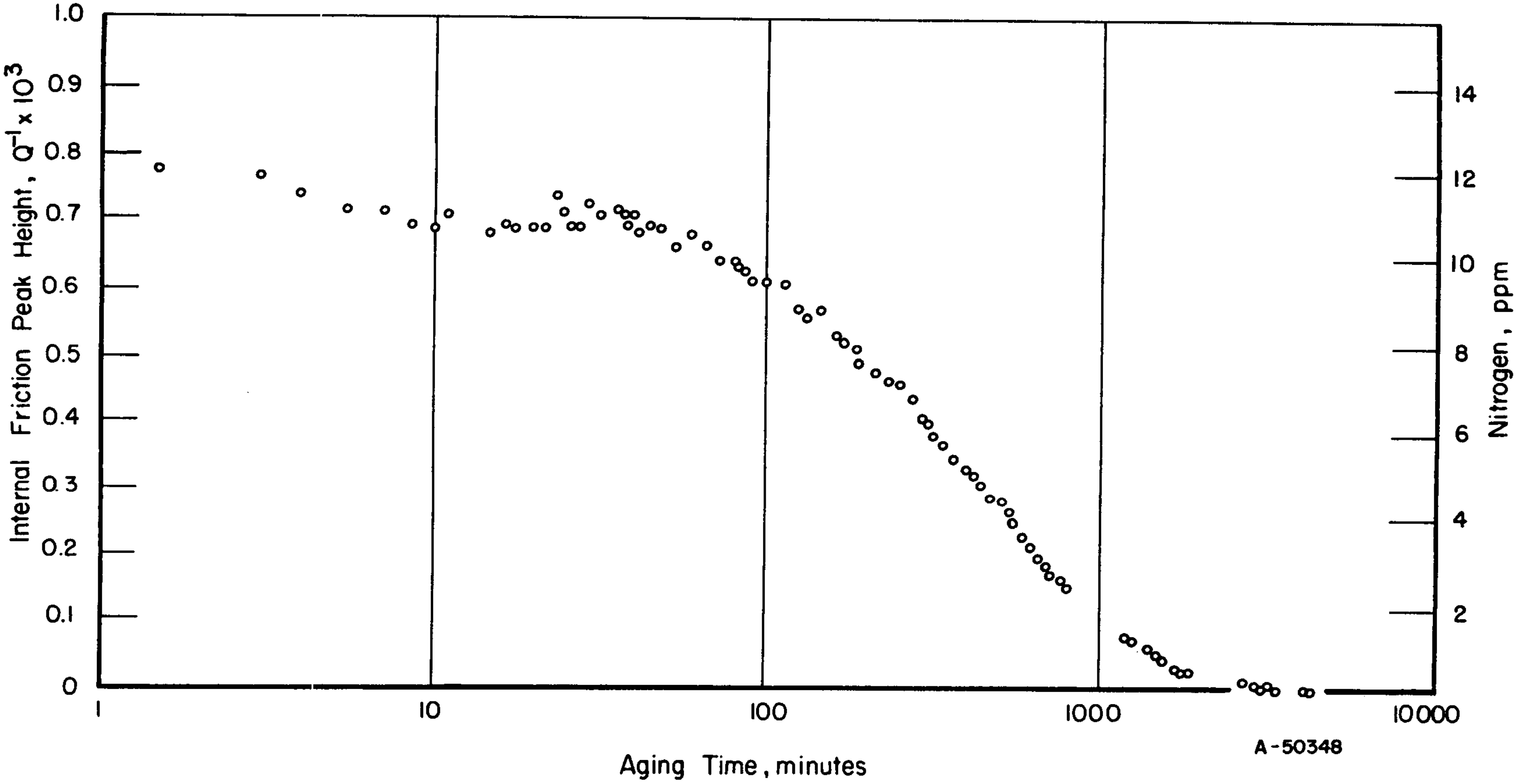

FIGURE 1. CHANGE IN HEIGHT OF THE NITROGEN INTERNAL FRICTION PEAK AND SOLUBLE NITROGEN CONCENTRATION FOR CHROMIUM AGED AT 152 C

TABLE 1. BEND-TRANSITION BEHAVIOR OF .017-INCH-DIAMETER Cr WIRE

Specimen	Test Temp., C	Bend Behavior	Upper Yield-Point Load, lb	Lower Yield-Point Load, lb	Yield Drop, percent	Brittle Fracture Load, lb
			Quenched Wire			
1	30	Brittle	Preliminary test; no load recorded			--
2	53	"	--	--	--	1.56
3	71	Ductile	1.08	0.84	29	--
4	85	Brittle	--	--	--	1.12
5	94	Ductile	1.07	0.86	24	--
6	98	Brittle	--	--	--	1.07
7	105	Ductile	0.96	0.72	33	--
8	113	"	1.30	1.14	12	--
9	129	"	1.52	1.32	15	--
10	142	"	1.03	0.75	37	--
11	164	"	1.12	0.98	14	--
			Quenched and Aged Wire			
12	30	Brittle	Preliminary test; no load recorded			--
13	105	"	--	--	--	1.10
14	128	"	--	--	--	1.30
15	145	Ductile	0.87	0.84	3	--
16	166	Brittle	--	--	--	1.36
17	192	Ductile	0.72	0.64	12	--
18	195	Brittle	--	--	--	0.71
19	225	Ductile	1.09	0.91	20	--
20	260	"	0.89	0.78	15	--

TABLE 2. NITROGEN RETAINED IN SOLUTION IN CHROMIUM AS A FUNCTION OF COOLING RATE

Cooling Times and Approximate Cooling Rates From 1000 to 100 C		Nitrogen, ppm
Time, sec	Rate, C/sec	
0.1	~9000	26
25	40	6
200	5	2
1,800	0.5	<1
10,800	0.09	--

of the present authors(10) in which quenched tensile specimens gave every indication of being dispersion hardened by a much finer precipitate than did slow-cooled specimens.

In the present work, however, the data in Figure 1, together with the nitrogen analysis, show that all the nitrogen present in the material is in solid solution as a result of the quench, and that after aging for times greater than 3000 minutes it is largely present as a precipitated phase in accordance with the predictions of equilibrium-solubility data(1). Thus, it appears that nitrogen completely in solution is less detrimental to ductility (see Table 1) than when present as a second phase. However, reference to earlier work(5-7) suggests that, given the presence of a second phase in both quenched and furnace-cooled Cr, a greater concentration of nitrogen retained in solution by a higher cooling rate can lead to further embrittlement.

SECTION II: THE EFFECT OF QUENCHING ON THE DUCTILE-BRITTLE BEND-TRANSITION TEMPERATURE OF Cr-35Re WIRE

by

A. Gilbert and M. J. Klein

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.(10-12) 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 Re has been attributed to a modification of the interstitial distribution,(13) it is desirable to investigate the effect of impurities on the ductility of a high-Re 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 Cr 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 at.% Re ingots were prepared by arc-melting iodide chromium crystals with sintered Re 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.(3)

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*See Section I of this report.

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 3.

TABLE 3. 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

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 2. 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, 3-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.

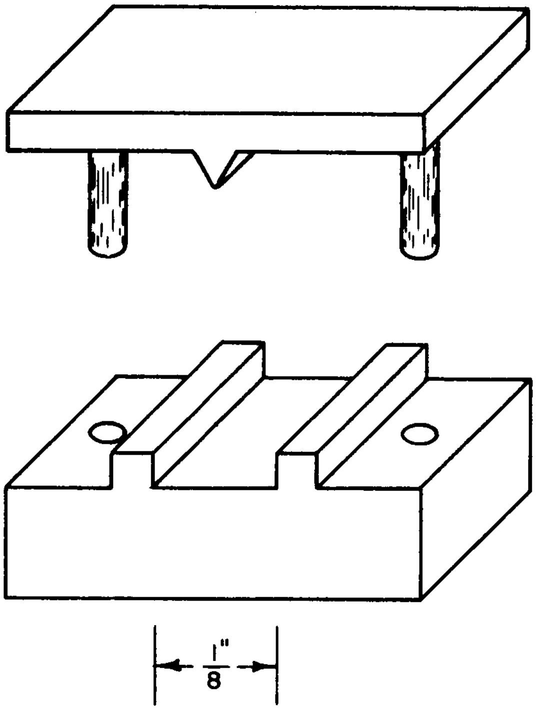

FIGURE 2. SCHEMATIC OF THE 3-POINT BEND JIG USED IN THESE TESTS

As-drawn 80-mil Mo 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 2 and the load at the proportional limit was measured as a function of diameter. The results are presented in Figure 3 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.

Experimental Results

Transition Temperatures

The bend data for Cr-35Re wire in various conditions is summarized in Table 4 and Figures 4 and 5. The important results are as follows:

(1) The nonnitrogen-loaded material is very much more ductile than the loaded (-150 C transition temperature compared with 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-treatment.
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.

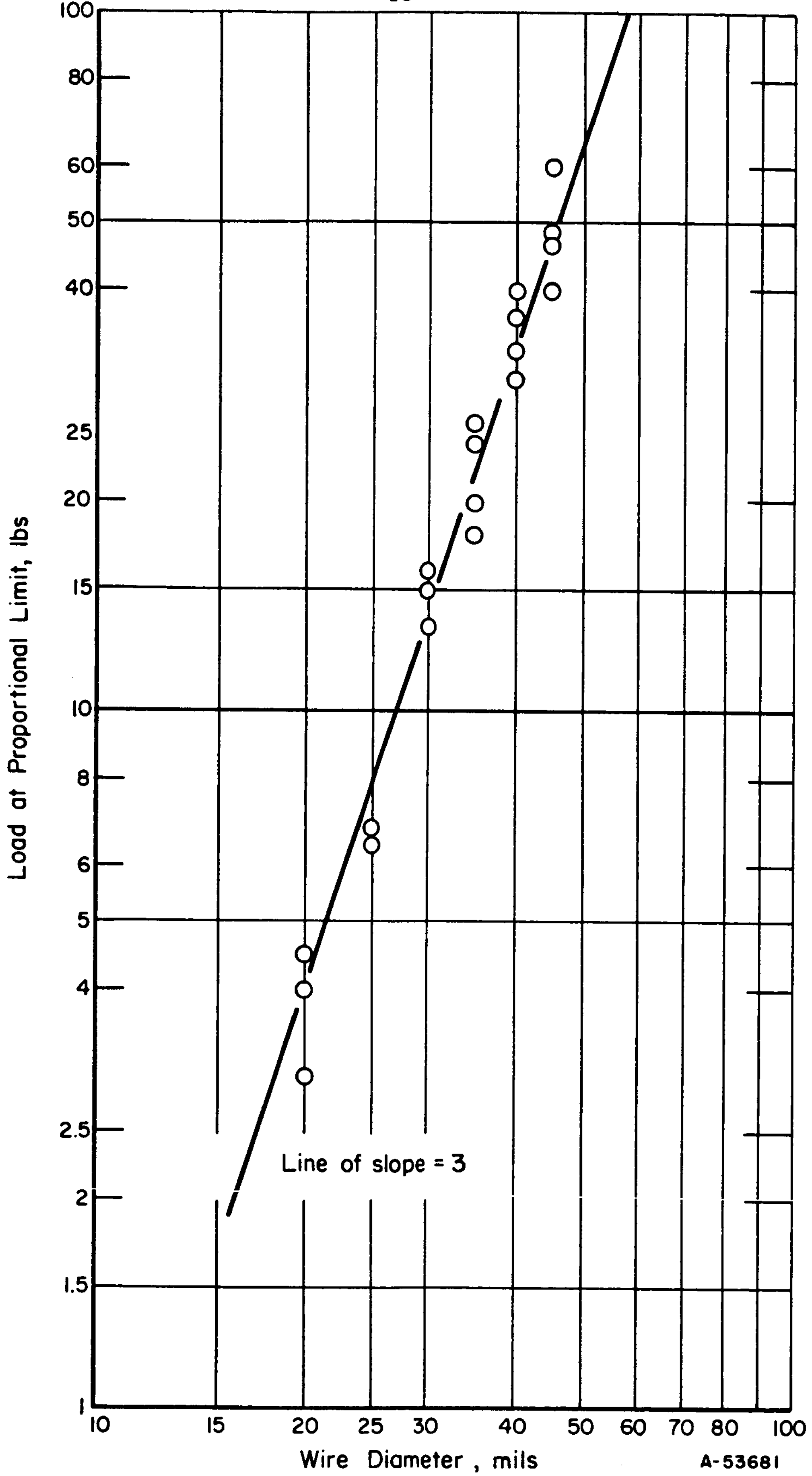

FIGURE 3. RELATIONSHIP BETWEEN DIAMETER AND LOAD AT THE PROPORTIONAL LIMIT FOR DRAWN Mo WIRE (USING THE BEND JIG OF FIGURE 2)

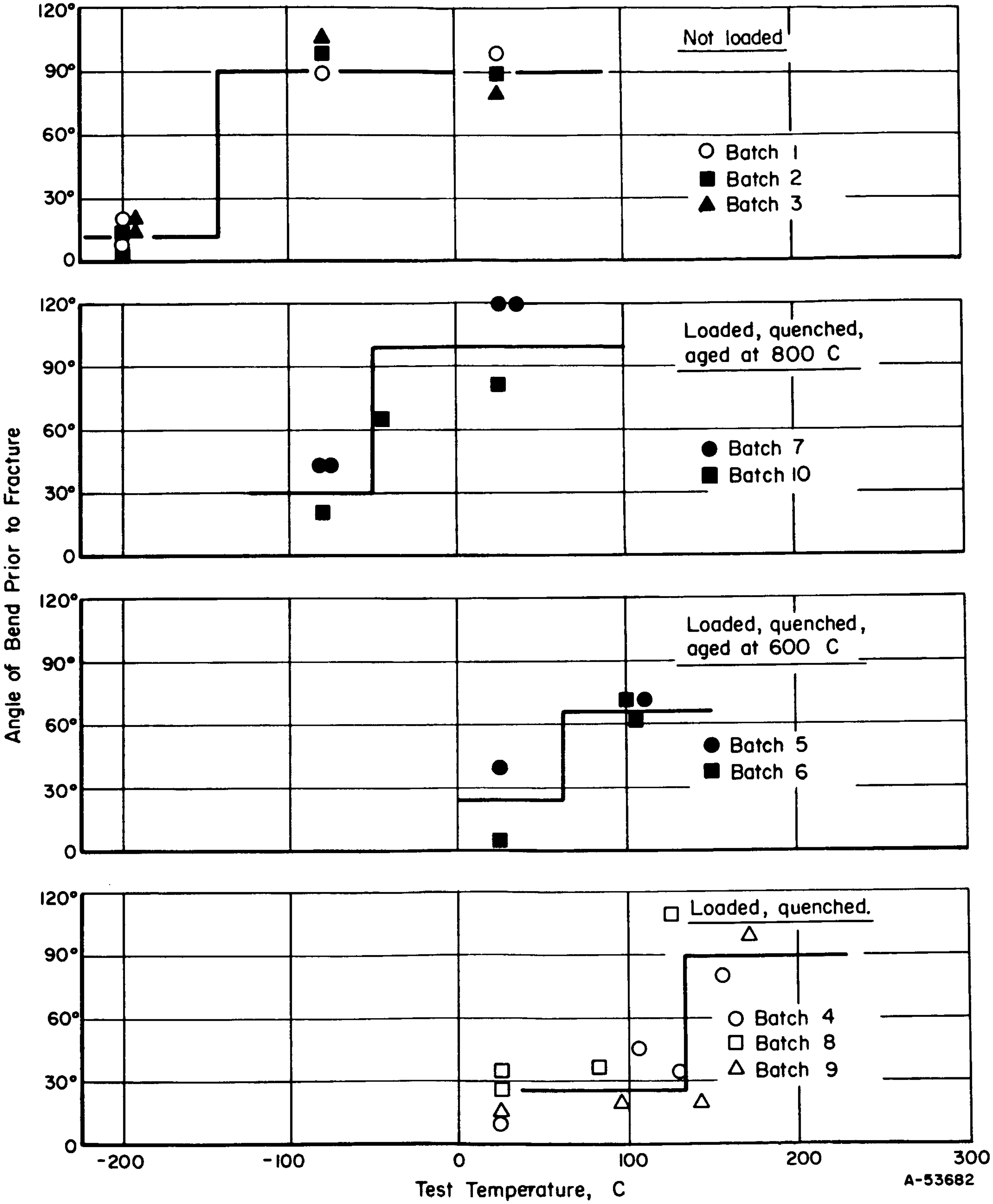

FIGURE 4. 60° BEND-TRANSITION TEMPERATURES FOR Cr-35Re WIRES IN VARIOUS CONDITIONS, 3-POINT BENDING

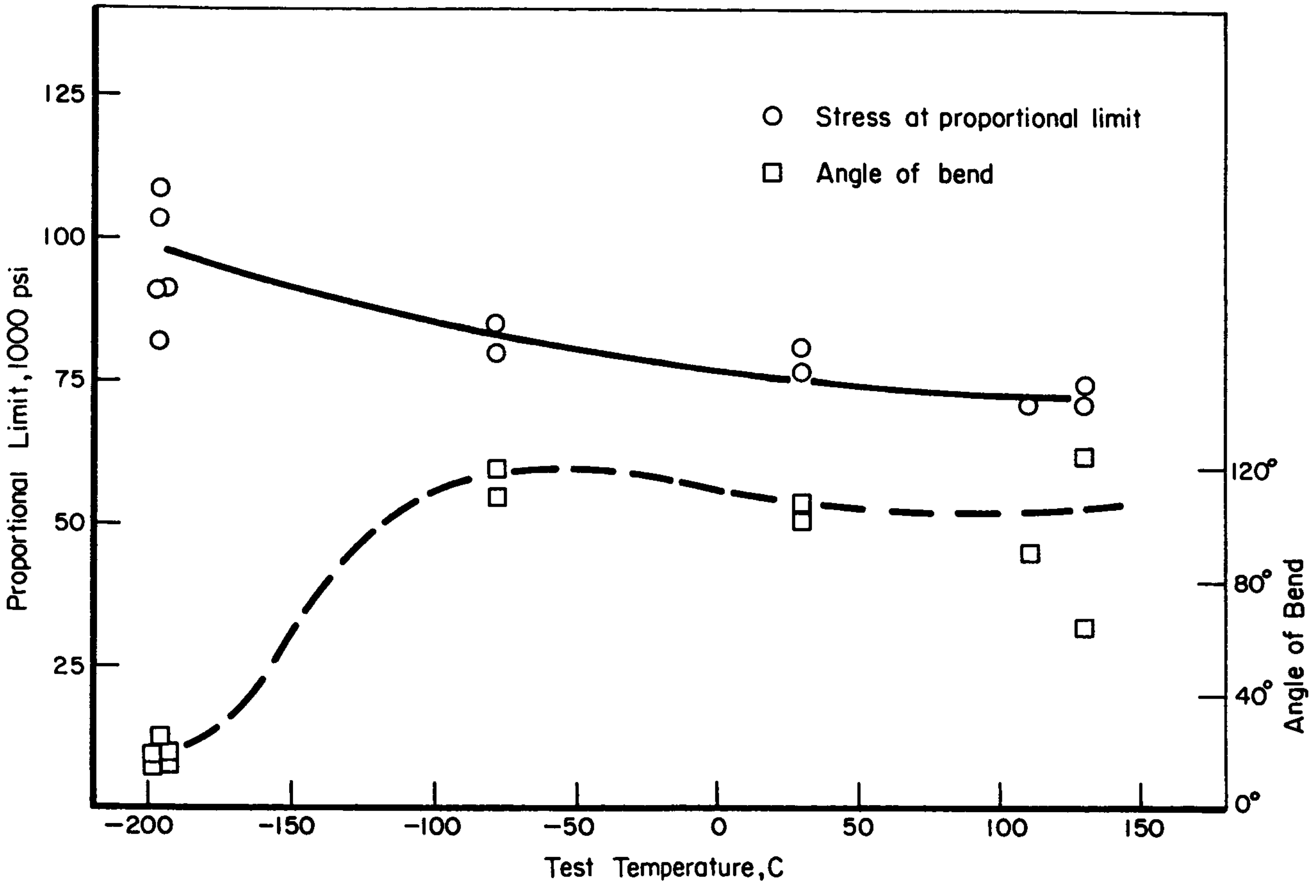

FIGURE 5. PROPORTIONAL-LIMIT AND ANGLE-OF-BEND DATA FOR BATCH 3 MATERIAL (TESTS 51-62)

TABLE 4. 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
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

TABLE 4. (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
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
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

TABLE 5. 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, mm[(a)]	Comments	Hardness at Room Temperature[(b)]	Average No. of Twins Surrounding Room-Temperature Hardness Impression[(c)]
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.

