TECHNICAL REPORT

on

MOLYBDENUM AND MOLYBDENUM-BASE ALLOYS

PART 1. HIGH-TEMPERATURE PROPERTIES OF A MOLYBDENUM-3 PER CENT THORIUM ALLOY

PART 2. EVALUATION OF A COLUMBIUM-ZIRCONIUM-TITANIUM CLADDING ALLOY

to

DEPARTMENT OF THE NAVY
OFFICE OF NAVAL RESEARCH
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by

G. W. P. Rengstorff, G. S. Root, F. C. Holden, and R. I. Jaffee

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TABLE OF CONTENTS

Page

PART 1. HIGH-TEMPERATURE PROPERTIES OF A MOLYBDENUM-3 PER CENT THORIUM ALLOY

PART 2. EVALUATION OF A COLUMBIUM-ZIRCONIUM-TITANIUM CLADDING ALLOY

LIST OF TABLES

LIST OF FIGURES

LIST OF FIGURES
(Continued)

MOLYBDENUM AND MOLYBDENUM-BASE ALLOYS

PART 1. HIGH-TEMPERATURE PROPERTIES OF A MOLYBDENUM-3 PER CENT THORIUM ALLOY

by

George W. P. Rengstorff

INTRODUCTION AND SUMMARY

Prior to 1954, studies at Battelle on the causes of brittleness of molybdenum showed that thorium imparted unusual room-temperature ductility to molybdenum in the as-cast state(1,2)*. Initial hopes that this finding would lead to the development of ductile weldments were quickly dashed when it was found that the as-cast alloys did not have adequate strength at elevated temperatures. The as-cast molybdenum-thorium alloys immediately failed under relatively low loads at 1800 F, apparently because each grain of molybdenum was completely surrounded by unalloyed thorium, and thorium is very weak at elevated temperatures. Thus, the same condition which apparently gave rise to highly ductile cast molybdenum, i.e., ductile thorium at the grain boundaries, also led to high-temperature weakness.

Some time later, a study was initiated to determine whether some combination of fabrication and heat treatment would impart high-temperature strength to the molybdenum-thorium alloys. This study, although very limited in scope, showed metallographically that: (1) fabrication dispersed the thorium in such a manner that it would not be expected to harm the high-temperature strength of molybdenum, and (2) the molybdenum-thorium alloys were resistant to recrystallization at temperatures where unalloyed molybdenum was fully recrystallized. Details and results of this study were presented as a special report(3) on a project which had as its primary objective a study of the improvement of ductility of molybdenum by means of rhenium additions. Later, on the same project, a single test was made to determine the actual high-temperature strength of a fabricated molybdenum-thorium alloy. Although the test showed the strength to be high at 2000 F, the testing equipment failed so that no quantitative information was obtained.

Finally, in 1959, it was decided to allocate enough effort from the over-all program on studies of molybdenum to obtain a limited amount of quantitative data on the molybdenum-3 per cent thorium alloy. This report presents the results of this recent study.

The prime objective of this study was to obtain enough information to determine whether molybdenum-thorium alloys should be rejected as valueless or whether a full research program should be proposed. It was, therefore, deemed important to evaluate the molybdenum-thorium alloy by extensively comparing the new experimental data with published data on commercial molybdenum. Properties of unalloyed arc-cast molybdenum and of the arc-cast molybdenum-0.5 per cent titanium alloy** were used

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*References appear on page 31.

**Some of the literature refers to a 0.5 per cent titanium alloy, and some to a 0.45 per cent titanium alloy. This distinction is retained in references to the literature in this report although, in fact, both designations are undoubtedly referring to the same alloy.

as bases for comparison. This alloy is one of the best which has been produced commercially and complete information is available concerning its properties.

The experimental work presented in this report leads to the following comparisons:

(1) The Mo-3Th alloy is very much stronger at 1800 and 2000 F than unalloyed molybdenum.

(2) The Mo-0.5Ti alloy is appreciably stronger than the Mo-3Th alloy at 1800 F, but the alloys begin to be comparable at 2000 F. For extended periods before rupture at 2000 F and for temperatures above 2100 F, indirect evidence indicates that the Mo-3Th alloy may be stronger than this well-known high-strength alloy.

(3) At temperatures above 2200 F, the Mo-3Th alloy appears to resist softening and recrystallization better than the Mo-0.5Ti alloy.

(4) The Mo-3Th alloy is softer than other molybdenum alloys in the annealed state, and it does not work harden as much during fabrication as other alloys. Generally, the work hardening was even less than for unalloyed molybdenum. This is particularly surprising when it is realized that the Mo-3Th alloy was fabricated entirely at temperatures below 1200 F and the comparisons are made with molybdenum and Mo-0.5Ti which were rolled at 1800 F.

