RESEARCH ON THE EFFECT OF SELECTED RARE-EARTH SCAVENGERS ON THE PROPERTIES OF TUNGSTEN AND MOLYBDENUM

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Introduction

One of the major limitations to the engineering utilization of the refractory metals molybdenum and tungsten is the lack of ductility and fabricability at conventional metal-working temperatures. This lack of ductility is generally attributed to impurity contents of oxygen and nitrogen either as interstitials in solid solution or as grain-boundary films. Consequently, any refining technique which will remove these impurities or any processing method which would significantly alter the impurity concentration in the matrix or along the grain boundaries should result in improved ductility.

This research program is an investigation of a processing method designed to remove the interstitial oxygen and nitrogen from tungsten and molybdenum, and also to convert the grain-boundary films to less harmful forms. Minor additions of yttrium or a rare-earth metal are arc melted with the tungsten and molybdenum to act as scavengers of the oxygen and nitrogen and form stable, inert oxides and nitrides. An additional objective of the program is to achieve grain-refinement of the as-cast structure simultaneously with the scavenging action as a result of the formation of nuclei in the melt. Small-diameter ingots (7/8-inch) are melted in a continuous-casting, non-consumable electrode arc furnace using compacted powder charges. The ingots are machined and then formed into rod from which test specimens are machined. Recrystallized specimens are tested in torsion and by impact loading at various temperatures, and the ductile-to-brittle transition temperature is determined. The lowering of the ductile-to-brittle transition temperature is the criterion for ductility. Commercially produced molybdenum and tungsten rods are fabricated into test specimens to function as standards. Also, swaged and recrystallized arc-cast molybdenum, tungsten, and molybdenum -0.5 percent titanium materials are included to provide additional base-line data.

This report is the first quarterly report for the contract period 1 February 1962 to 31 July 1962 required on Research Grant No. NsG 61-60, Supplement No. 1-61, sponsored by the National Aeronautics and Space Administration. The report describes the research progress for the period 1 February to 30 April 1962.

During this report period the effort was directed toward the production and evaluation of molybdenum and molybdenum-yttrium alloys. Thirty-four additional alloys were arc-melted and fabricated into impact specimens. These new specimens, as well as previously produced impact and torsion specimens were tested over a range of temperatures and the ductile-to-brittle transition temperatures determined. Work is continuing in the evaluation of the influence of the amount of yttrium addition on the transition temperature of molybdenum.

Preparation of Specimens

A major effort was expended during the current report period in the production and preparation of impact-test specimens. Consequently, a large number of arc-cast molybdenum-yttrium, molybdenum-0.5-percent titanium, and molybdenum-lutetium ingots are presently in various stages of processing.

Thirty-four ingots were produced by melting compacted-powder charges under an inert atmosphere in the continuous-casting, non-consumable electrode arc furnace. A second arc-furnace was modified to be used as a continuous-casting furnace for the melting of the molybdenum and is presently in operation. Experience to date indicates that the additional melting capacity results in approximately a three-fold increase in the rate of ingot production.

Sixteen of the arc-cast ingots were swaged after being machined to a 5/8-inch diameter and twelve were successfully reduced to the final 5/16-inch diameter. Nine good quality ingots remain to be swaged. The 0.2- and 0.4-percent yttrium addition alloy ingots did not present any particular difficulties during swaging, and swaging losses of these ingots were relatively low. These observations are in contrast to those made earlier in the research program when considerable difficulty was experienced when the lower yttrium content ingots were swaged. The improved swageability is attributed to better preheat temperature control now achieved in the hydrogen-atmosphere furnace. The 0.5-percent titanium ingots were readily swaged to the final diameter.

A total of forty molybdenum alloy specimens have been recrystallized and machined into impact test specimens. The recrystallization was accomplished by holding the specimens for one hour at 1550C in a vacuum furnace. Details of the recrystallization procedure and furnace were given in the previous quarterly report.