(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 5 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 5 also lists the extent of grain-boundary cracking and values of room-temperature hardness. The following experimental conclusions can be drawn from Table 5.

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

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

(3) In the loaded specimens of .04-mm grain size, quenched material twins more than aged material. 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 specimens, the extent of grain-boundary cracking was about the same as the loaded and aged specimens, and less than the loaded and quenched specimens.

(5) As can be seen from Table 6, the transition temperature of this material increases as the room-temperature hardness increases.

TABLE 6. 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)	~-140	.005
	357 (Batch 3)		
Loaded, aged 800 C	389 (Batch 10)	~ -50	.008
Loaded, aged 600 C	392 (Batch 5)	~ +60	.05
Loaded, quenched	414 (Batch 4)		.04
	419 (Batch 9)	~+130	.03

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*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 Section IV of this report show that this holds true for Cr-35Re.

Temperature Variation of Proportional Limit

The measurements of the proportional limit stress summarized in Table 4 are not sufficiently reproducible that one determination at one temperature can be assumed to be meaningful. Thus, the hardness measurements given in Table 5 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 5, 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 that was obvious on the exposed fracture surface. Figure 6 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 7. 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.

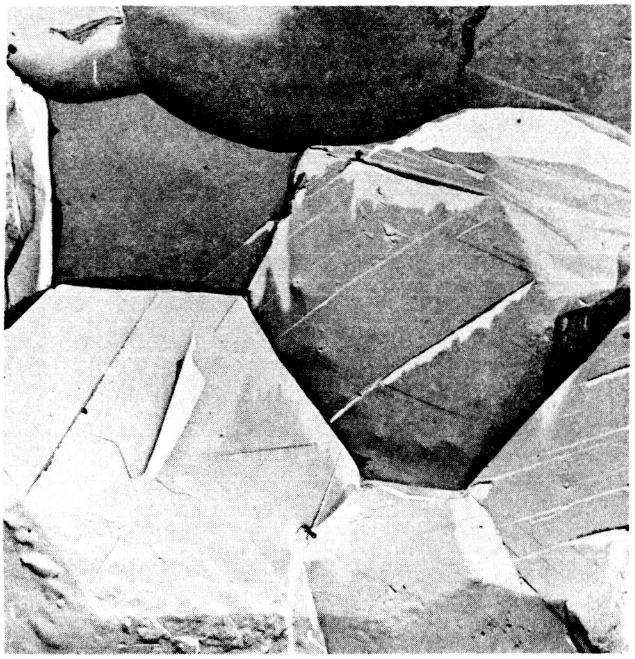
An example of twin-induced grain boundary cracking is shown in Figure 8.

Discussion

It is clear from Figure 4 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



a. Loaded-Quenched Wire (Batch 9)

b. Loaded-Aged Wire (Batch 10)

FIGURE 6. ELECTRON REPLICA FRACTOGRAPHS OF EXPOSED GRAIN BOUNDARIES

1500X 14979

Metallographic Section of Specimen in Figure 6b

FIGURE 7. GRAIN-BOUNDARY PRECIPITATES IN BATCH 10 WIRE

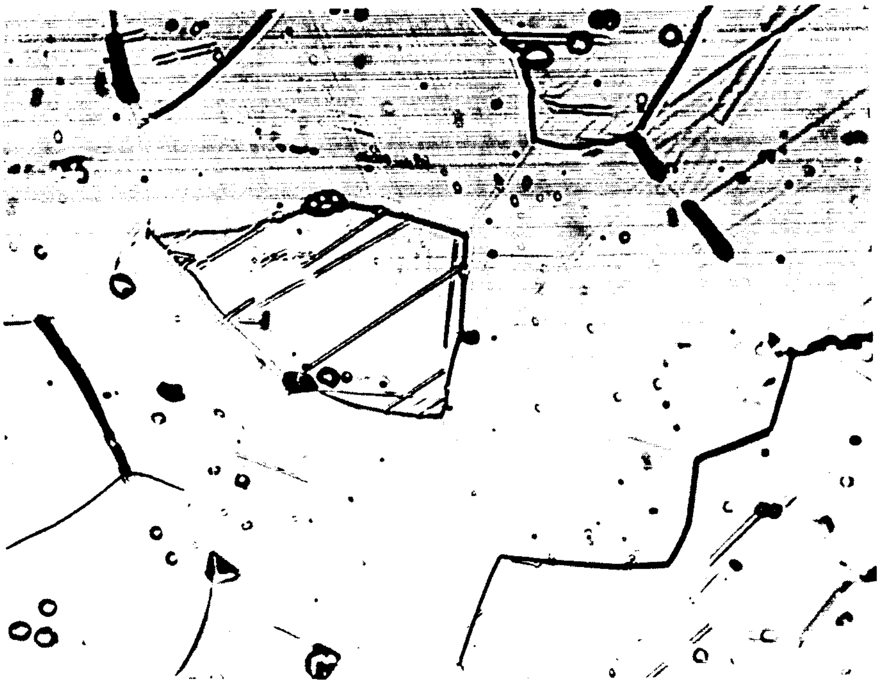


FIGURE 8. TWIN-INDUCED GRAIN-BOUNDARY CRACKS IN BATCH 4 MATERIAL TESTED AT -196 C

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 5 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 5.

The proposed mechanism is shown schematically in Figure 9, where the mechanism has been simplified so that the fracture stress has been considered equivalent

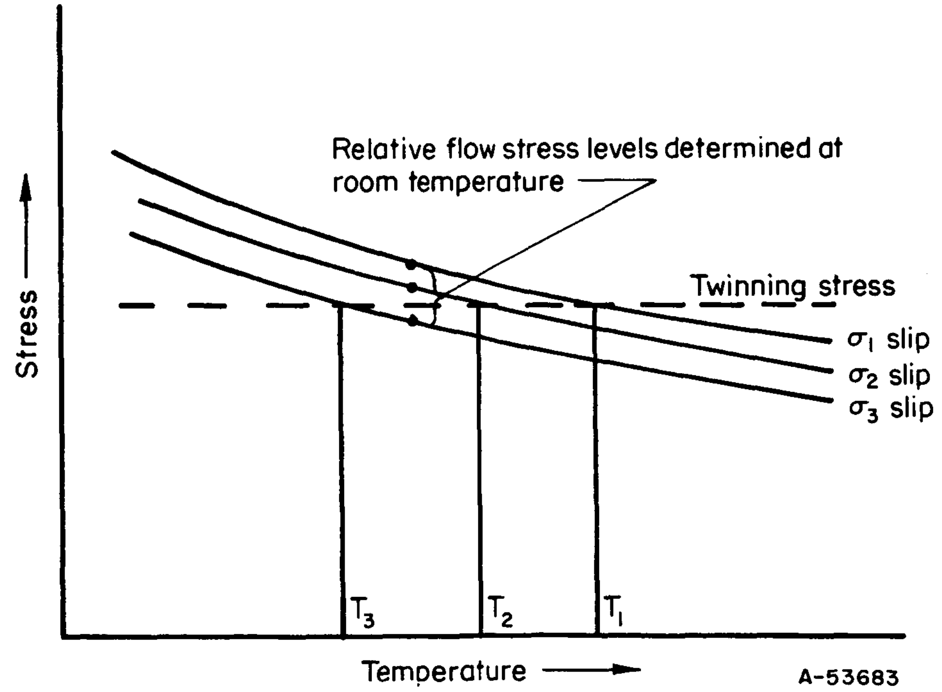


FIGURE 9. SCHEMATIC OF THE RELATIONSHIP BETWEEN SLIP, TWINNING, AND TRANSITION TEMPERATURE FOR TWIN-INDUCED FRACTURE

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 9 have been drawn to the form shown experimentally to exist (see Figure 5). 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 5 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 5, twinning produced around 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.

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 seriously affect the transition temperatures. It would thus seem that the properties of the matrix rather than the boundary control the transition temperature.

The results of this part of the overall investigation are very significant with respect to the relative importance of twinning in the rhenium-produced enhancement of ductility in the Group VI-A metals. Rather than promoting ductility, the evidence suggests that under the appropriate conditions (i. e., a matrix in which slip is difficult as a result of loading and quenching) twins can be in large part responsible for brittle failure. This aberration emphasizes that the mechanism by which ductility is improved by rhenium additions depends to a large extent on relatively easy movement of slip dislocations at low temperatures. This point of view will be enlarged upon in Sections III, IV, and VI.

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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*It should be emphasized that this is virtually the opposite view to that taken by the Russian workers - see Sections III and VI of this report.

N67-15836

SECTION III. THE EFFECT OF TEMPERATURE ON THE HARDNESS OF Cr-Re ALLOYS IN THE RANGE 0-40 AT.% Re

by

A. Gilbert

Introduction

Although in previous years' work it has been demonstrated that a recrystallized alloy of Cr-35 at.% Re can show several percent extension at -196 C(10), there has been no systematic investigation into the effect on the mechanical properties of Cr of increasing amounts of Re. It was known, however, that very low additions of Re to Cr did not have the beneficial effect observed on dilute additions of Re to W(13). In fact, a Cr-1 at.% Re alloy had been shown to have a tensile transition temperature several hundred degrees centigrade higher than that of unalloyed Cr(10). From the limited evidence available(12), dilute additions of Re to Mo seem to behave in much the same way as in the case of W-Re alloys – at any rate there is no evidence of increased brittleness in dilute Mo-Re alloys such as was found in dilute Cr-1 at.% Re. There was thus some evidence that the Cr-Re system behaves in a significantly different way to either the Mo-Re or W-Re system at low Re concentrations although all three show enhanced ductility at compositions close to the phase boundary. It was pointed out by R. I. Jaffee(14) that this apparent difference in behavior at low Re compositions was a parallel to the difference in superconducting properties exhibited by the 3 systems. In brief, Mo-Re and W-Re alloys are superconducting (at sufficiently low temperatures) for all Re compositions whereas Cr-Re alloys only become superconducting for Re contents greater than 20 at.%. Since the superconducting properties are a reflection of the electronic structure of an alloy as are ultimately the plastic properties, it seemed reasonable to look for a change in the mechanical properties of Cr-Re alloys at approximately the same composition as that at which Cr-Re alloys become superconducting. Accordingly, it was decided to run tests on a series of Cr-Re alloys to see at what composition the behavior changed from that characteristic of Cr to that characteristic of Cr-35 at.% Re.

Because of the inherent simplicity of the technique and the ease with which it could be adapted to low temperatures, hardness determinations were chosen as the investigative tool.

In addition, a feature common to the bcc metals as a whole, and one which is thought to be associated to a greater or lesser extent with the brittleness problem, is the pronounced increase in strength occurring at low temperatures. Tests were therefore made at temperatures below ambient to assess the effect of Re on the temperature dependence of strength in chromium. In order to determine as closely as was readily possible the effect of Re on the Peierls stress of Cr, hardness determinations were made at liquid hydrogen temperature, 20 K.

Experimental Procedure

The alloys were prepared by nonconsumable tungsten arc melting on a copper hearth the appropriate amounts of iodide chromium (containing <50 ppm total interstitials) and rhenium (>99.9 percent pure). The melting was carried out under helium at 1/3 atmosphere pressure and each casting was inverted and remelted 6 times to promote homogeneous mixing. Nine button castings were made containing Re in 5 at.% increments from 0-40 at.%. Because of known problems of working and recrystallizing each individual alloy by the same procedure, the alloys were tested in the cast condition before and after a 1-hour homogenization treatment at 1300 C in a vacuum of 10^{-5} mm of Hg. Although the alloys were not analyzed individually, density determinations showed that the actual compositions were a linear function of nominal composition, and a chemical analysis of the alloy highest in Re showed it to contain 38.5 at.% (40 at.% nominal). The compositions were thus very close to the nominal compositions.

For hardness testing at low temperatures, the apparatus shown in Figure 10 was constructed. It was found that the double Dewar construction in conjunction with the close-fitting polystyrene cap made a well-insulated container to permit up to 60 hardness impressions to be made while consuming only 5 liters of liquid hydrogen. In order to minimize conduction of heat into the container along the extension of the arm holding the indenter, a Fiberglas segment was inserted along its length*.

Slices approximately 0.8 x 0.3 x 0.1 inch were cut from the button castings and clipped to the base of the cradle whose outer legs stood on the moveable table of a Vickers hardness tester. In this way, up to 15 hardness indentations could be made on a specimen without removing it from the liquid hydrogen. The hole in the polystyrene cap was made elliptical in order to permit the necessary movement. Hardness determinations were made at 300 K, 197 K, 78 K, and 20 K. Ten to fifteen hardness impressions were made at each temperature for each alloy.

On completion of this work on the series of Cr-Re alloys, selected alloys that were available from previous work were tested using the same procedures.

Experimental Results

Figure 11 summarizes the results of the hardness determinations made at four temperatures on the series of cast homogenized Cr-Re alloys. Results on the as-cast alloys were qualitatively the same but showed greater scatter. The room-temperature measurements followed the same trend as was reported by Allen and Jaffee(15) but showed slightly less scatter and less evidence of the hardness minimum reported previously at ~35 at.% Re.(15) At lower temperatures, the variation of hardness with composition changes drastically and in fact at 20 K and 78 K solid solution softening is observed rather than hardening. The drastic reduction in low-temperature hardness occurs at between 10 and 20 at.% Re. Above 20 at.% Re the hardness stays sensibly constant as it does at all four temperatures.

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*This permits an electrostatic charge to be carried by the indenter that was therefore grounded to the body of the testing machine in order to avoid a sparkover as the indenter was being attached.