(5) The Mo-3Th is much softer than the Mo-0.5Ti alloy at temperatures where it has nearly equivalent strength. It thus deviates considerably from the hardness-strength relationship which was found to exist for other arc-cast alloys.

On the basis of the above comparisons and the other discussions contained in the report, it is concluded that molybdenum-thorium alloys, although not superlatively outstanding, have a unique combination of properties which warrant further research. A justifiable full-scale research program might have the following objectives:

(1) To determine whether the softness and low-temperature fabricability of the Mo-3Th alloy combined with its high-temperature strength might make it particularly suitable for rivets, bolts and other fasteners for high-temperature service, as well as for high-temperature parts requiring special machining and forming operations

(2) To determine whether the Mo-3Th alloys actually are superior to other molybdenum alloys in the 2200 to 2500 F temperature range

(3) To determine whether thorium can be combined with other alloying additions to give a truly superior molybdenum alloy.

A program having these objectives necessarily would also include a study of one of the most vexing problems concerning the alloy; that is, the need to develop a commercially usable process for making alloys containing thorium. It would also include a study of fabrication temperatures and techniques.

EXPERIMENTAL WORK*

The experimental program comprised the following operations:

(1) A 1-pound ingot was made consisting of molybdenum plus 3 per cent thorium. No carbon or other alloying element was added to the alloy.

(2) After scalping, the ingot was directly rolled and swaged at 1200 F or less to a reduction of approximately 50 per cent.

(3) The fabricated bar was cleaned, flaws removed, and recrystallized for 1/2 hour at 2600 F.

(4) The recrystallized bar was swaged at 1000 to 1100 F for a total reduction in area of 84 per cent after the recrystallization treatment.

(5) Sections of the bar which had been saved after the bar had been swaged 43, 55, 80, and 84 per cent were annealed for 1/2 hour at 2200, 2300, 2400, 2500, and 2600 F. Room-temperature hardnesses were obtained on these specimens before and after the heat treatments. They were also studied metallographically to determine evidence of recrystallization.

(6) Portions of the bar which had been swaged 84 per cent were given the following tests:

    (a) Tensile test at 1800 F

    (b) Tensile test at 2000 F

    (c) Stress-rupture test at 2000 F

    (d) Hot hardness at 1200, 1500, 1800, and 2000 F

    (e) Time-dependent hot hardness at 1800 F

    (f) Time-dependent hot hardness at 2000 F.

(7) From the information obtained in Item (6), strength parameters (Larson-Miller) were determined and comparisons made with unalloyed molybdenum and the Mo-0.5Ti alloy.

Preparation of the Ingot

Unlike other molybdenum alloys, molybdenum-thorium alloys form a slag during arc melting. This slag is a thin, tenacious oxide film which neither the arc nor melting metal breaks, once enough of the slag has developed to completely cover the surface of the melt. Therefore, when an ingot has been built up to a critical thickness during arc melting, the continuity of the ingot is broken by a layer of this slag. The new metal is melted on top of the slag, so that the final ingot has serious periodic flaws caused by layers of oxide.

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*Experimental data may be found in Battelle Laboratory Record Book No. 13,322.

A solid ingot can be formed by the process used in this work which was:

(1) The molybdenum was partially prepurified to minimize its oxygen content, and hence to minimize the amount of slag. For the ingot prepared here, fabricated molybdenum rod prepared by the powder-metallurgy process (hence low in carbon) was arc melted as a consumable electrode at a measured pressure of less than 0.1 micron.

(2) The purified molybdenum ingot was crushed and melted with turnings from a Mo-10Th alloy which had been made previously under high-purity conditions. By melting very slowly in argon using a nonconsumable tungsten electrode, it was possible to build up three ingots of the Mo-3Th alloy weighing 1 to 1-1/4 pounds each before the slag prevented further buildup. No tungsten was observed to be lost during this melting operation. The ingots were each approximately 1 to 1-1/4 inches high and about 2 inches in diameter with a partially rounded bottom.

(3) The ingots were scalped and ground to remove slag from the top, sides, and bottom before they were each cut into half-cylinders.

(4) Five of the half-cylinders were welded together to form a rough rod for arc melting as a consumable electrode.

(5) The electrode was melted at a pressure of less than 0.1 micron into a mold 1-5/8 inches in diameter.

(6) As is usual in the preparation of molybdenum-thorium alloys, the arc voltage was extremely low, less than 5 volts, apparently because of the low energy required to emit electrons from thorium or thorium oxide. This, plus the small amount of slag which formed during melting caused the ingot to be poorly melted. It was possible, however, to scalp to an ingot 1.185 inches in diameter, 2-1/2 inches long, and weighing 410 grams, which had only a few flaws.