Impact Testing Program

At the time of the last quarterly report, a number of cylindrical impact specimens had been produced, but had not been tested, pending fabrication of special anvils to accommodate the cylindrical specimens. The impact tests proposed were as follows:

1. impact tests on standard Charpy V-notch specimens and the 0.300-inch diameter unnotched round Charpy specimens of 1090 steel to determine the effects of specimen size and geometry.

2. impact tests on standard Charpy keyhole specimens and the 0.300-inch diameter unnotched round Charpy specimens of commercial molybdenum to check the reproducibility of the results obtained by Barr[1] and to determine the approximate ductile-brittle transition for the nonstandard molybdenum specimens.

3. impact tests on scavenged molybdenum alloys to determine the effect of various yttrium additions on the ductile-brittle transition.

The tests were performed as planned, and the results obtained to date are shown in Tables I and II.

The tests on the 1090 steel standard Charpy V-notch specimens were generally inconclusive as can be seen in Table I. A faulty heat treatment prior to the tests caused serious oxidation of the specimens, and is probably responsible for the poor results obtained.

Tests on the unnotched round nonstandard Charpy specimens were characterized by considerable scatter as shown in Table II. Examination of the specimens indicated that excessive jamming had occurred. The source of such jams was traced to the design of the standard striking tup, which incorporates a triangular "slot" of metal machined from each side. The "slots" serve to let the standard V-notch or keyhole specimens fold around the striking edge of the tup where they are caught by the flat face at the throat of the pendulum. The standard tup does not perform satisfactorily in tests on the nonstandard cylindrical specimens, however, as the specimens tend to jam between the anvils and the pendulum throat. For this reason a new tup without side slots was designed and fabricated from tool steel. The overall weight,

[1] Molybdenum Metal, Climax Molybdenum Company, 1960, p. 33.

TABLE I

IMPACT TESTS ON STANDARD CHARPY SPECIMENS
(Standard anvils and striking tup. Impact velocity: 12.75 ft. sec. $^{-1}$)

Nominal Composition	Temperature of Test C	Energy Absorbed ft. lbs.	Observations
1090 steel[1]	500	10	--
	235	4	--
	100	2	--
	100	~100	severe jamming
	25	9	slight jamming
100% Mo (comm.)[2]	500	99	bent-ductile
	450	103	" "
	400	110	" "
	375	102	" "
	350	3	brittle fracture
	200	2	" "

[1] 1090 steel specimens were standard Charpy V-notch.

[2] Molybdenum specimens were standard Charpy keyhole.

TABLE II

IMPACT TESTS ON UNNOTCHED ROUND SUBSTANDARD CHARPY SPECIMENS

(0.300-in. diameter × 2.165 in. long. Modified anvils and striking tup except where noted. Impact velocity: 12.75 ft. sec.$^{-1}$)

Nominal Composition	Temperature of Test C	Energy Absorbed ft. lbs.	Observations
1090 steel[1]	260	59[3]	severe jamming
	100	17[3]	" "
	25	8[3]	" "
	25	10[3]	" "
100% Mo (comm.)	375	52[2]	bent-ductile
	300	56[2]	" "
	268	63[2]	" "
	256	4	brittle fracture
	245	3	" "
	235	4	" "
	93	10[3]	" "
	26	2	" "
99% Mo-1.0% Y	303	3	brittle fracture
	288	6	" "
	268	9	" "
	268	2	" "
	247	2	" "
99.2% Mo-0.8% Y	262	55[2]	bent-ductile
	255	28[2]	brittle fracture
	255	1	" "
	252	56[3]	bent-ductile
	246	2	brittle fracture
	242	1	" "
	222	3	" "
	181	2	" "
	93	1	" "

TABLE II (Cont.)

IMPACT TESTS ON UNNOTCHED ROUND
SUBSTANDARD CHARPY SPECIMENS
(0.300-in. diameter × 2.165 in. long. Modified anvils and striking tup except where noted. Impact velocity: 12.75 ft. sec.$^{-1}$)

Nominal Composition	Temperature of Test C	Energy Absorbed ft. lbs.	Observations
99.4% Mo-0.6% Y	93	54[2]	jammed-faulty run
99.5% Mo-0.5% Ti	242	5	brittle fracture

[1] Tests on 1090 steel cylindrical specimens were conducted with the standard striking tup.