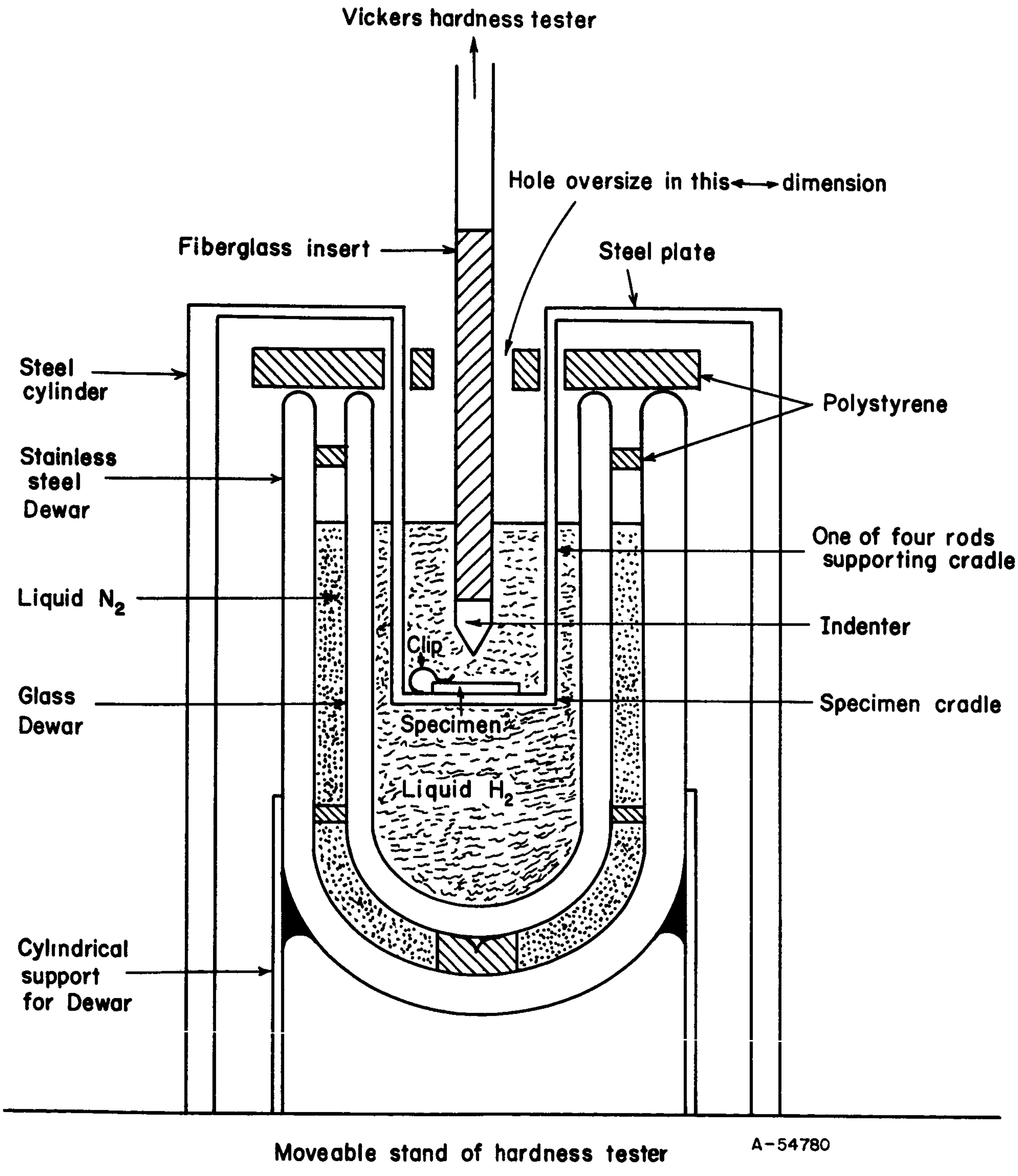

FIGURE 10. DIAGRAM OF THE APPARATUS CONSTRUCTED TO PERMIT HARDNESS MEASUREMENTS TO BE MADE AT 20 K

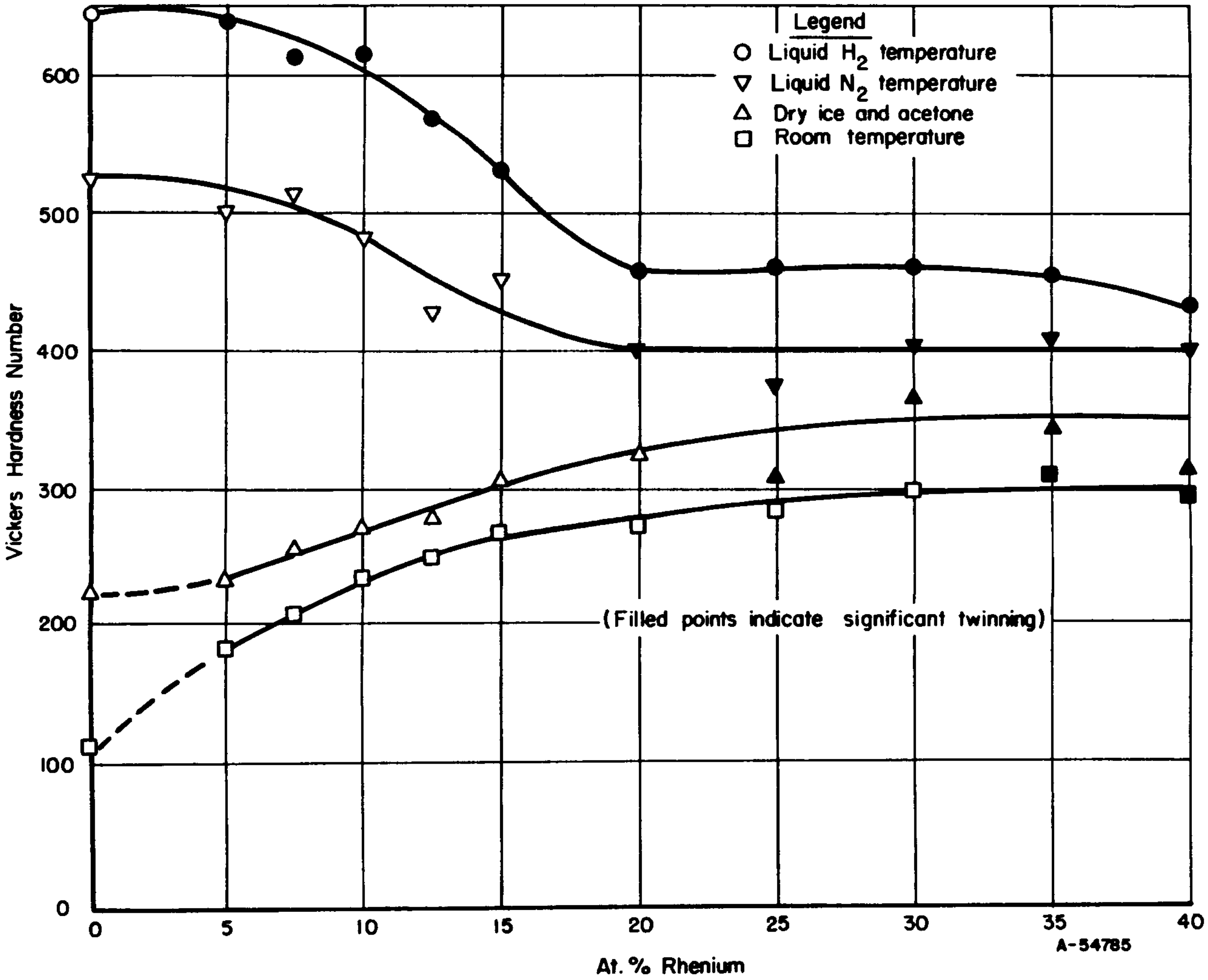

FIGURE 11. HARDNESS OF CAST HOMOGENIZED Cr-Re ALLOYS AT ROOM TEMPERATURE, 197 K, 77 K, AND 20 K

Cr-Re alloys annealed at 1300 C, 6 hours in vacuum.

Figure 12 presents selected data from Figure 11 to show more graphically the effect of Re on the temperature variation of hardness for Cr and Cr-Re alloys. As the Re content is increased, a marked reduction in the temperature sensitivity is observed. This reduction in hardness is not associated solely with the onset of twinning since at 20 K all samples twinned. Furthermore, it is generally thought that slip must precede twinning. It was observed, however, in accord with previous investigations, that twinning was more profuse in the higher Re alloys. In contrast to the results of Allen and Jaffee,(15) twinning at 30 C was observed only at Re contents >30 at.% in the homogenized material and >20 at.% in the as-cast material.

The results of hardness determinations made at 20 K and 300 K for series of Cr-Rh, Mo-Re, and W-Re alloys are presented in Figure 13. In general, it was found that the variation of hardness with composition at both temperatures was similar for these alloys, as for the Cr-Re system, with the exception that a decrease in hardness occurs at more dilute alloy compositions.

Discussion

While hardness measurements are an inexact method of determining the mechanical properties of a material, there is nonetheless a well-documented relationship between hardness and ultimate tensile strength. A similar correspondence between yield strength and hardness breaks down only if the materials being compared show very different work-hardening characteristics. As can be seen from data to be presented in Section IV, the work-hardening characteristics of Cr and Cr-35Re are very similar. Accordingly, it will be assumed that the hardness reflects the effect of Re on the flow stress at a common low strain or on the twinning stress. The results of Figure 11 therefore show that Re additions dramatically change the critical stress for plastic flow in Cr. Both the sign and magnitude of the change are dependent on temperature.

At room temperature, Re additions produce the commonly accepted form of solid-solution strengthening. The most interesting aspect of the experimental results, however, is the softening that occurs (at Re additions of from 10-20 at.%) at 20 K. Within the limits of the experiments performed, it seems that Mo-Re, W-Re, and Cr-Rh alloys show a similar hardness decrease (at 20 K) with the difference that the reduction appears to begin at much lower alloy compositions than for Cr-base material. This therefore may be, as was suggested by Jaffee,(14) a reflection of the difference in electronic structure between Cr and Mo and W, which is also responsible for the differences in superconducting behavior. The Cr-Rh results, however, do not support this contention, since a significant hardness decrease occurs in this system at alloy additions as low as 2 at.%, at which composition the alloy is not superconducting.

In general, however, results of all four of the alloy systems investigated follow the trend exemplified by the Cr-Re alloys. At 20 K increasing additions of Re (or Rh) produce a progressive decrease in hardness down to a certain level (which for Cr-Re occurs at about 20 at.% Re) beyond which the curve is parallel to the room-temperature hardness curve, but a little displaced from it. The implication of this observation is that Re additions are bringing about a reduction in strength through an effect on some mechanism other than that responsible for solid-solution strengthening in the athermal region. The mechanism generally considered to control the rate of plastic flow at low temperatures is the thermally assisted movement of dislocations over the Peierls

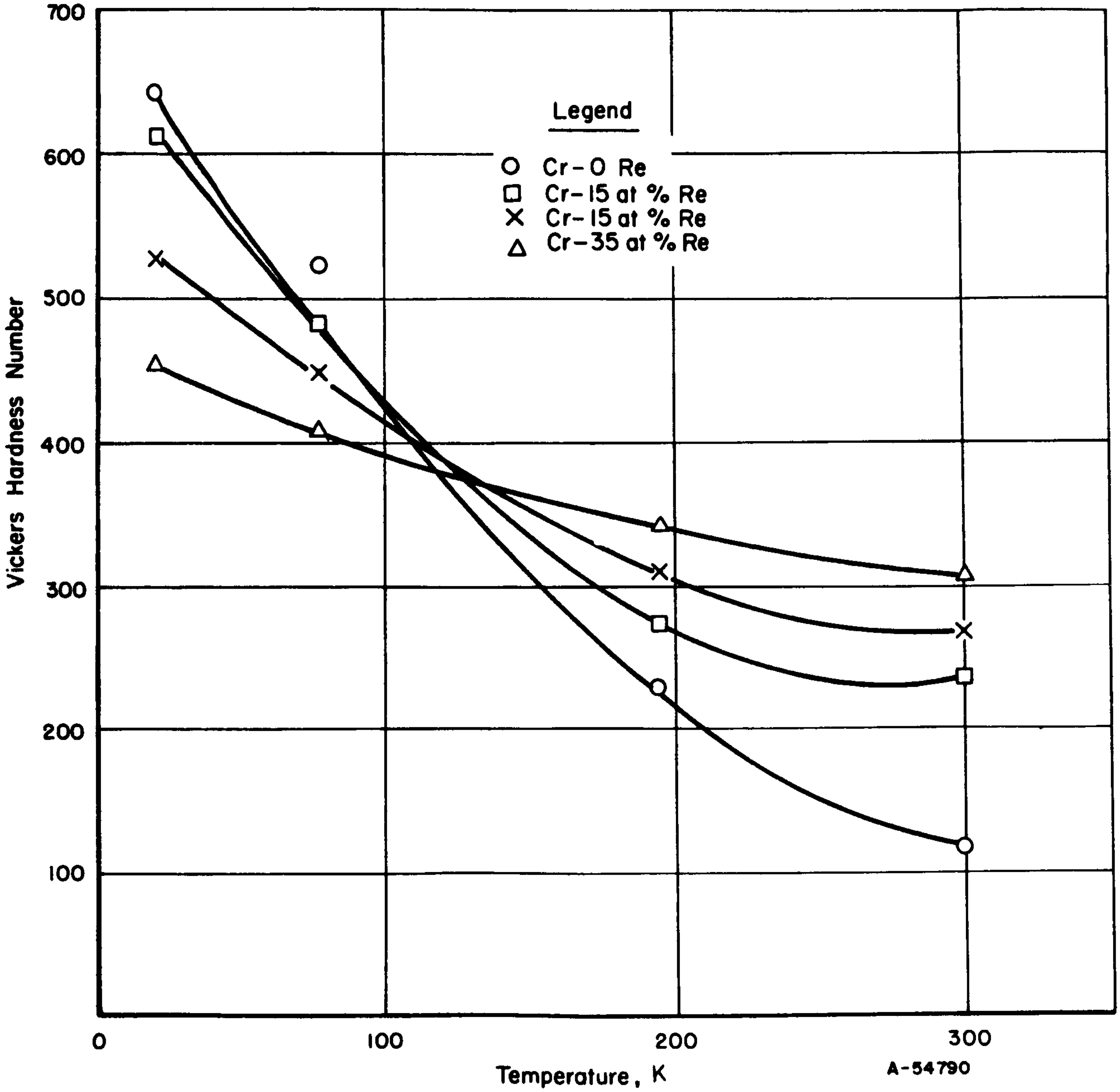

FIGURE 12. THE TEMPERATURE DEPENDENCE OF HARDNESS IN SELECTED Cr-Re ALLOYS

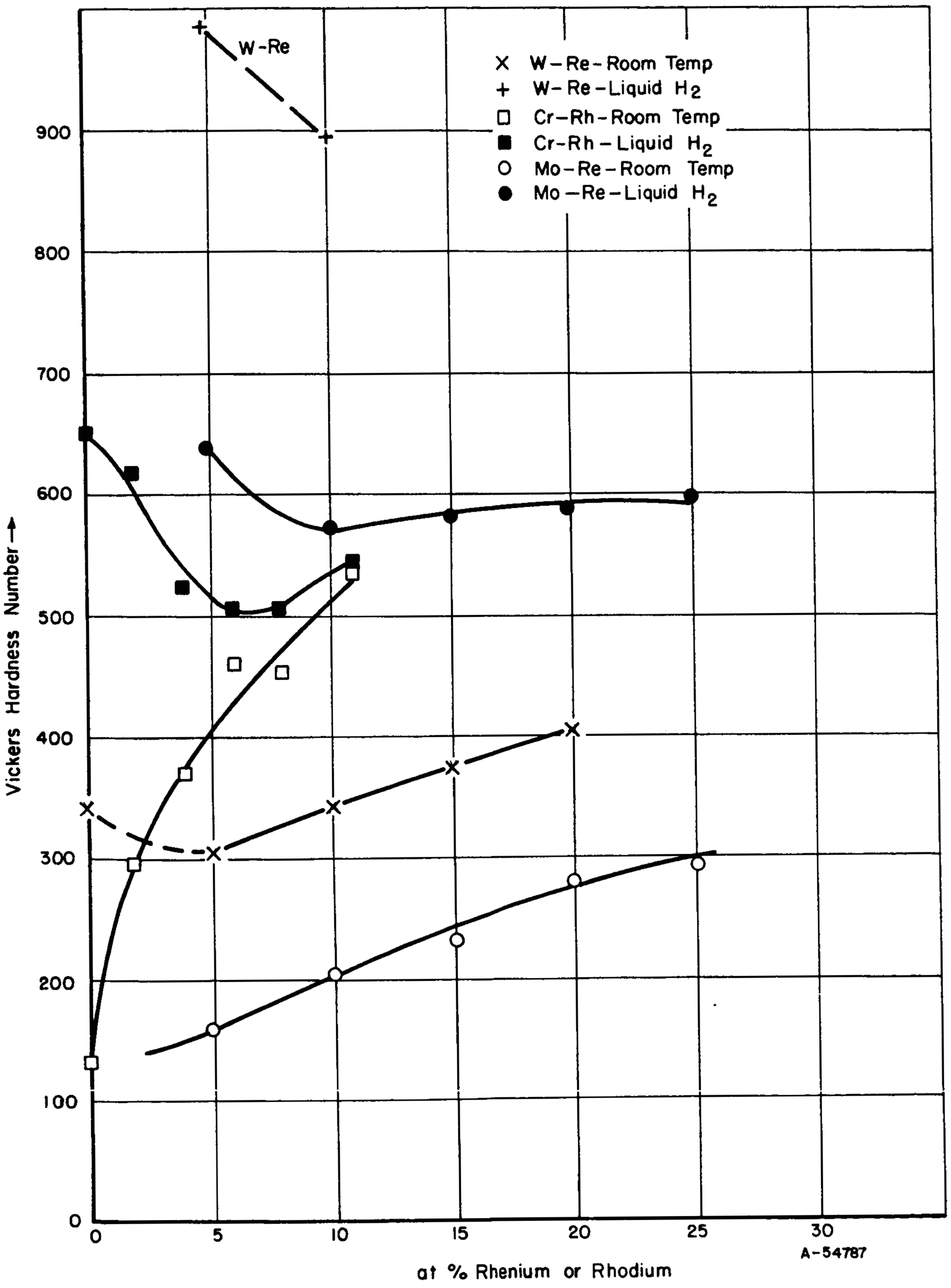

FIGURE 13. HARDNESS OF Mo-Re, W-Re, AND Cr-Rh ALLOYS AT ROOM TEMPERATURE AND 20 K

barrier. Accordingly, it is suggested that the role played by Re may be to reduce the height of the Peierls barrier*. This would bring about a decrease in the temperature dependence of the flow stress such as is shown for the Cr-Re system in Figure 12. A reduction in the height of the Peierls barrier is a particularly attractive possibility in view of the facts:

(1) Brittleness in the Group VI-A metals is thought to arise partly because of the strong temperature dependence of the flow stress at lower temperatures

(2) Rhenium, which is known to enhance ductility in the Group VI-A metals, now seems also to lower this temperature dependence.

Although there is a clear need for a controlled investigation into the related effects of a solute softening at low temperatures and improved ductility at the same compositions, there is some evidence that such a correspondence exists. First, there is the evidence presented here for Cr-Re, W-Re, and Mo-Re alloys. In addition, in an investigation on the Cr-Fe system, Mil'man, et al,(17) show that in the region from 0-30 at. % Fe, increasing amounts of solute raise both the high- and low-temperature hardness of Cr and also increase the ductile-brittle transition temperature (see Figure 14). Between 30 and 40 at. % Fe, however, increasing solute additions bring about a dramatic decrease in the transition temperature and also produce a reduction in the low-temperature strength – or in terms of the present suggestion, reduce the height of the Peierls barrier.

Mil'man, et al,(17) believe that the promotion of ductility by high additions of Fe is explained entirely by the promotion of twinning as a deformation mode. This seems to be an oversimplification of the situation, however, as previous work by the present author in the Cr-Fe system(19) has shown that it is the twins themselves that are responsible for the generation of grain-boundary cracks (see the insert to Figure 14 taken from Gilbert(19)) which nucleate cleavage failure. Evidence to support this assertion is presented in Figure 15 and 16 also taken from Gilbert(19). It is apparent that although twinning occurs at 400, 500, and 600 C, it does not enhance ductility. Rather, some measure of ductility is observed only at 700 C where there is no evidence of twinning. A similar question as to the part played by twinning is raised in the discussion to Section II of this report where even in nitrogen-loaded Cr-Re alloys twinning was found to be responsible for the initiation of grain-boundary cracks at ~150 C. The importance of twinning in the promotion of ductility in rhenium-type alloys is thus an unresolved issue. While on the one hand twins are undoubtedly capable of generating cracks both at grain boundaries and at twin/twin intersections, twinning is a means by which deformation can occur very rapidly and which therefore, in principle, is capable of promoting ductility by relieving stress at the head of a crack. It could be that the enhanced ductility and increased twinning are both causes of a common effect – the promotion of $\{112\}$ slip planes rather than $\{110\}$. Rhenium additions have been shown to produce such a change in Mo-Re(19), Cr-Re(20), and W-Re(21) alloys. Since Cr-Fe alloys also exhibit pronounced twinning, it may well be that in these alloys too, such a change in slip plane is produced. The detrimental effect of Fe additions on the ductility of Cr would then have to be accounted for by some factor such as the very high critical stress for twinning in this system (see Figure 16) – over 100,000 psi at 600 C compared

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*Such a suggestion was also made by Booth, Jaffee, and Salkovitz(43), in explaining the reduced temperature and strain-rate sensitivity of Cr-Re and Mo-Re alloys. Also, reduced Peierls barrier recently was suggested by Raffo and Mitchell(16) to explain a solution softening observed at low Re compositions in Ta-Re alloys. This reduction occurs at levels much lower (~2 at.%) than the levels at which the softening occurs in the present alloys.

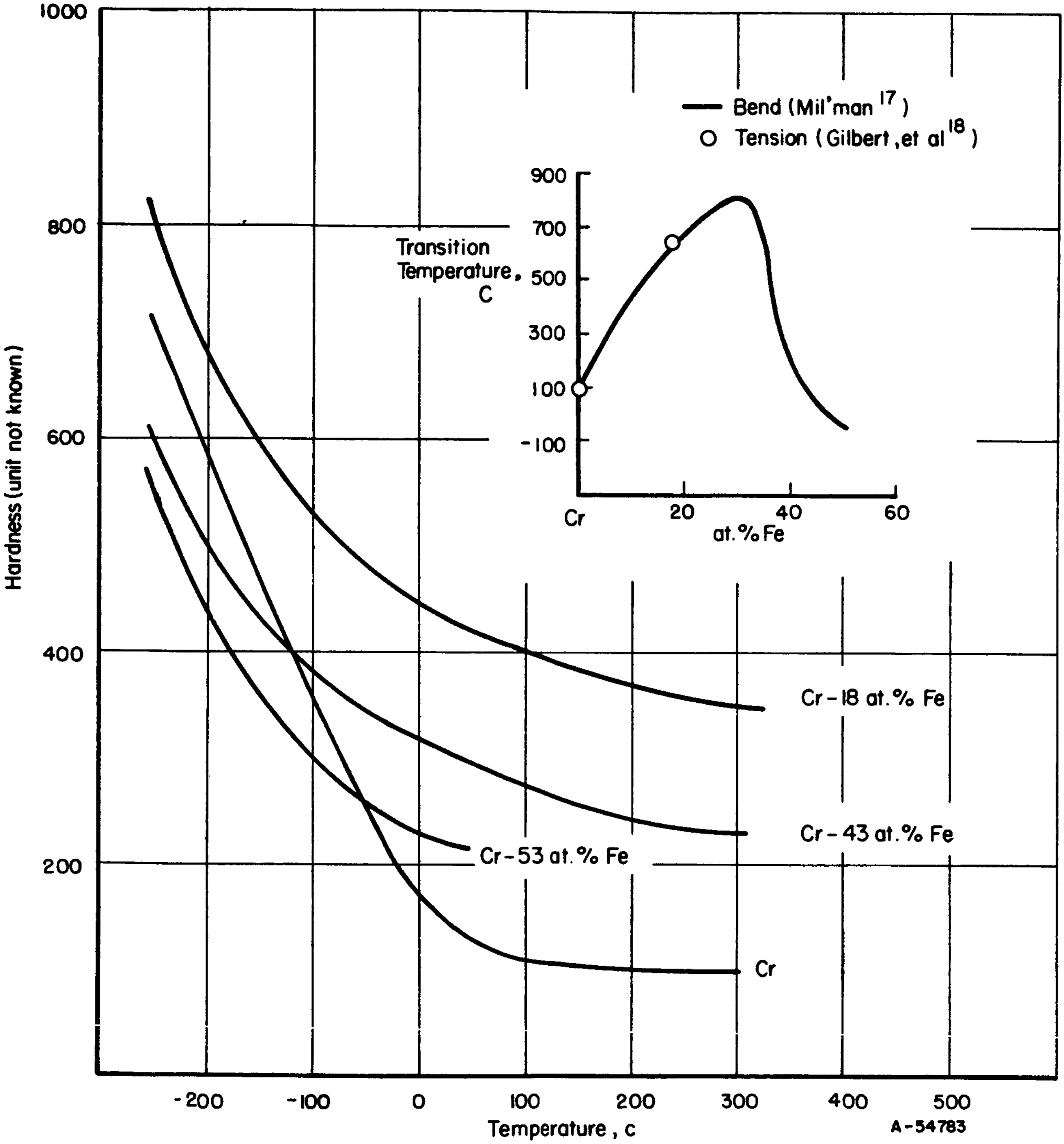
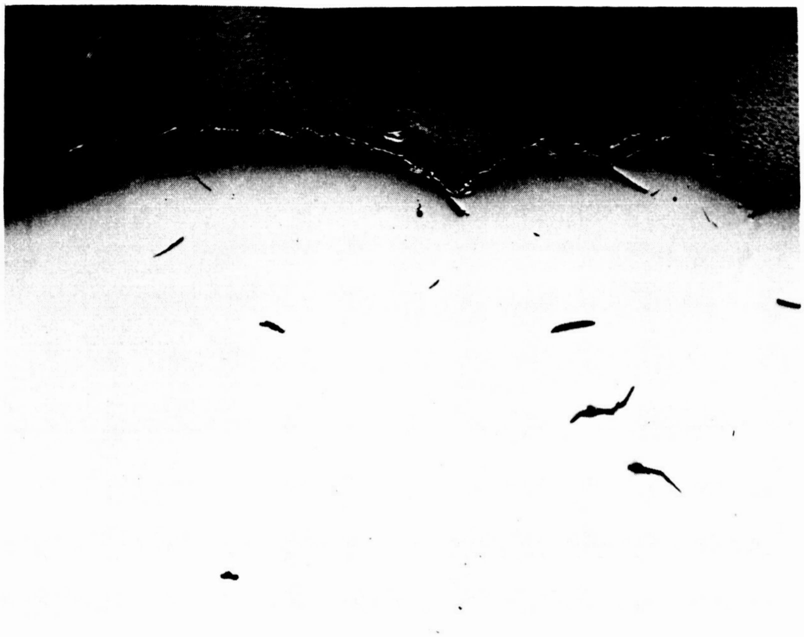
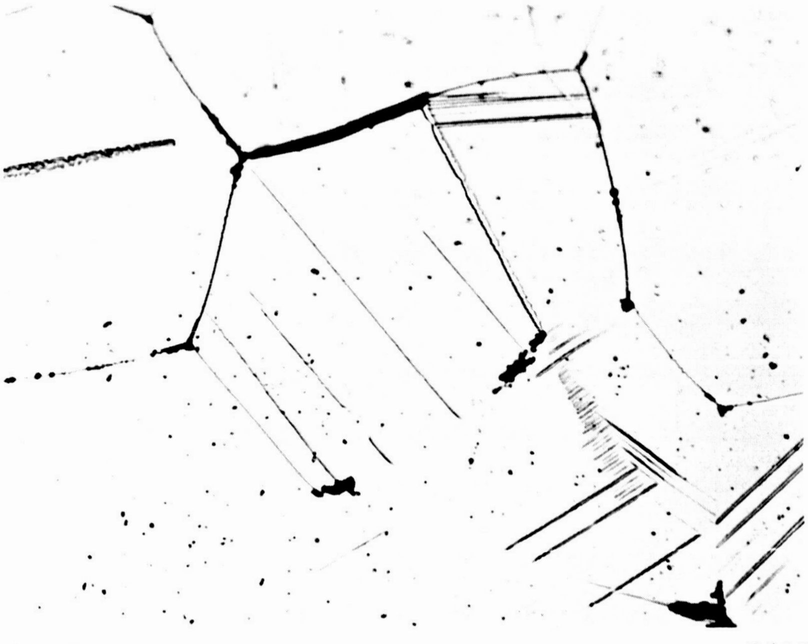


FIGURE 14. THE TEMPERATURE DEPENDENCE OF HARDNESS OF Cr-Fe ALLOYS (MIL'MAN, ET AL)



80X 9417

a. Before Etching



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b. After Etching

FIGURE 15. METALLOGRAPHIC SECTION THROUGH A RECRYSTALLIZED SAMPLE OF Cr-17.5 At.% Fe TESTED AT 600 C

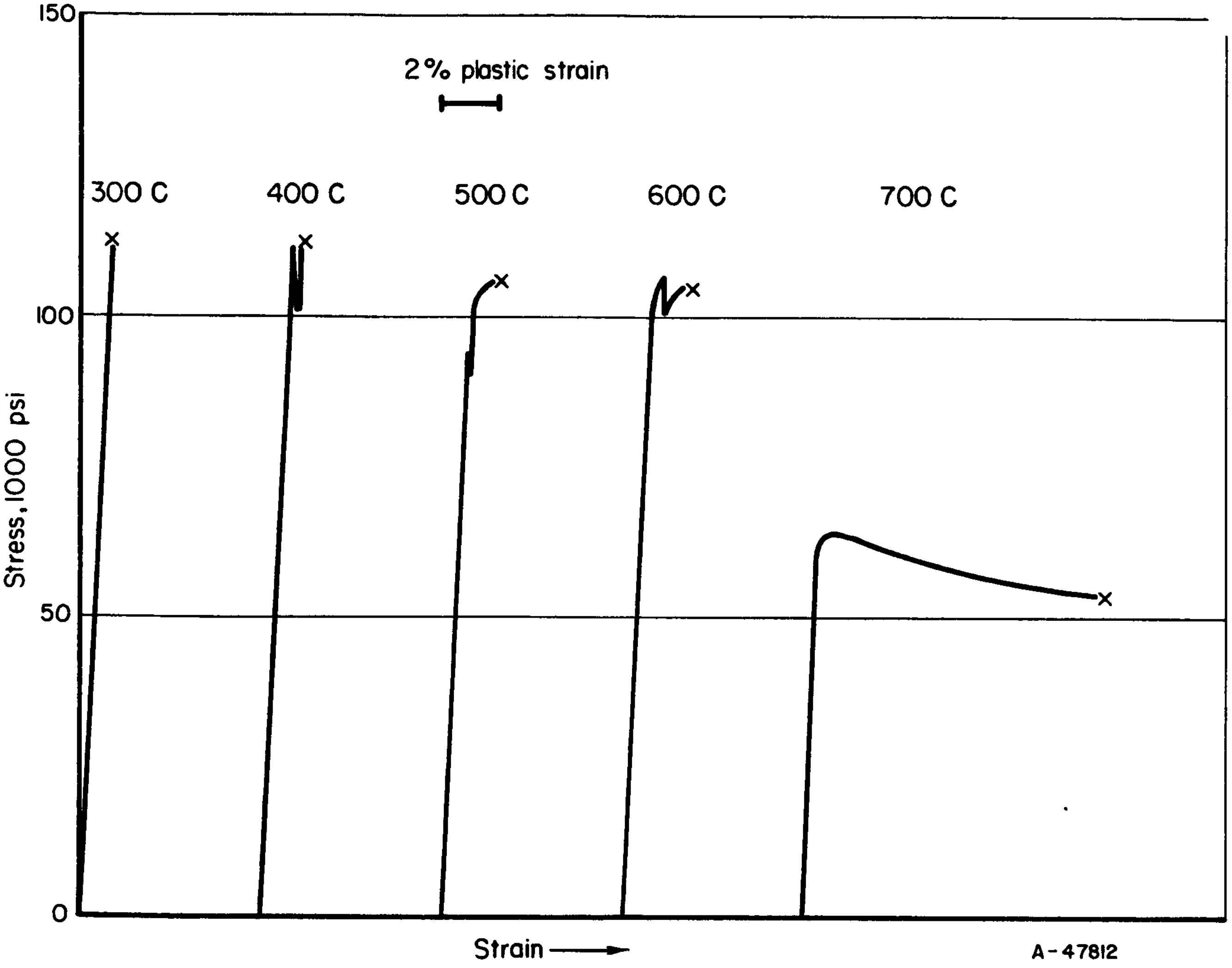

FIGURE 16. TYPICAL STRESS-STRAIN CURVES FOR RECRYSTALLIZED Cr-17.5 At.% Fe

with ~80,000 psi for Cr-Re at room temperature. To the best of the author's knowledge, however, there is no detailed knowledge, either experimental or theoretical, as to the variation of the critical stress for twinning or for slip on $\{110\}$ planes compared with that on $\{112\}$ planes. Accordingly, further speculation at this time seems unwarranted.

In summary, the marked solid-solution softening at low temperatures produced in Cr by Re additions of >20 at. % may well be a critical factor in the concurrent enhancement of ductility. It is suggested that the mechanism underlying this softening is a lowering of Peierls barrier by addition of Re. It may also be that the presence or absence of such an effect represents a critical test for the operation of a "Re-type" enhancement of ductility. The limited data available seem to support this contention, but final proof awaits more complete documentation.

N67-15837

SECTION IV. ACTIVATION VOLUME ANALYSIS FOR Cr AND Cr-35 Re

by

A. Gilbert

Introduction

In Section III of this report it was shown that additions of Re in amounts >20 at. % produce a pronounced decrease in the temperature dependence of the hardness of Cr and, therefore, presumably of the flow stress. A low-temperature dependence of the flow stress is characteristic of a fcc or cph material in which the temperature is thought to control the ease of dislocation motion through its effect on the dislocation intersection mechanism or on the conservative motion of jogs. In bcc materials, on the other hand, the strong temperature dependence of the flow stress is thought to be a result of a thermally activated "climbing" by dislocations of the Peierls Nabarro energy barrier.(22) The change in the temperature dependence of the flow stress produced by Re alloying could thus be a reflection of a change in the mechanism controlling flow. In order to investigate this possibility a series of strain-rate cycling experiments was carried out at different temperatures in order to evaluate the stress dependence on the activation volume of the process controlling deformation in Cr and Cr-35Re.

Experimental Procedure

Single-shoulder tensile specimens having a gage length of 0.5 inch and a width of 0.1 inch were prepared from a .030-inch-thick strip of cold-rolled Cr-35 Re and cylindrical compression samples 0.2 inch in diameter and 0.5 inch long were machined from wrought Cr rod. An impurity analysis for both materials is given in Table 7. The specimens were all vacuum annealed at 1200 C, which produced grain sizes of 0.5 mm and .01 mm, respectively, in the Cr and the Cr-35Re samples. The coarse grain size was chosen for the Cr samples in order to promote ductility in compression at lower temperatures, and the fine grain size for the Cr-35Re strip samples in order to assure the presence of a sufficiently large number of grains across the specimen thickness. Two different types of tests were performed on both materials – constant-strain-rate tests (either to failure in the case of the tensile specimens or to strains of >10 percent

TABLE 7. INTERSTITIAL CONTENT, IN PPM, OF THE TEST MATERIALS

Test Material	0	N	H_2	C
Cr	20	4-10	0.5	15-30
Cr-35Re	350	14	0.8	15-30

for the compression) and strain rate cycling from .002 to .02 inch per minute. The latter tests were performed on specimens that had all been strained to a predetermined stress at a temperature that from previous experimental work(23) was known to be in the athermal region[*] in order to put all the specimens in the same state in terms of dislocation density. Cr-35Re samples were strained at 650 K and the Cr samples at 425 K.

Experimental Results

Figure 17 shows typical engineering stress-strain curves for the samples tested. Results taken from previous work on Cr-35Re(23) are included in the same figure in order to illustrate the effect of grain size on the deformation process in Cr-35Re. It is apparent the very-fine-grain-size material deformed by slip at room temperature whereas the medium-grain-size material tested earlier deformed by twinning. This effect of refinement of grain size is in accord with the grain-size effect observed in other materials(24). In addition, it is apparent that the fine-grained material is stronger at all strains than the medium and, furthermore, is very much more ductile at 77 K (~40 percent elongation compared to ~5 percent).

The effect of temperature on the mechanical properties of Cr and Cr-35Re is illustrated in Figure 18 from which the effect of grain size on both slip and twinning can be assessed. In common with previous work(24) the grain-size dependence of the twinning stress (K_t) is about three times that for slip.

Despite the very coarse grain size of the Cr compression samples, the twinning stress for Cr is ~15,000 psi higher than for the medium-grain-size Cr-35Re samples, and it thus appears that, as was observed in Mo and Mo-35 at.% Re[†], Re additions lower the critical stress for twinning.

At low temperatures, in the region where the deformation process is thought to be thermally activated, the shear flow stress τ is usually considered to be made up of two components:

$$\tau = \tau_o + \tau^* ,$$

where τ_o is the athermal component and τ^* the thermally activated component. The athermal component τ_o varies with temperature through the variation of the shear modulus with temperature. The variation of the shear modulus over the temperature range investigated is essentially small and negligible. So in present work τ_o was taken to be invariant with temperature. In the present tests, $\tau_o (= \sigma_o/2$, when σ_o is the tensile flow stress) can be taken as half of the flow stress at 650 K for the Cr-35Re samples and at 475 K for the Cr.

In order to assess the effect of Re on the thermally activated component of the flow stress, Figure 19 compares the τ^* $(= \tau - \tau_o)$ evaluated at 8 percent strain[††] for

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[*] That is, when the temperature dependence of the flow stress (and accordingly the strain-rate sensitivity) is zero. For the Cr samples, the behavior never became truly athermal, and 425 K was chosen as a prestraining temperature at which the strain rate sensitivity was reasonably low.

[†] See reference (33).

[††] In bcc metals, in general, it has been found that since the work hardening rate is not very temperature dependent(22) (also see Figure 17) the temperature dependence of the thermally activated flow stress is not dependent on the strain at which the flow stress is determined.