[2] Values of energy absorbed are not representative of fracture energy because specimens bent, but did not fracture.

[3] Values of energy absorbed are probably not correct because of faulty test, i.e. jamming etc.

and center of mass were preserved by drilling a hole of the proper dimensions in the bottom of the tup, and closing it with a plug of the correct weight. Figure 1 shows the modified tup with the standard tup for purposes of comparison. Performance of the modified tup on cylindrical specimens was entirely satisfactory.

The impact tests on the keyhole Charpy specimens machined from commercial molybdenum produced much more satisfactory results than were obtained with the steel specimens. A ductile-brittle transition was found between 350 and 375C, which agrees well with the data of Barr.[2]

Impact transition data obtained in tests on the cylindrical specimens of commercial molybdenum indicate a ductile-brittle transition temperature between 256 and 268C. The decrease in transition temperature from the standard keyhole Charpy transition range was expected. The decreased constraint of the smaller section and the absence of triaxial stresses due to notches are, of course, responsible for the lower transition temperatures observed.

The ductile-brittle transition determined for commercial molybdenum served as a starting point for similar determinations on scavenged molybdenum alloy specimens. As shown in Table II, a sharp transition was observed between 242C and 252C for the 0.8-percent yttrium specimens. Figure 2 shows the condition of the specimens after testing. The decrease of about 15 degrees centigrade from the commercial molybdenum transition indicates that the yttrium addition may have produced a slight improvement in ductility. The transition for the 1.0-percent yttrium alloy could not be determined with the five specimens available. All of the specimens failed in a more or less brittle manner, however, even at the 303C temperature, and it is probable that the yttrium content is too high.

Figure 3 is a graphical comparison of the impact data obtained on 1.0 and 0.8-percent yttrium specimens and on specimens of commercial molybdenum.

During the next report period, molybdenum specimens containing 0.2, 0.4 and 0.6-percent yttrium will be tested to determine the ductile-brittle transition for each composition. The 0.5-percent titanium composition will also be tested, and additional tests on the 0.8 and 1.0-percent yttrium additions are contemplated. It is anticipated, however, that the properties will be improved most significantly by the lower yttrium (0.2, 0.4, and 0.6 percent) compositions.

[2] Ibid, p. 33.