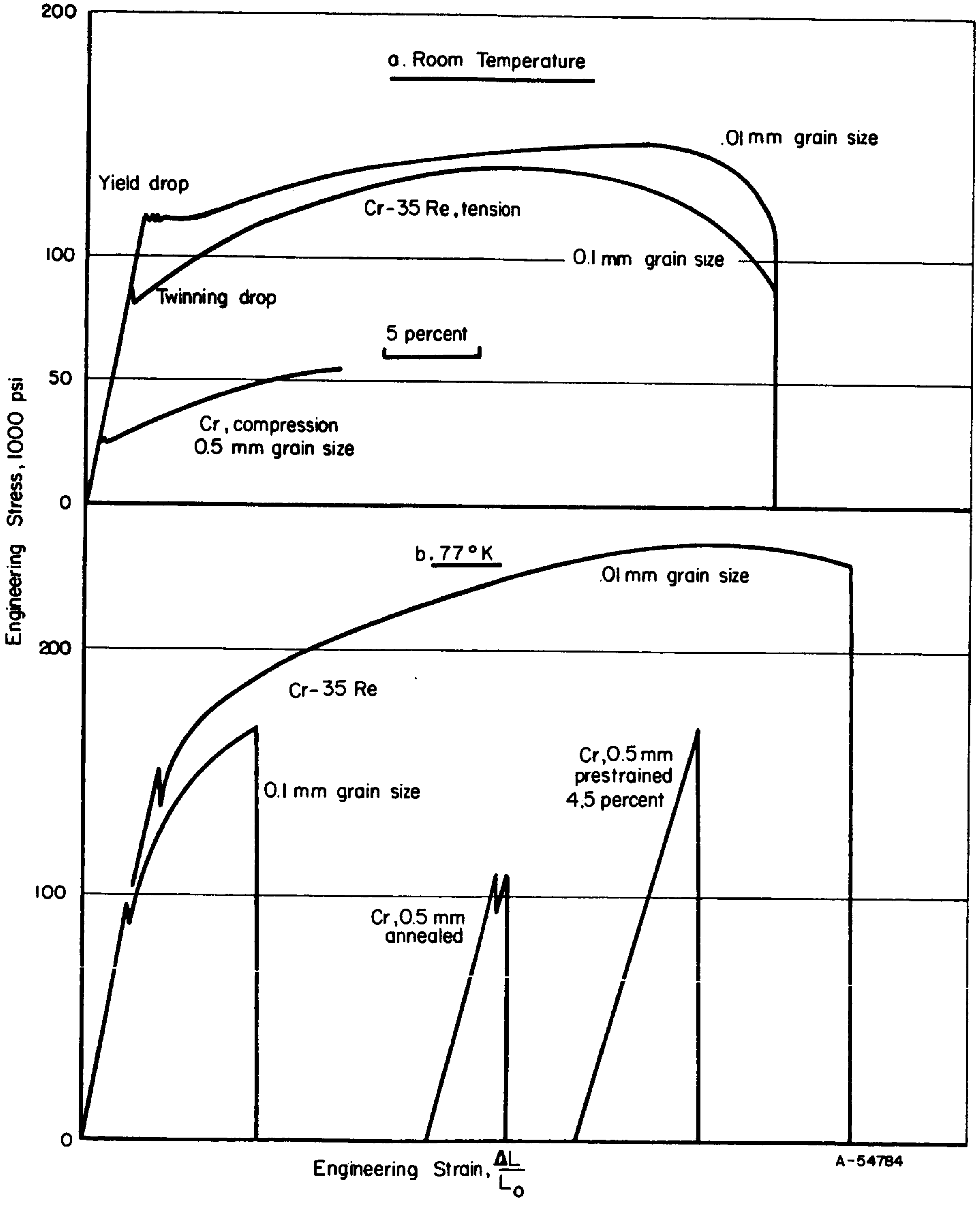

FIGURE 17. REPRESENTATIVE ENGINEERING STRESS-STRAIN CURVES FOR COARSE-GRAIN-SIZE CHROMIUM COMPRESSION SAMPLES AND FINE- AND MEDIUM-GRAIN-SIZE Cr-35Re

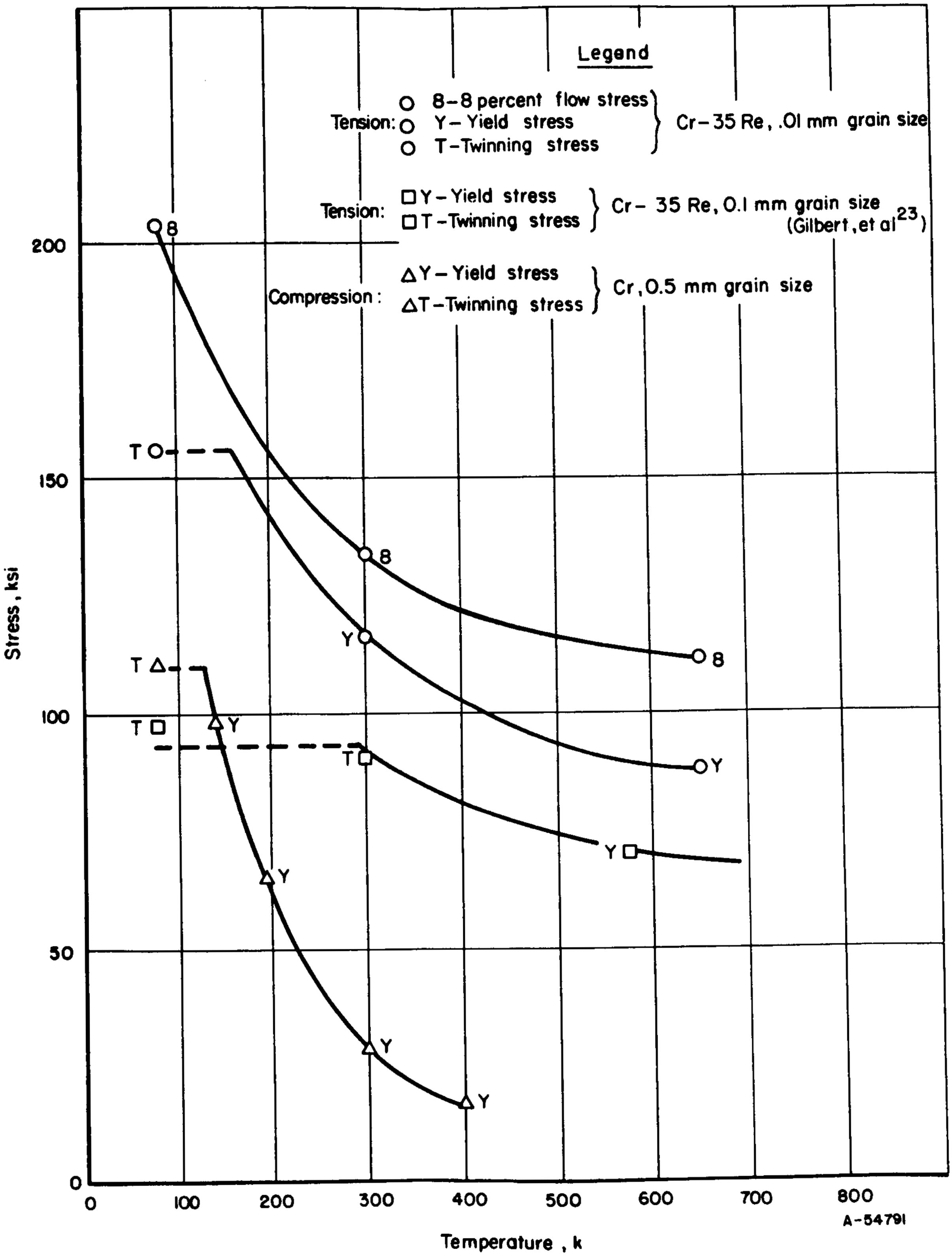

FIGURE 18. THE EFFECT OF TEMPERATURE ON THE MECHANICAL PROPERTIES OF Cr AND Cr-35Re

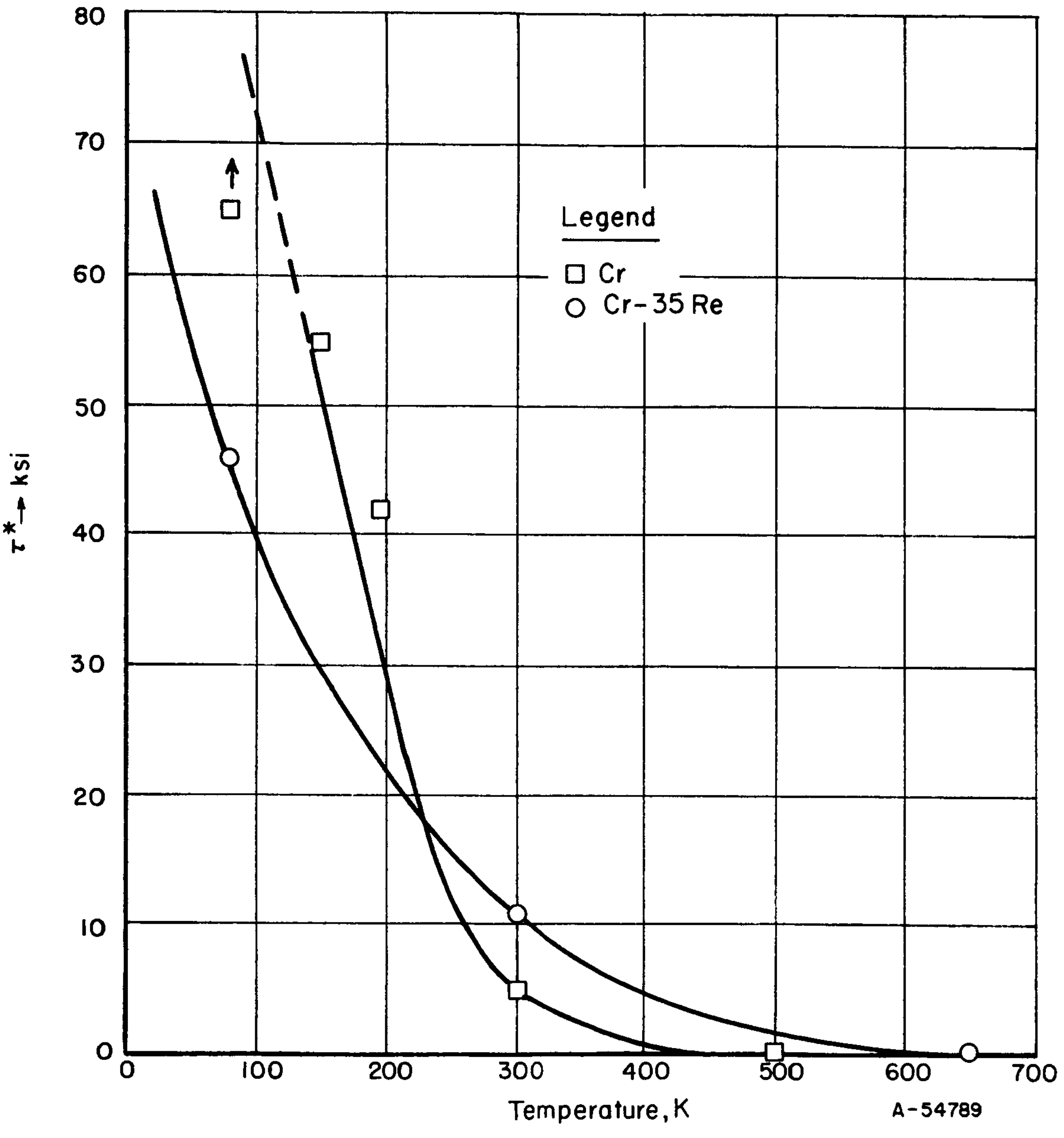

FIGURE 19. A COMPARISON OF THE THERMAL COMPONENT OF THE 8 PERCENT FLOW STRESS IN Cr AND Cr-35Re

Cr and Cr-35Re as a function of temperature. The results provide firm support for the conclusion drawn from the hardness determinations described in Section III, that Re does in fact lower the temperature dependence of the flow stress.

A summary of the results of the strain rate cycling tests is given in Table 8 and Figure 20.

Although the data are sparse, it is apparent that the activation volume in the thermally activated region is typical of that for other bcc materials (~10 to $30b^3$) where the activation process is the nucleation of a pair of kinks and furthermore is clearly the same for both Cr and Cr-35Re.

Discussion

From the mechanical property evaluations made in this phase of the work, it is apparent that Cr-35Re exhibits typical bcc behavior in terms of the effect of grain size on both flow stress and ductility. The fine-grained material is both stronger and more ductile than the coarse, whereas in unalloyed Cr, while it is observed that fine-grained material is stronger, it is less ductile than is the coarse-grained material. In addition, the Cr-35Re samples tested in this work exhibited a Lüders plateau in the stress-strain curve that is also characteristic of fine-grained bcc material. Finally, from the activation volume analysis it is apparent that the process controlling flow in both Cr and Cr-35Re is thermally activated climbing of the Peierls barrier. Accordingly, the effect of Re is to reduce the height of this barrier.

This reduction in activation energy must be at least in part a reflection of the modification of the preferred slip plane (from $\{110\}$ to $\{112\}$) which has been observed previously.(19) Ultimately, both effects must be due to some modification in the electronic structure – particularly with respect to atomic bonding – produced by the addition of Re that alters the intrinsic lattice resistance to motion of dislocations as reflected by the decrease of the barrier height. At present, there does not seem to be an acceptable theoretical model on the basis of which such phenomena can be explained from a truly basic standpoint, but in Section VI of this report elastic calculations are summarized which indicate that the effect may be due to a modification made by Re additions to the elastic anisotropy of the base metal.

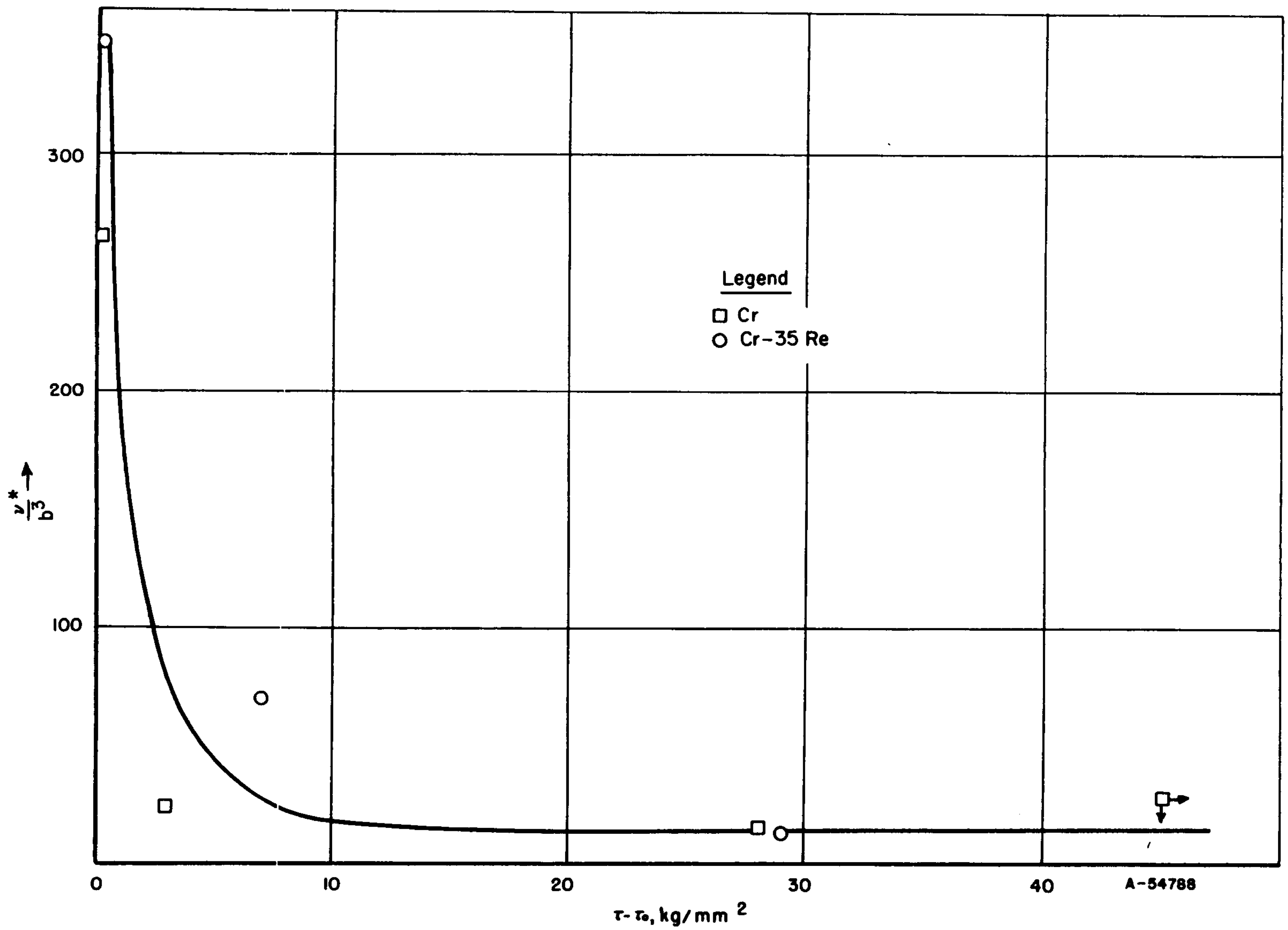

FIGURE 20. ACTIVATION VOLUME VERSUS STRESS FOR CHROMIUM AND Cr-35Re

TABLE 8. SUMMARY OF EXPERIMENTAL DATA AND ACTIVATION VOLUME CALCULATION FOR Cr (PRESTRAINED ~4. 5 PERCENT AT 425 K) AND Cr-35Re (PRESTRAINED ~5. 0 PERCENT AT 650 K)

Material	Temperature, K	Strain at Temperature, percent	$\Delta\sigma$, ksi	$v^* = kT\frac{\Delta\ \ell\eta\ \dot{\epsilon}}{\Delta\tau}$ (units of b^3)	τ^* $(= \tau - \tau_0)^{(a)}$, kg/mm^2
Cr	400	1. 5	0. 9	264	0. 35
	345	1	3. 3	62	1. 7
	345	2	3. 3	62	
	345	3. 5	3. 4	60	
	300	1	8. 0	22	2. 8
	300	3	8. 4	21	
	300	5	8. 6	21	
	195	0. 5	4. 1	28	
	195	1	7. 1	16	28. 0
	195	3	8. 2	14	
	195	6	8. 8	13	
	78	<0. 5	>1. 5	<31	>45
Cr-35Re	600	1	1. 0	345	0. 2
	300	1	2. 6	69	6. 7
		5	2. 5	71	
	78	1	3. 9	12	29
		15	3. 5	13	

(a) Evaluated at 6 percent engineering strain.

N67-15838

SECTION V. EFFECT OF RHENIUM ON THE STRAIN-RATE SENSITIVITY OF CHROMIUM AT ROOM TEMPERATURE*

by

A. Gilbert

Introduction

The response of a metal to a rapidly increasing stress (such as exists ahead of a propagating crack) depends on the way dislocations can move in response to an increase in stress. It has been shown for many materials that over a limited range dislocation velocity obeys an equation of the form

$$v \propto \sigma^m \quad , \tag{1}$$

where v is the dislocation velocity, σ is the stress experienced by the dislocation, and m is a constant for a particular material.

Thus,

$$\log v = m \log \sigma \quad . \tag{2}$$

In order for plastic flow to occur in advance of a moving crack sufficiently rapidly to blunt and arrest the crack, let us assume that dislocations must move at velocity, v'. Other things being equal, this velocity, v' (or rather log v'), can be attained at a stress which from Equation (2) is seen to be inversely proportional to m. Thus, for high values of m, dislocations can attain this velocity, v', at a much lower stress than for low values of m. Since the stress-concentrating effect of a crack falls off approximately inversely with distance ahead of the crack, large values of m permit plastic flow to occur well ahead of the crack, thus maximizing the possibility of the crack stopping.

In order to devise an experimental technique for determining m for a given material, the following reasoning is invoked.

Since plastic flow occurs by the movement of dislocations, the plastic strain rate, $\dot{\epsilon}_p$, can be written as a produce of ρ, the number of dislocations moving, and v, their average velocity:

$$\dot{\epsilon}_p \propto \rho v \quad . \tag{3}$$

Using Equation (1),

$$\dot{\epsilon}_p \propto \rho \sigma^m \quad . \tag{4}$$

If it is assumed that the number of dislocations moving is independent of strain rate, then Equation (4) can be written

$$\log \left(\frac{\dot{\epsilon}_p'}{\dot{\epsilon}_p''} \right) = m \log \left(\frac{\sigma'}{\sigma''} \right) \quad , \tag{5}$$

where σ' is the flow stress at strain rate $\dot{\epsilon}_p'$, and σ'' is the flow stress at $\dot{\epsilon}_p''$.

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*This section of the report is a conclusion of work which was described in partial form in an earlier report.

It has been experimentally determined that the yield stress or flow stress is usually related to the strain rate by an equation very similar to this, that is,

$$\log \frac{\sigma'}{\sigma''} = n \log \frac{\dot{\epsilon}'_p}{\dot{\epsilon}''_p} \quad . \tag{6}$$

Comparing Equations (5) and (6), it can be seen that $m = 1/n$. Thus, a highly strain-rate-sensitive material is characterized by a large value of n and a small value of m.

The preceding argument shows that, other things being equal, a material which is very strain-rate sensitive should be more susceptible to cleavage propagation than one which is insensitive to strain rate. Qualitatively, the reason is that under the high loading rates existing in front of a propagating crack, a highly rate-sensitive material will permit the buildup of a high stress which ultimately can lead to the development of stresses sufficient to cause cleavage. A material insensitive to strain rate, however, can deform at stresses not significantly different from the yield stress at low loading rates which are normally much below the stresses necessary to produce cleavage.

In an earlier report(23), it was shown that for strain-rate cycling by a factor of 10, Cr-35Re was an order of magnitude less sensitive to strain rate than was Cr. The object of this portion of the present work is to document the effect of Re on the room-temperature strain-rate sensitivity of Cr over a wide range of strain rates.

Room temperature is an appropriate temperature at which to compare the rate sensitivities since it is about the middle of the temperature range over which recrystallized Cr is brittle, while recrystallized Cr-35Re is ductile.

Experimental Program

Cylindrical compression samples of Cr and Cr-35 at.% Re, with a gage length of ~0.75 inch and a diameter of ~0.25 inch, were ground from rods of worked material. The specimens were given 1-hour vacuum anneals at 1200 C and 1500 C, respectively, and were electropolished prior to testing at room temperature. For strain rates in the range 10^{-5} to 10^{-2} per second, an Instron machine was used, and strain rates in the range 10^{-2} to 10 per second were obtained on a gas-operated, hydraulically stiffened machine designed at the Naval Research Laboratories.(25) For the latter tests, stresses were recorded by using a strain gage (attached to an elastically stressed portion of the loading chain), the output from which was displayed on the tube face of an oscilloscope.

Finally, strain rates of the order of 10^3 to 10^4 per second were obtained by the use of a pneumatically operated Hopkinson bar apparatus(26). In this case the load is applied by means of an input bar that is propelled towards the specimen at a high rate. As the material is being deformed after impact, it transmits a load that can be measured by strain gages attached to an output bar. The load-time history recorded by the output bar can be interpreted to provide the stress-time history of the specimen.

Experimental Results

The variation of yield stress with strain rate is illustrated in Figure 21. The Cr samples tested at rates below 10 per second yielded at a well-defined yield point, but the alloy samples and the Cr samples tested at the highest rates yielded continuously and, in these cases, the yield point was taken as the first macroscopic deviation of the load-time curve from linearity. There is some doubt as to the validity of this determination as made on the load-time curves recorded for the Hopkinson bar tests. However, at all stages of plastic strain at which the load was recorded, the load transmitted by the Cr-35Re samples was ~5 percent lower at 10^3/sec and ~25 percent lower at 10^4/sec than that transmitted by the Cr samples. Accordingly, the same definition of "proportional limit" was applied and is plotted in Figure 21. This approach is partially justified by the good correspondence between the proportional limits (recorded by different techniques) at ~10 and ~100 per second.

Although the Cr-35Re samples are much stronger than the Cr samples at low rates of strain, the alloy samples are much softer at the highest.

Discussion

As would be expected if the plastic flow process is thermally activated, the decrease in the temperature dependence of the flow stress produced by Re additions is reflected in a corresponding decrease in strain-rate sensitivity. The results obtained in this phase of the program substantiate results obtained by earlier strain-rate cycling(23) which indicated that Cr-35Re is very much less strain-rate sensitive than unalloyed Cr. In addition, however, it is apparent that at the strain rates reached during brittle crack propagation, Cr-35Re can actually deform at lower stresses than can Cr. As outlined in the Introduction, such insensitivity to strain rate may be vital with regard to enhancing the ductility of the alloy over that of Cr in that it permits plastic flow to occur rather than cleavage.

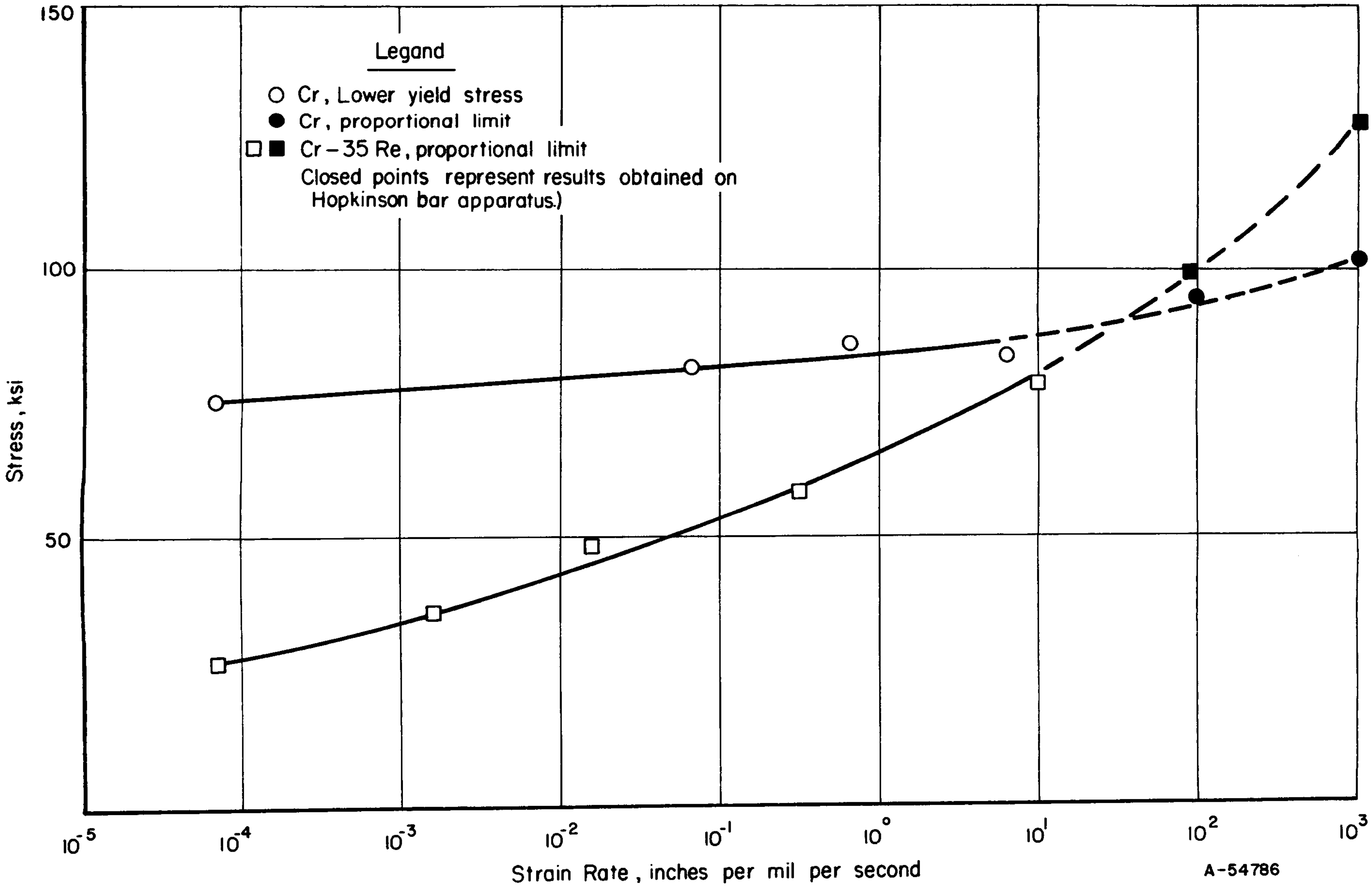

FIGURE 21. EFFECT OF STRAIN RATE ON THE YIELD OF CHROMIUM AND Cr-35Re

N67-15839

SECTION VI. GENERAL DISCUSSION: THE RHENIUM ALLOYING EFFECT

by

A. Gilbert

From a practical standpoint, the most important effect produced by additions of Re to W, Mo, and Cr is that their high-Re alloys* can deform plastically at room temperature and below, rather than fail in the brittle manner characteristic of the recrystallized unalloyed base metals. In addition, however, other effects are observed, such as the promotion of twinning at temperatures above ambient, a change in the fracture mode from cleavage (in unalloyed material) to grain-boundary failure (in the alloys), a change in the recrystallization behavior and possibly modifications to the precipitate morphology. It has been the aim of this experimental program to determine which of these or any number of other modifications is or are primarily responsible for the enhancement of ductility. Much of the work has therefore been devoted to delineating just what modification to the physical or mechanical properties is made by Re additions and then trying to assess the importance of the contribution of a particular modification to the promotion of ductility. In this section the conclusions of the author will be presented as to the relative importance of the contributions of the various facets of the Re effect so far known to exist.

In order most conveniently to assess the role of Re in promoting ductility in Cr, the behavior of Cr-35Re samples tested at or below room temperature can be contrasted with the behavior of recrystallized Cr samples under the same conditions. Recrystallized Cr can prove completely brittle at temperatures between -50 and 300 C depending on the purity and conditions of testing. Factors that induce brittleness are a fine grain size, a high impurity content (primarily with respect to nitrogen), a high strain rate, and a poor surface finish (of which notches may be considered an extreme example). Conversely, ductility is promoted by a large grain size (particularly taken to the limit of a single crystal), high purity, a good surface finish, a low straining rate, or even in the absence of all other beneficial factors by testing in a prestrained condition. Depending on the conditions of testing, completely brittle fractures occur at stresses in the range 15 - 40,000 psi and propagate by cleavage that is usually initiated at a grain boundary or inclusion. The fractures are thought to be initiated by the intersection of a slip band with a grain boundary. A critical aspect of fracture is that once a crack has been initiated, it can propagate at a fairly low stress (even in a single crystal(4)) at temperatures below 300 C. Evidence is available that suggests that the temperature above which cracks cannot propagate is typically in the neighborhood of 400 C. It is therefore the ease of crack propagation which in Cr is the root of the brittleness problem.** In contrast to this behavior, nonpropagating microcracks have been observed in Cr-35Re, an example of which is shown in Figure 22(19) at temperatures as low as -196 C. Furthermore, when Cr-35Re samples fail, they do so mainly by grain-boundary failure*** (although some cleavage has been observed)(18) at stress

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*Cr-35 at.% Re, Mo-35 at.% Re, and W-23 at.% Re.

**This point of view is generally but not universally accepted [see Reference (6)].

***See Section II of this report.

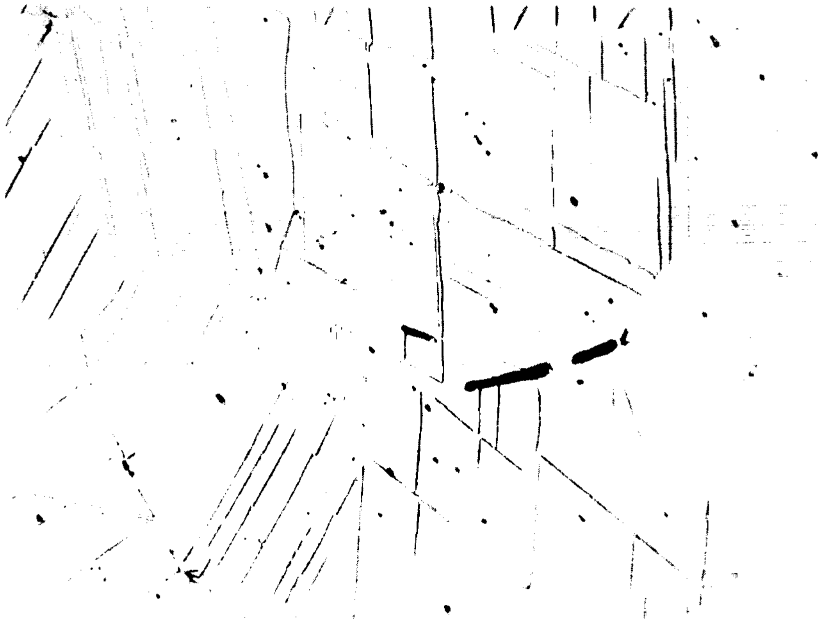

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FIGURE 22. Cr-35Re ALLOY DEFORMED IN TENSION AT -196 C SHOWING NONPROPAGATED MICROCRACKS AT TWIN INTERSECTIONS

levels of ~200,000 psi. Thus, while the addition of Re may to some extent make crack initiation more difficult, the primary effect is to reduce the susceptibility of the Cr matrix to cleavage to such an extent that the crack-propagation transition temperature is reduced some 600 C. There are several factors that may have the controlling influence on this change in crack-propagation characteristics, all of which appear to be important with respect to the ability, or lack of ability, of the matrix to deform by plastic flow under the influence of the stress concentration existing at the head of a newly initiated or growing crack. If the matrix can deform ahead of the crack, the stress can be relieved. If the matrix cannot deform, the stress may be relieved by cleavage and immediate failure. Thus, any factor that enhances the ability of the matrix to deform plastically should promote ductility. This ability is most important at low temperatures (when brittleness is a problem) and at the high rates at which brittle cracks usually propagate. It may be in this respect that the promotion of twinning by Re additions is most important, since twinning becomes a preferred method of deformation (and therefore of stress relief) under just these conditions of low temperature and/or high strain rates. However, it seems to the author that the importance of twinning per se in enhancing ductility has been overestimated(27, 28) since as was observed in Section IV of this report, fine-grained Cr-35Re deforms at room temperature without twinning and yet is very much more ductile than Cr of the same grain size.* The true relevance of the twinning phenomenon may be that the increased tendency to twin may itself be a reflection of a more basic effect produced by the addition of Re, a modification of the preferred slip plane. Since in the systems Mo-Re(19), Cr-Re(20), and W-Re(21), Re additions have been shown to induce slip on {112} planes (the twinning habit plane) rather than {110}, the increased twinning may simply be a reflection of the greater availability of dislocations on those planes that are thus available for

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*Which would have a ductile-brittle transition temperature higher than 200 C.

dissociation and subsequent twin nucleation. The change of the slip plane from {110} to {112} may also be important in two other ways. First, it increases the number of available slip planes from 6 {110} to 12 {112}, or even as was suggested in Cr-35Re(20) and Mo-35Re(19) to 24 {123} planes. An increase in the number of planes available increases the possibility that a slip plane should be available for stress relief along the same crystallographic direction as the shear stress distribution is maximized. Alternatively, either the temperature sensitivity of the flow stress or the strain-rate sensitivity of the flow stress could be significantly reduced for {112} slip as opposed to {110} slip, which would again make dislocation movement easier under conditions where crack propagation would otherwise occur. This may well be the explanation of the effect of Re on hardness described in Section III and for the strain-rate-sensitivity results summarized in Figure 21. From these last results it is apparent that at the strain rates reached during propagation of brittle cracks, the Cr-35Re samples actually deform at a lower stress than the Cr samples despite the very much greater strength of the alloy at low rates.

It seems to the author that the effect of Re in lowering the Peierls stress and the strain-rate sensitivity is the most likely prime factor in enhancing ductility. Although a complete correlation between solution softening at low temperatures and increased ductility is hampered by a lack of complete documentation, a good preliminary correlation can be made from data already in the literature. The results summarized in Figures 12, 13, and 14 are support for a causal relationship with respect to enhanced ductility, and the results summarized in Figures 23 and 24 can be used to show a correlation between low-temperature hardening and increased brittleness. It is apparent that additions of Re to Nb actually increase the temperature dependence of the hardness (see Figure 23) while at the same time promoting brittleness in the alloys(29). The data in Figure 24 contrast the behavior of Ta and Re additions to W in terms of their effect on the temperature dependence of hardness. While Re, a ductilizing addition(12), greatly reduces the temperature dependence of the hardness, embrittling Ta additions(16, 30) have a much smaller effect on hardness, causing a reduction in hardness at temperatures only lower than ~100 K. On the basis of these admittedly indirect yet fairly convincing correlations, it seems that enhanced ductility is associated with a reduction in the temperature sensitivity of hardness, and a tendency towards greater brittleness with an increase in temperature sensitivity.