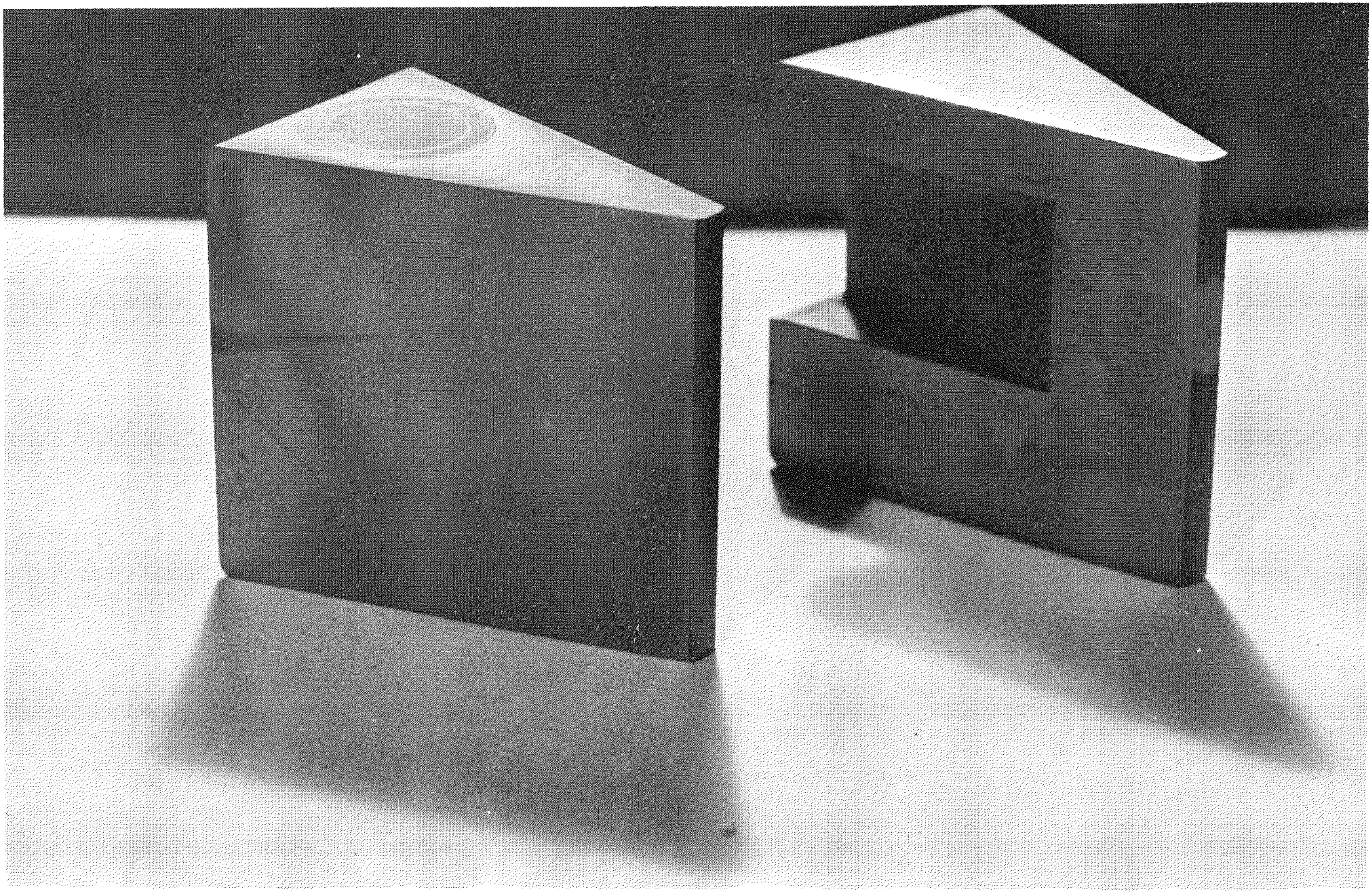

Figure 1. Modified (left) and Standard Striking Tups for the Riehle Impact Testing Machine

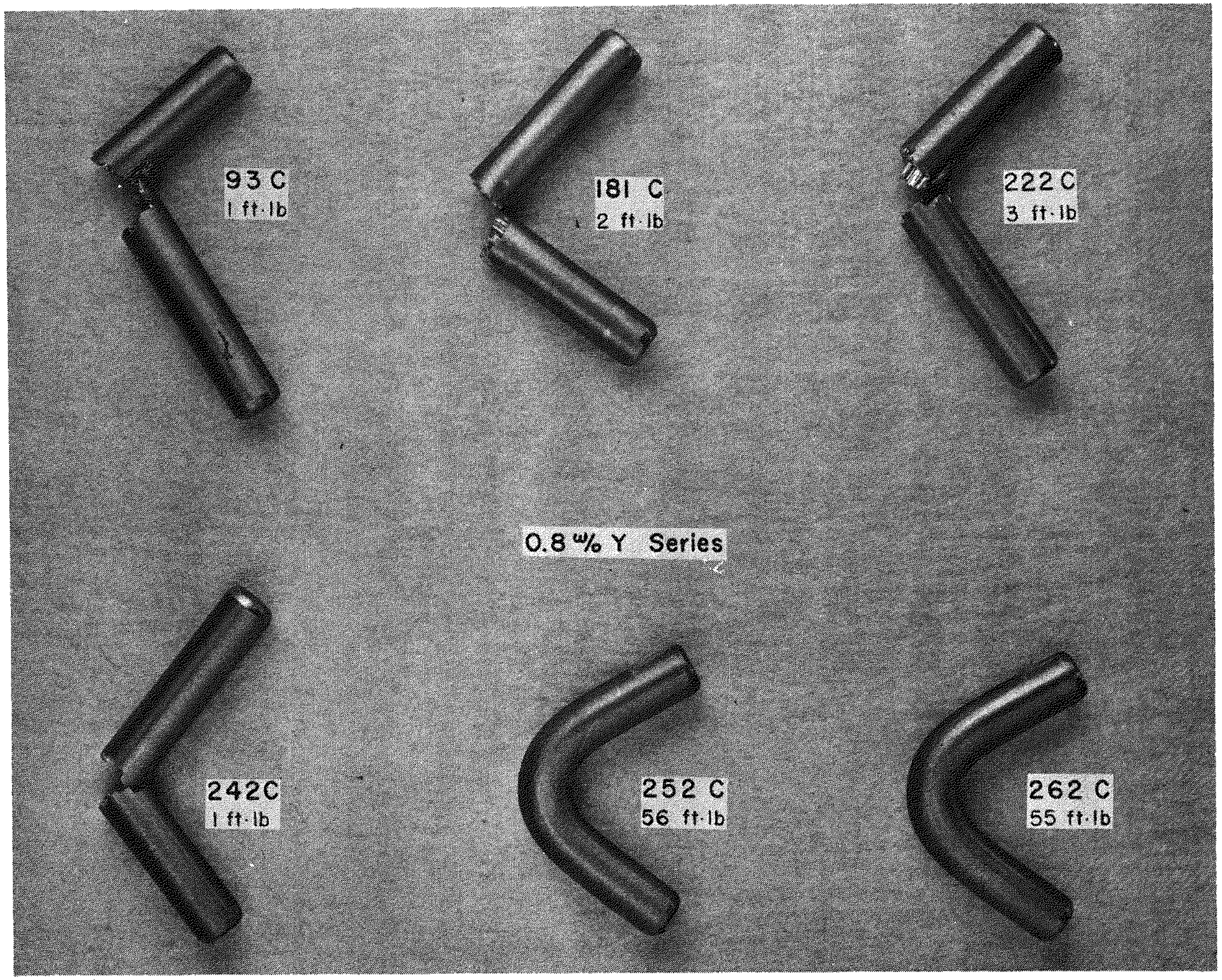

Figure 2. Photograph of the 0.8-Percent Yttrium Alloys Specimens After Testing Showing the Abrupt Ductility Transition Between 242 and 252C