In order to completely understand the mechanism of the Re effect, it is necessary to understand the processes that occur on an atomic scale by means of which Re additions actually are able to reduce the Peierls stress. Since there is at present no well-established theory to describe the effect of solute atoms on either the electronic bonding or ease of dislocation motion, it is not yet possible to explain these effects in detail. However, it is possible to discuss in general terms one factor that may be important – possibly to the extent of being controlling. Qualitatively, the ease of dislocation motion is determined by the "width" of the dislocation: a wide dislocation is easier to move – moves at a lower stress – than a narrow one. The width of the dislocation is in turn ultimately determined by the details of the electronic bonding – strongly directional bonds will tend to promote narrower dislocations than will less strongly directed bonds. Another reflection of the details of the electronic bonding is to be found in the shear modulus of a material and, in confirmation of this qualitative correlation, it is observed that, in general, materials with a high shear modulus have narrow dislocations.(31)

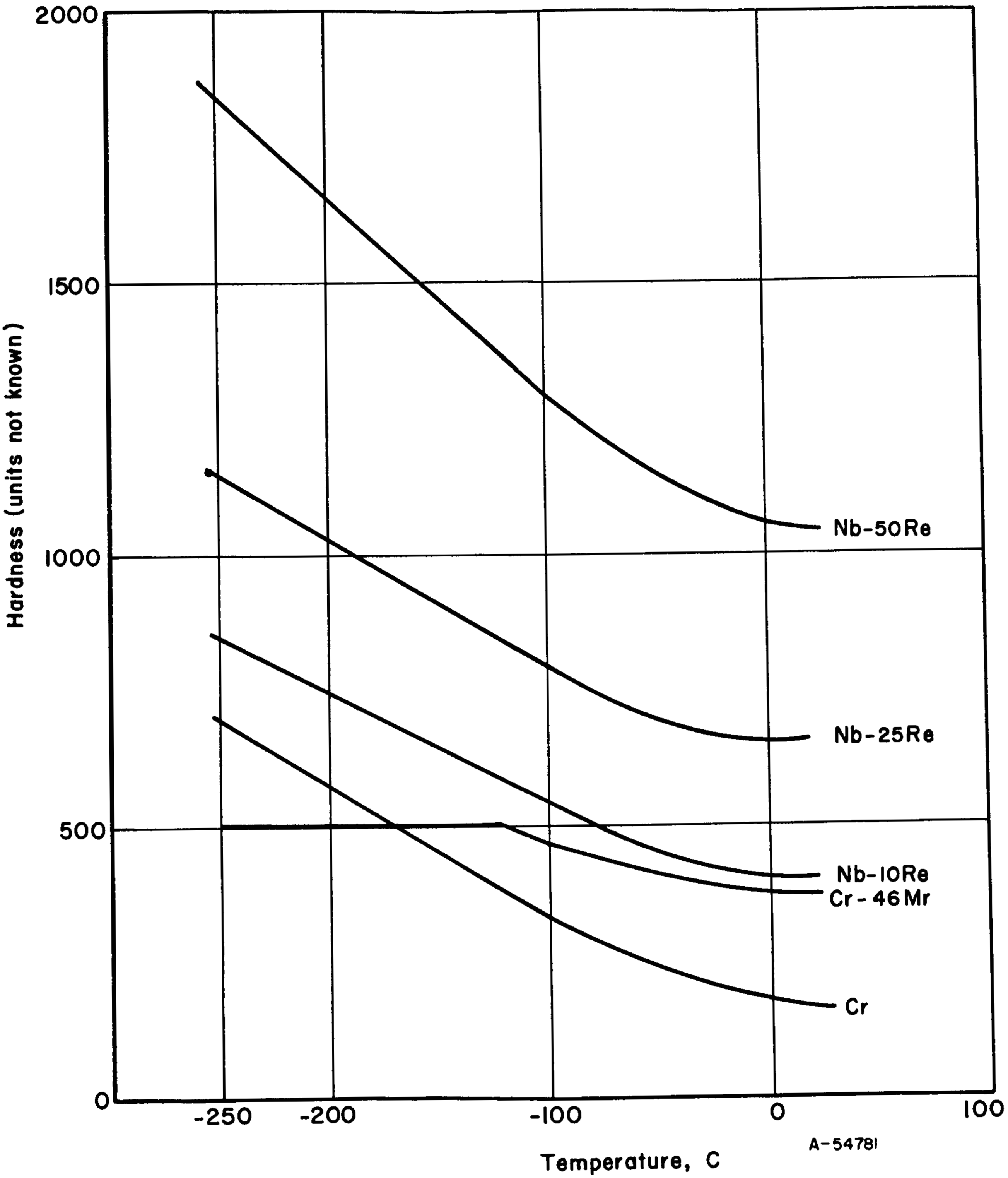

FIGURE 23. THE TEMPERATURE DEPENDENCE OF HARDNESS IN Nb-Re AND Cr-Mn ALLOYS (MIL'MAN, ET AL)

In order to get a more quantitative estimate of the effect of Re in this respect, the elastic constants were determined for a single crystal of Mo-35Re* and were used to calculate the Peierls-Nabarro stress for comparison with a similar calculation already performed on Mo. The appropriate constants* and a summary of the calculation are presented in Tables 9 and 10. The values of S listed in the last column of Table 10 represent the ratio of the stress to move a dislocation to the stress to shear the lattice rigidly. Two points are worthy of discussion. First, the calculation shows that the stress to move dislocations in Mo is higher on both {110} and {112} slip planes than for Mo-35Re**, which is in accord with the marked hardness decrease promoted by Re additions at 20 K. Second, it is apparent that the mobility of edge dislocations on {110} planes compared with the mobility of screw dislocations is very much greater in Mo-Re than in Mo. If a similar ratio of mobilities exist for dislocation movement of {112} planes, it would explain the preponderance of screw segments observed in the transmission electron microscopy of Mo-35Re samples (the edge segments moving easily will leave behind long segments of screw). Thus, while the quantitative results of the calculation cannot necessarily be taken too literally, they nevertheless provide support for the qualitative arguments made as to the effect of Re in modifying the bonding.

Since Re additions tend to inhibit cleavage in the Group VI-A metals, the elastic constants have been manipulated to evaluate Youngs modulus along various crystallographic directions, since this parameter would be expected to be proportional to the cleavage strength of a metal or alloy across a particular crystallographic plane(32). However, as can be seen from the final column of Table 11, the results do not seem to be connected in any meaningful way with the preferential cleavage planes in Mo (for example, Youngs modulus along a <100> direction is greater than along any other direction, and yet Mo frequently cleaves on this plane). Accordingly, it is difficult to draw any meaningful conclusion from the changes in E brought about by the addition of Re.

One other factor that has frequently been discussed in connection with the effect of Re is the possibility of a Re-induced modification (lowering) of the stacking-fault energy. Such an effect is highly likely to exist, since Re additions promote twinning for which, according to present concepts, dislocation dissociation (and accordingly formation of stacking faults) is a prerequisite.

Up to the present time, attempts to provide direct experimental evidence of the independent existence of stacking faults in Re alloys have not been productive. Some evidence has been presented, however, of both stacking faults and extended nodes*** in a Cr-50 at. % Fe alloy.(28) In view of the possible similarity of this system to Re-type alloys, this observation must be considered to keep open the possibility that under the correct conditions stacking faults and/or extended nodes may yet be observed. The photographs available to the author, however, that are intended to show the stacking faults and extended nodes in Cr-50 at. % Fe have suffered in reproduction to such an extent that they no longer represent convincing evidence of the effect. Attempts to reproduce this interesting observation are needed.

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*The Mo-35Re data were kindly supplied by Professor G. C. Smith, of the Department of Physics, Case Institute of Technology, and have not been published previously.

**The calculation of the K factor for screw segments of a dislocation of { 112 } planes cannot be obtained from an analytical solution of the equations and, thus, this comment applies only to the edge components of such dislocations.

***Both features are characteristic of a reduction in stacking-fault energy.

TABLE 9. SINGLE CRYSTAL ELASTIC CONSTANTS FOR Mo AND Mo-35 Re

Mo			Mo-35 Re		
C_{11}	C_{12}	C_{44}	C_{11}	C_{12}	C_{44}
10^{12} dynes/cm^2			10^{12} dynes/cm^2		
4.696	1.676	1.068	4.43	2.05	1.36

TABLE 10. SUMMARY OF CALCULATION OF DISLOCATION ENERGY FACTORS AND PEIERLS STRESS FOR Mo AND Mo-35Re

Material	Dislocation	Energy Factor, 10^{11} dynes/cm^2	C, 10^{11} dynes/cm^2	ξ/b	S
Mo	$\{110\}$ $\langle\bar{1}11\rangle$	$K_e = 16.6$	13.6	0.5	0.27
	$\{110\}$ $\langle\bar{1}11\rangle$	$K_s = 13.7$	13.6	0.4	0.41
	$\{212\}$ $\langle\bar{1}11\rangle$	$K_e = 17.3$	13.6	0.3	0.57
Mo-35 Re	$\{110\}$ $\langle\bar{1}11\rangle$	$K_e = 18.7$	12.5	0.61	0.165
	$\{110\}$ $\langle\bar{1}11\rangle$	$K_s = 12.8$	12.5	0.42	0.38
	$\{212\}$ $\langle\bar{1}11\rangle$	$K_e = 18.7$	12.5	0.35	0.47

TABLE 11. CALCULATION OF YOUNG'S MODULUS FOR VARIOUS CRYSTALLOGRAPHIC DIRECTIONS IN Mo AND Mo-35Re

For Mo $S_{11} = 0.262 \times 10^{-12}$	$E = \dfrac{1}{\left\{0.262 + 0.275\left(\Sigma l_1^2 l_2^2\right)\right\}}$		
100, $\Sigma l_1^2 l_2^2 = 0$	$0.275\ \Sigma l_1^2 l_2^2 = 0$	$1/E_{100} = 0.262$	$E_{100} = 3.82 \times 10^{12}$ dynes/cm^2
110, $\Sigma l_1^2 l_2^2 = 1/4$	$0.275\ \Sigma l_1^2 l_2^2 = .069$	$1/E_{100} = 0.331$	$E_{110} = 3.02 \times 10^{12}$ dynes/cm^2
111, $\Sigma l_1^2 l_2^2 = 1/3$	$0.275\ \Sigma l_1^2 l_2^2 = .091$	$1/E_{100} = 0.353$	$E_{111} = 2.83 \times 10^{12}$ dynes/cm^2
112, $\Sigma l_1^2 l_2^2 = 1/4$	$0.275\ \Sigma l_1^2 l_2^2 = .069$	$1/E_{100} = 0.331$	$E_{112} = 3.02 \times 10^{12}$ dynes/cm^2
For Mo-35Re $S_{11} = 0.319 \times 10^{-12}$	$E = \dfrac{1}{\left\{0.319 - 0.11\left(\Sigma l_1 l_2^2\right)\right\}}$		
100, $\Sigma l_1^2 l_2^2 = 0$	$0.110\ \Sigma l_1^2 l_2^2 = 0$	$1/E_{100} = 0.319$	$E_{100} = 3.14 \times 10^{12}$ dynes/cm^2
110, $\Sigma l_1^2 l_2^2 = 1/4$	$0.110\ \Sigma l_1^2 l_2^2 = .027$	$1/E_{110} = 0.292$	$E_{110} = 3.43 \times 10^{12}$ dynes/cm^2
111, $\Sigma l_1^2 l_2^2 = 1/3$	$0.110\ \Sigma l_1^2 l_2^2 = .037$	$1/E_{111} = 0.282$	$E_{111} = 3.52 \times 10^{12}$ dynes/cm^2
112, $\Sigma l_1^2 l_2^2 = 1/4$	$0.110\ \Sigma l_1^2 l_2^2 = .027$	$1/E_{112} = 0.292$	$E_{112} = 3.43 \times 10^{12}$ dynes/cm^2

In addition to the effects so far discussed, Re additions make other significant modifications to the properties of the Group VI-A metals that may or may not be important in enhancing ductility.

In concluding the discussion of the Re alloying effect, some remaining hypotheses previously advanced to explain the beneficial effect of Re additions will be evaluated in the light of present knowledge.

Hypothesis 1. A Rhenium-Induced Change in Precipitate Morphology Promotes Ductility

It is well known that fracture in Group VI-A metals is initiated at the grain boundary(1), and it would thus be expected that any factor which removed this weakness would reduce the tendency to brittleness. Jaffee, et al, have shown that the continuous grain-boundary oxide film occasionally present in Mo is replaced by a discontinuous globular grain-boundary precipitate in Mo-35Re(27). The effect of Re in breaking the continuity of this film may be important in promoting ductility in the more impure materials where grain-boundary failure may occur to a significant extent, but in commercially pure present-day material, brittle failure in the Group VI-A metals occurs primarily by cleavage and, thus, during propagation at least, any modification to grain-boundary precipitate morphology is not relevant. The effect is probably not too important in crack initiation either, since cleavage is frequently initiated at grain boundaries where there is no evidence of either precipitate globules or film.(19) Finally, work described previously shows that in dilute W-Re alloys, which show improved ductility over that of unalloyed W, no modification of grain-boundary precipitate morphology was observed.(19) Instead, it appeared that Re exerted an effect primarily through a change in the recrystallization kinetics.

On the whole, it does not now seem that this is one of the more important effects produced by Re additions.

Hypothesis 2. Alloying With Rhenium Improves Ductility by Lowering the Solubility of Interstitial Impurities

This hypothesis is actually twofold: that the solubility is lowered, and that the result of a reduced solubility is an increase in ductility.

This hypothesis appears to have had its origin in the Cottrell theory of the yield point and brittle fracture. The crux of this theory was that the phenomena of the yield point and brittle fracture were entirely due to the immobilization of dislocations by impurity atmospheres that had formed at the expense of interstitial atoms in solution. The argument ran that if the amount of interstitial in solution were reduced, the extent of dislocation locking would likewise be reduced leading to a diminution of the tendency for discontinuous yielding and brittle fracture. However, the current theory of yielding and crack propagation considers that the pinning of dislocations is not the only factor which determines the yield point and the tendency towards brittle fracture, so the original basis for this hypothesis is now accepted less widely. In fact, an argument can be made that good ductility is exhibited by bcc metals only when they exist as a single bcc phase and that, when impurity phases are present as well, the ductility deteriorates. With the current state of industrial practices, the commercially produced metals are single phase only when their interstitial solubilities are high (e.g., V, Cb, and Ta), when significantly their ductility also is high. On the other hand, the metals with low solubilities are generally available only as multiphase materials due to the presence of precipitated impurities, and accordingly these metals (Cr, Mo, and W) have high transition temperatures, of the order of 300 K. Iron is an intermediate case. Furthermore, Lawley, et al(33), have shown that if polycrystalline Mo is purified past the limits of chemical analysis it has ductility down to below 4 K. Therefore, at this time it would seem to be more likely that good ductility is associated with increased rather than reduced solubility.

In Cr in particular the evidence presented in Section I of this report shows that Cr samples in which all the nitrogen is retained in solution are more ductile than when second phases are precipitated on aging. Furthermore there is evidence that nitrides precipitate on the {100} planes of Cr(34), a fact that may possibly contribute to the ready propagation of cleavage on these planes(35).

There is no known experimental evidence to indicate that the already low solubilities of Cr, Mo, and W(1) are further reduced by alloying with Re. On the other hand, there are three pieces of evidence to indicate that the solubility of interstitial impurities is actually increased:

(1) Experiments on Snoek damping due to nitrogen in Cr and Cr-35 at.% Re have been carried out by Klein.(36) The interpretation of the results indicates that after furnace cooling from typical recrystallization temperatures, the amount of nitrogen retained in solution in Cr-35 at.% Re is about 1000 times greater than in unalloyed Cr. This effect apparently resides in a Re-induced modification of the precipitation kinetics rather than in true equilibrium solubility, but the practical result is that under normal conditions, a very much greater amount of interstitial solute is retained in solution in Cr-35Re than in Cr.

(2) The height of the strain-aging peaks (on the graph of tensile flow stress versus temperature) are considerably increased by adding 35 at.% Re to Cr(23) and Mo(37). The phenomena of dynamic strain aging, according to the current theories of both Cottrell(38) and Schoeck and Seeger(39), is due to interstitial impurities in solution, and, other things being equal, the increase in strength is proportional to the interstitial-solute concentration. Accordingly, then, these observations suggest that the concentration of retained interstitial solute is higher in the high-Re alloys than in the respective pure metals.

(3) Bryant(40) has investigated the solubility of oxygen in alloys of the bcc crystal structure extending from an average group number of 5.0 to 6.2. Similarly, Jones(41) has measured the hydrogen solubility in bcc alloys from an average group number of 5.0 to 6.4 and has correlated this with the height of the density-of-states curve, $n(E_f)$, at the Fermi level, as inferred by a variety of physical-property measurements, such as magnetic susceptibility, low-temperature specific heat, and the superconducting transition temperature; the

> correlation is good. The solubilities and $n(E_f)$ have large values at N = 5.0, above which they fall progressively until at about N = 5.7 they reach a minimum that persists until about N = 6.0. Then an increase occurs that leads to a small maximum at N = 6.25. The hydrogen-solubility measurements between N = 6.0 and N = 6.4 were actually carried out on Mo-Re alloys and so are particularly relevant to this discussion. If it is accepted that the variation of $n(E_f)$ may be correlated with the solubility of all interstitial elements, in addition to the specific cases treated by Bryant and Jones, then one is forced to conclude that the interstitial solubilities in the high-Re alloys (with N between 6.25 and 6.4) are greater than in the corresponding Group VI-A metal.

Thus, on both counts Hypothesis 2 can apparently be discounted.

Some of the considerations discussed here bear on the mechanisms suggested by Wukusick(42) to account for the Re alloying effect. Wukusick discussed the possibility that spinodal decomposition occurs in high-Re alloys, and that the resulting Re-rich clusters form sites of high interstitial solubility. As was suggested earlier, however, such an explanation presupposes that interstitials in solution are the primary cause of brittleness, and such has not been shown to be the case. Further speculation as to the possible effects of spinodal decomposition does not seem warranted until some evidence has been provided to show that it exists. However, it is worthy of note that, according to Wukusick, ordered Re-rich arrays could be responsible for promoting paths of easy dislocation motion along <111> directions on {110} planes.*

Hypothesis 3. The Criterion for Enhancement of Ductility by "Rhenium-Type" Alloy Additions is the Attainment of a Critical Electron-to-Atom Ratio

The alloy additions that have been shown to exert a beneficial effect on the ductility of the Group VI-A metals, Re, Ru, Co, and possibly Fe, show several features in common:

(1) They all occur to the right of Cr in the periodic table – that is, on a Group Number basis they have a higher valency

(2) All have a high solubility in the base metal and the maximum ductilizing effect occurs near to the phase boundary

(3) The solid solubility range is limited by the appearance of sigma phase.