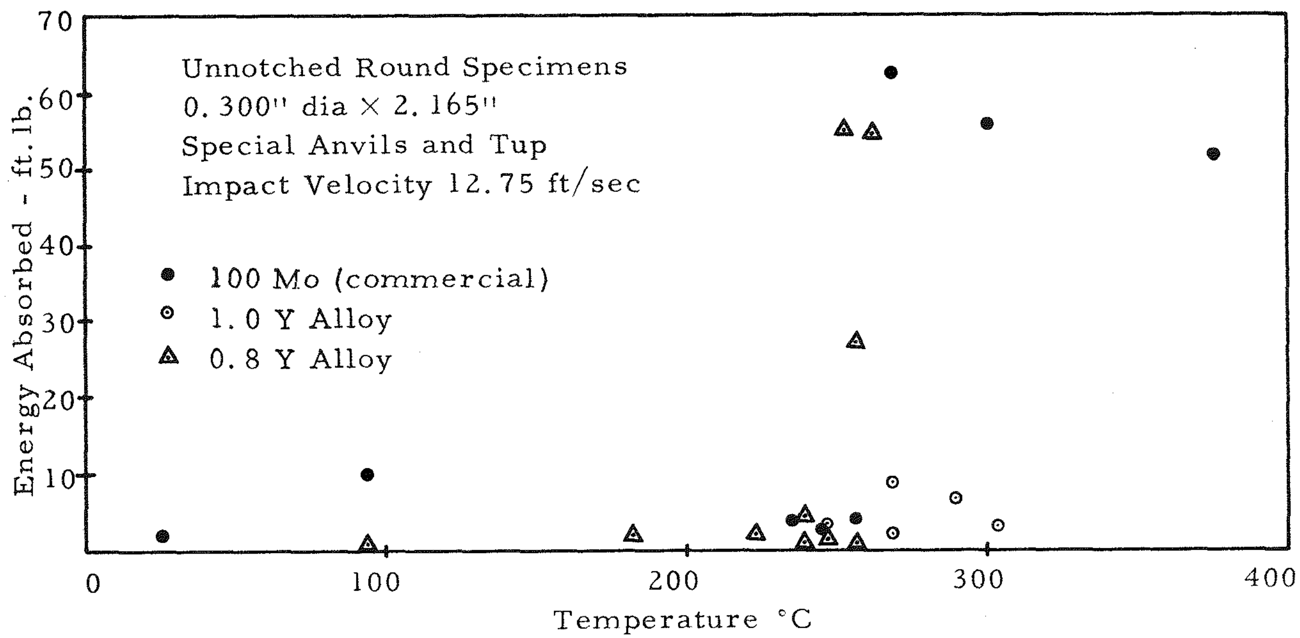

Figure 3. Comparison of Ductile-Brittle Transition of Two Molybdenum-Yttrium Alloys with Commercial Molybdenum

Torsion Testing

Two torsion specimens each of 0.6-percent yttrium, 0.8-percent yttrium and 0.5-percent titanium compositions were tested at temperatures down to -190C to obtain additional data on the ductile-to-brittle transition temperatures. The data from these tests were compared with earlier torsion data obtained on the same alloy compositions as well as 0.4-percent yttrium and commercial molybdenum materials. A summary of these torsion results is presented in Table III. It is significant that the commercial molybdenum showed considerably more ductility at -190C than any of the arc-cast and swaged molybdenum specimens. However, the differences in fabrication history and starting materials would account for these results.

To date, it has not been possible to produce unalloyed molybdenum arc-cast ingots which are of sufficient quality to yield sound torsion specimens. Consequently, the commercial molybdenum rod has been used as a standard comparison material.

The torsion data indicate that the ductile-to-brittle transition temperature of the 0.5-percent titanium alloys may be lower than the 0.6- and 0.8-percent yttrium alloys, but of the same order as the 0.4-percent yttrium alloys. However, the small number of tests which have been conducted are by no means conclusive and the results serve therefore only as a qualitative indication of the ductility characteristics of the alloys.

TABLE III
SUMMARY OF TORSION TEST RESULTS ON MOLYBDENUM ALLOYS

Spec. No.	Composition	Test Temperature, C	Rotation to Fracture, Degrees	Comments
21-B	99.5% Mo-0.5% Ti	-190	2	
38	99.5% Mo-0.5% Ti	-190	4	
3-B	99.6% Mo-0.4% Y	-190	2	
6	99.4% Mo-0.6% Y	-190	1-2	
20-A	99.2% Mo-0.8% Y	-190	1-2	
23-B	99.2% Mo-0.8% Y	-190	1-2	
$12-T_1$	99.2% Mo-0.8% Y	-190	5	
29	100% Mo (commercial)	-190	12+	(load limit of test machine reached before specimen fractured)
39	99.5% Mo-0.5% Ti	-90	180+	Ductile
3-A	99.6% Mo-0.4% Y	-90	5+	(test discontinued before fracture of specimen)
$31-T_2$	99.4% Mo-0.6% Y	-190	5-6	
28	100% Mo (commercial)	-90	180+	Ductile
$31-T_1$	99.4% Mo-0.6% Y	-15	180+	Ductile
$11-T_1$	99.2% Mo-0.8% Y	-15	24	Ductile