The question thus arises as to which of these factors is or are important in the promotion of ductility. Earlier efforts to interpret the mechanisms of the effect sought to establish a correlation between electron to atom ratio (e/a ratio) and ductilization, since improved ductility is observed at what would be a common e/a ratio of about 6.3 if the valency of the solute atom is taken to be 7. However, the e/a ratio was

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*Mo-Re has been shown to slip on {112} planes rather than the {110} planes preferred in Mo.

thought to be important in determining the distribution of interstitial impurities, and this does not now seem to be a critical factor. Furthermore, in order to establish a fair correlation between e/a and ductility, it would be necessary to have a much more detailed understanding of the valency of the transition metals than one has at present, and so a correlation cannot at the present be made*. The possibility still does exist, however, and ultimately the improved ductility must arise as a result of a modification to the electronic bonding. However, nearness to the sigma-phase boundary may actually be a more important criterion. Stephens and Klopp(44) have recently shown that a Cr-30 at.% Co alloy that in the quenched state** shows typical Re-type enhancement of ductility also shows super-plasticity at higher temperatures. Since high-temperature super-plasticity appears to be associated with the potential stress inducement of a phase transformation, it may be that closeness to a phase boundary is also important to the enhancement of low-temperature ductility. Unfortunately, the correlation is again hampered by lack of data. Since the Re effect is of most practical importance at low temperatures, most testing of Re alloys has been done at low temperatures, and little attention has been paid to the possibility that super-plastic effects may also be present at very high temperatures.

With respect to the third possibility, Wukusick's model is the only one that attaches any significance to the nucleation or prenucleation of the sigma phase. Nonetheless, it could be that the potential precipitation of a sigma phase is the critical criteria for the appearance of enhanced ductility, though not necessarily by the mechanism proposed by Wukusick. On the other hand, as is thought to be the case for twinning, it could be that the enhanced ductility and the limiting sigma phase are both effects of the same underlying cause.

In conclusion, as is found to be the case in other respects, the determination of which criterion is the main one for producing a Re-type alloying effect is hampered by lack of sufficient experimental data. However, the observation of the effect in the Cr-Co system, which permits the fabrication of alloys at much lower cost than Re alloys, should make possible the type of comprehensive research program that is necessary to settle the issue.

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*A fairly complete discussion of a possible effect of Re additions on electronic properties is given by Booth, et al(43).

**The need for quenching in this system simply reflects the greater slope of the solvus line in the Cr-Co alloy system compared with the slope in typical Re solute systems.

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APPENDIX

QUENCHED-IN DEFECTS IN Mo-35Re

APPENDIX

QUENCHED-IN DEFECTS IN Mo-35Re

by

A. Gilbert and J. W. Edington

Introduction

Experiments performed in an earlier phase of this program showed that a major effect of high Re additions to Mo was to modify the preferred slip plane.(1)* In brief, whereas Mo slips exclusively on {110} planes, both {112} and {123} slip planes were observed in Mo-35Re. In order to shed further light on the mechanism underlying this modification of the slip plane, some approach is necessary that is sensitive to the way in which Re affects various physical properties of the lattice. It was considered that such information could be derived from a study of the factors affecting the formation and stability of quenched-in vacancy clusters in Mo and Mo-Re alloys, since previous experiments performed on a wide range of face-centered cubic (fcc) metals and alloys quenched from close to the melting point have been a rich source of information on the fundamental properties of the fcc lattice. Examples of such information are as follows:

1. The relationship between the type of vacancy clusters and the stacking-fault energy of the metal.

It has been found experimentally that several types of lattice defects may be produced in quenched and aged metals and alloys supersaturated with vacancies. Materials of low stacking-fault energies frequently produce three-dimensional tetrahedra consisting of stacking faults on the {111} planes such as those seen in Au(2) and Ni-Co alloys. Al and al alloys, on the other hand, with a higher stacking-fault energy, produce two-dimensional loops(3) of various kinds. By controlled aging studies allied to electron microscope observations, it is possible to make estimates of stacking-fault energies for alloys exhibiting either type of defect.

2. The crystal plane on which vacancy loops condense, and their Burgers vector.

In fcc materials, loops condense on {111} planes with an $\frac{a}{2}$ <110> or an $\frac{a}{3}$ <111> Burgers vectors. In irradiated body centered cubic (bcc) mat materials, however, loops with Burgers vectors of $\frac{a}{2}$ <111> and also a <100> have been observed on {110} planes.(4) In both fcc and bcc materials, a particular configuration is chosen so as to minimize the energy of the defect. Such observations can thus point to the parameters that are the most important in determining this energy.

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*References are given on page A-7.

3. The binding energy of a vacancy to a solute atom.

A type of defect known as a helical dislocation can be formed when dislocations in the screw orientation absorb vacancies. Such helices are found to be most stable in alloys, and the stability of this type of defect is thought to be a function of the binding energy between a vacancy and a solute atom.(5)

In bcc metals, however, until very recently there was no evidence from either annealing studies or transmission microscopy that high vacancy supersaturations could be quenched-in. Part of the reason for this may be that, in general, bcc materials have much higher melting points than fcc. This makes it difficult to achieve a sufficiently high quenching rate to produce the necessary supersaturation of vacancies, since the amount of heat that must be rapidly dissipated from the quenched sample increases with the annealing temperature. Even in Ni, a fcc metal with a moderately high melting point (1453 C), there is as yet no good evidence that vacancy clusters have successfully been quenched-in.

Another contributing factor, as pointed out by Gregory(6), may be that, while for fcc materials the energy of vacancy formation E_f and of movement E_m are roughly in the ratio 3:2, the ratio E_f:E_m for bcc metals is estimated to be closer to 4:1. Thus, vacancies are relatively much more mobile at a given temperature in bcc materials than in fcc and quenching experiments correspondingly more difficult. In addition, because of the relatively high formation energy, the original equilibrium vacancy concentration at the annealing temperature may be much lower than for the fcc metals.*

Finally, if the concentration of vacancies is intrinsically low in bcc materials, it may well be that the commonly observed interstitial impurity levels of 10 to 1000 ppm can tie up and effectively prevent clustering of the thermal vacancies generated.

Despite these difficulties, however, Lawley, Meakin, and Koo(7) have successfully quenched pure Mo single crystals from 2600 C to produce a high supersaturation of vacancies at room temperature, which on annealing at 400 C agglomerated to produce loops.

The relevance of the preceding discussion to the present program is that one of the original hypotheses advanced to explain the beneficial effect of Re additions to the ductility of the Group VI-A transition metals was the effect of Re in changing the stacking-fault energy. Now that it is known that vacancy defects can be quenched into Mo, the development of a technique for quenching vacancies into Mo-35Re would perhaps permit a comparison to be made between the stacking-fault energy of Mo and that of Mo-35Re. Furthermore, it has been observed in another phase of the Integrated Chromium Alloy Program that precipitation kinetics in Cr-35Re are very much slower than in pure Cr.(8) Comparative quenching experiments in Mo and Mo-35Re should show whether or not there is a preferential binding between the substitutional solute, Re, and vacancies that could explain this kinetic effect. Finally, it has been observed that Mo-35Re prefers different slip planes to those of unalloyed Mo. In this context, it would be interesting to know whether vacancy loops also prefer to condense on different planes in Mo and Mo-35Re. Thus, a study of vacancy-annealing processes by transmission electron microscopy could be a powerful tool in explaining the mechanism underlying several affects already experimentally verified in earlier phases of this program. The present

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* The thermal vacancy concentration, c, at temperature, T, is given by $c = e^{-E_f/kT}$

report describes a preliminary attempt to examine the feasibility of developing the appropriate techniques.

Experimental Procedures

Because of the known difficulties involved in quenching bcc materials, it is desirable to start with as few vacancy sinks (random dislocations, dislocation networks, or grain boundaries) as possible and also, in order to minimize immobilizing interactions between interstitials and vacancies, to use as pure starting material as possible. In addition, in order to attain a sufficiently high cooling rate, quenching specimens should be in the form of sheet.

Accordingly, sheet samples were prepared by cross rolling 1/2-inch lengths of 1/8-inch-diameter Mo-35Re rod donated by the Chase Brass and Copper Company. Sheet thicknesses in the range 10 to 20 mils were employed. After rolling, samples were annealed for periods of 2 to 8 hours in a hydrogen atmosphere at temperatures in the range 2100 to 2300 C, in order to produce some degree of purification. Sheet quenching samples, approximately 1 inch long by 1/2 inch wide, were then slowly heated up in a tantalum-element furnace to temperatures in the range 2400 to 2500 C, keeping the vacuum better than 2×10^{-4} mm of Hg. Specimens were annealed at the maximum temperature for periods from 5 to 20 minutes, and then were quenched into liquid tin. The specimens were dropped either mechanically or by suspending the quenching sample and a small tungsten weight by a 5- to 10-mil wire of Mo-35Re, which crept to failure at a temperature close to its melting point.

After retrieval from the molten tin, the sheet samples were cleaned (from remaining tin) in hydrochloric acid, and thin foils were prepared for transmission microscopy by electrolytic dissolution in alcohol and sulfuric acid. The foils were mounted in a tilting holder and examined in a Siemens Elmiskop 1A.

Experimental Results

The grain sizes produced by the annealing treatment prior to the quench were generally very fine (of the order of 0.2-mm grain diameter), reflecting the great difficulty of grain growth even at temperatures close to the melting point. In addition, depending on the exact history of a particular specimen, there were many instances of dislocation networks inhomogeneously distributed within the grains and also on occasions a fairly high density of random dislocations. This, unfortunately, provides a large number of grain-boundary sinks to which vacancies can diffuse during the quench. Nonetheless, in spite of these fairly severe restrictions on what might be expected, evidence was obtained that vacancies had been quenched-in. This evidence was in the form of helical dislocations, examples of which are presented in Figures A-1 and A-2.

Figure A-1(a) shows an example of a stable helix at the left-hand side of the figure and, parallel to it, several rows of dislocation loops that were probably produced by degeneration of helices. A twin is visible at the right-hand side of the figure. Figure A-1(b) shows examples of loops and helices in another area of the same foil.

Figure A-2(a) shows an area containing short left-handed and right-handed helices similar to those observed in aluminum alloys by Westmacott, et al.(9), and Figure A-2(b) shows rows of aligned loops.

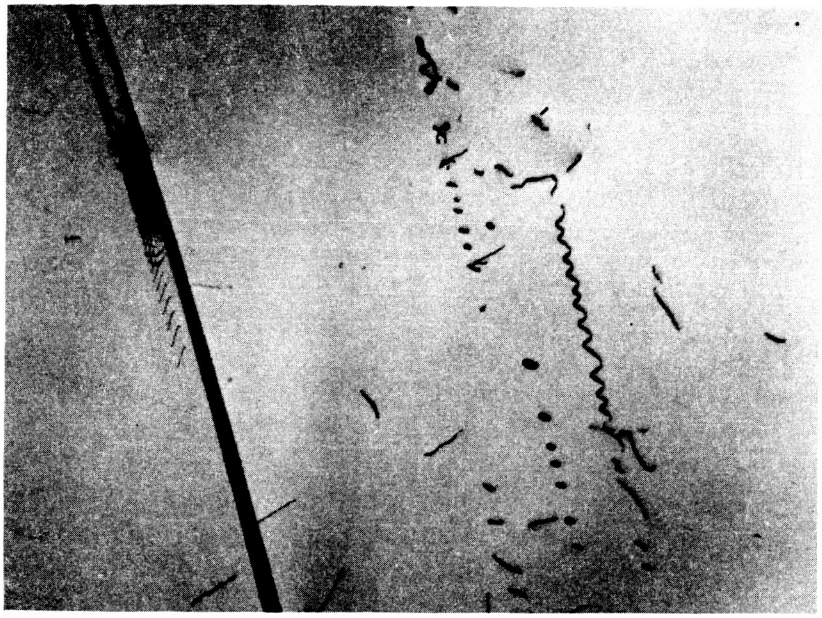
In different areas of one grain in this particular foil, helices were observed with axes lying along three different <111> directions. This is consistent with dislocations having a <111> type Burgers vector since helices are formed by the absorption of vacancies by screw dislocations, and the Burgers vector of a screw dislocation is parallel to its length. No direct determination of Burgers vector has yet been made. However, one series of photographs and associated diffraction patterns showed out-of-contrast loops under 2-beam conditions consistent with a <101> or <111> type Burgers vector, but not a <100> type Burgers vector.

The loops visible in Figure A-1 lie on {110} planes. The projected loops in Figure 2 however are sufficiently close to being circular that it is difficult to determine the major and minor axes. One {112} and two {110} type planes satisfy the geometrical considerations within experimental error.

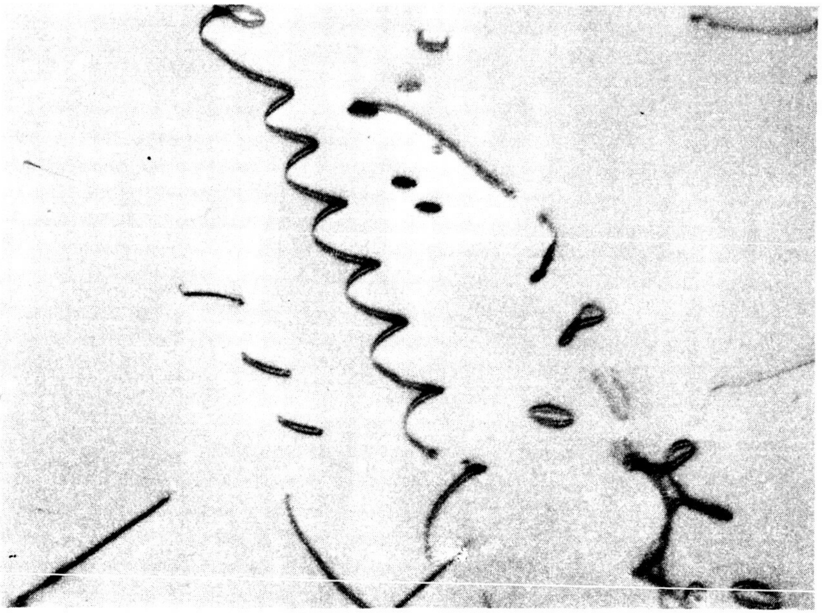
Discussion

The loops and helices shown in Figures A-1 and A-2 are thought to be the first examples of such defects observed in quenched bcc materials. The observation of helices rather than loops (as observed in unalloyed molybdenum) may be a result of a different quenching temperature as an alloy effect. It has been observed in fcc materials that helical dislocations are formed where the annealing temperature has been too low to produce a sufficiently high vacancy supersaturation for a more homogeneous loop nucleation to occur.(10) Alternatively, helices are also formed in alloys having a high binding energy between a vacancy and a solute atom.(5) Until a more complete investigation into the effect of quenching temperatures on quenched-in defects has been made, it will not be possible to distinguish between the two possibilities.

The purpose of the preliminary experiments described in this report was primarily to investigate the feasibility of using this type of quenching experiment to study the effect of Re on vacancy clustering in Mo. This has clearly been established. Experiments planned for the future will investigate the effect of prequench annealing temperatures and postquench aging temperatures on the type of defect observed.

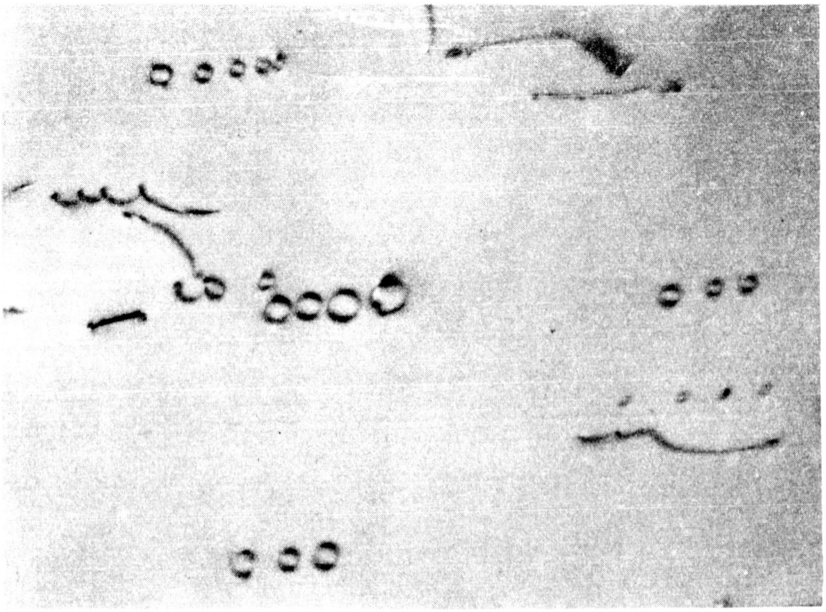


a. (15,000X)

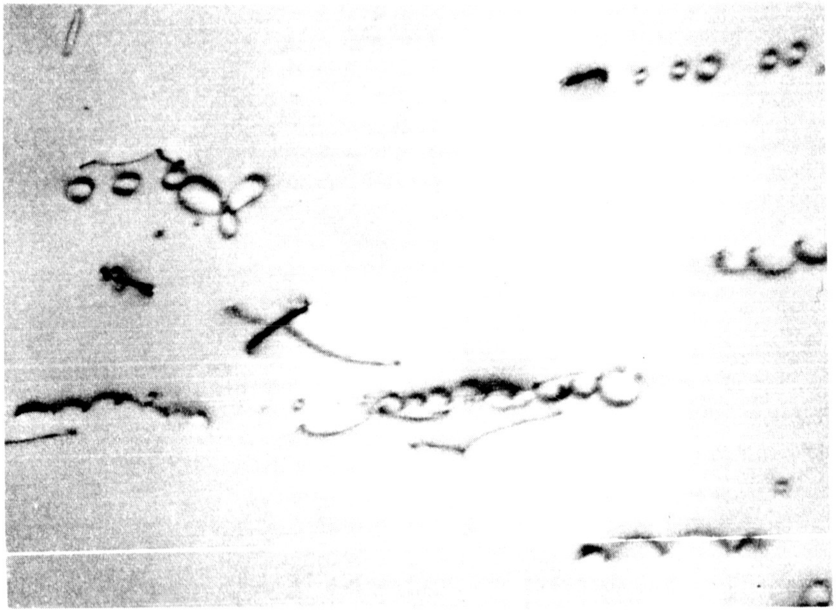


b. (30,000X)

FIGURE A-1. HELICAL DISLOCATIONS AND DISLOCATION LOOPS IN QUENCHED AND AGED Mo-35Re



a. (30,000X)



b. (30,000X)

FIGURE A-2. HELICAL DISLOCATIONS AND DISLOCATION LOOPS IN QUENCHED AND AGED Mo-35Re

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