Fabrication to Break Down the Ingot

Previous work had shown that the Mo-3Th alloy could be fabricated at 1000 to 1200 F. Little was known about optimum fabrication conditions except that rolling the as-cast alloy at temperatures above 1800 F caused severe cracking, apparently for the same reasons that the alloy failed in tensile tests at the same temperature.

All previous fabrication of the alloy had been done by flat rolling directly from the as-cast state. Because bar was desired from this ingot, however, it was necessary to choose some other technique. Swaging was preferred, but available equipment could not handle the large size of the initial ingot. An effort was therefore made to reduce the ingot in shaped rolls of the type normally used for rolling steel. These rolls impart rather severe working to the bars, and a few passes of the Mo-3Th alloy showed them to be too severe. The sound parts of the ingot remaining after this treatment were machined to a diameter of 0.75 inch and swaged at 1000 to 1100 F to a diameter a little over 0.65 inch.

It is estimated that the total reduction of area resulting from both the rolling and swaging operations was about 50 per cent. The hardness at this stage was 226 VHN.

Recrystallization

Previous work had indicated that 15 minutes at 2600 F would fully recrystallize a molybdenum-thorium alloy. Actually, as subsequent metallographic observation showed, 30 minutes at 2600 F, the time and temperature used for this ingot, did not quite complete recrystallization. A few patches of fine, apparently distorted grains remained.

Prior to this recrystallization treatment, the bar was filed to remove the oxidized surface and most of the flaws remaining from the severe rolling operation. The recrystallization treatment was made on the bar after sealing it in an evacuated quartz tube. The tube was placed in a furnace at 2600 F, timed from the time the bar appeared to reach furnace temperature, removed from the furnace, and cooled in air in the quartz tube.

The hardness after this treatment was 191 VHN. This is harder than the 174 to 184 obtained later when bars were again annealed at 2600 F for 1/2 hour after being swaged various amounts.

Final Swaging

The recrystallized bar was swaged from 0.625 inch to a final diameter of approximately 0.25 inch for a total reduction of area of 84 per cent. Between swaging passes, it was placed in a furnace at 1100 F for very short periods. Occasional checks with Tempilstix indicated the temperature of the bars to be over 1000 F when they entered the swager.

Specimens were removed for hardness and recrystallization tests at reductions of 43, 55, 80, and 84 per cent.

Annealing and Recrystallization Treatments

Earlier studies had shown that no observable recrystallization occurred in 15 minutes at temperatures of 2200 F and below, and that recrystallization was apparently completed in 15 minutes at 2600 F. The swaged specimens in this study were therefore annealed for 1/2 hour at 2200, 2300, 2400, 2500, and 2600 F. The resulting specimens were observed metallographically and their hardness determined.

Specimens were encapsulated in quartz tubes for the annealing tests.

Hot-Hardness and Time-Dependent Hot-Hardness Tests

The 0.25-inch-diameter bars (84 per cent reduction) were ground flat on opposite sides and tested in a hot-hardness tester which operated in a vacuum. Initially, indentations were made wherein the load was applied for 15 seconds at 1200, 1500, 1800, and 2000 F. Hardness tests were made at room temperature before and after this series of tests. Later, the same specimens were given time-dependent hot-hardness tests at 1800 and 2000 F. In these tests, the load was applied for 5, 80, 500, and 2000 seconds at each temperature. The hardness was again checked at room temperature after this series of tests.

Hot-Tensile and Stress-Rupture Tests

Temperature-dependent and time-dependent hot-hardness data, combined with a limited number of tensile and stress-rupture tests, can give considerable information about the high-temperature strength properties of a material.(4) This combination of tests was ideal for a preliminary study of this sort where the maximum amount of information was needed for minimum effort, but engineering data were not required.

It was decided that it would be possible to make three tensile or stress-rupture tests. These could be readily made at 1800 F, and with only a little more difficulty at 2000 F. Tests at higher temperatures would have been considerably more difficult. Also, the hot-hardness tests had been limited to 2000 F because of experimental difficulties. It appeared best to make the three tests as follows:

(1) A tensile test at 1800 F.

(2) A tensile test at 2000 F.

(3) A stress-rupture test at 2000 F, where the load would be adjusted so that failure would occur before 100 hours. This load would be selected from the analysis of the hot-hardness and tensile data.

As will be discussed later, the alloy had a tensile strength of 49,700 psi at 1800 F and 44,700 psi at 1980 F (the 2000 F test). From this, it was predicted that a load of approximately 33,000 psi would cause failure at 1000 hours. The test was made at 37,000 psi to assure failure in a shorter time. Failure occurred at 6.5 hours, well within the estimated 5 to 8 hours.

The specimens for these tests were machined from the 1/4-inch-diameter rod which had been reduced 84 per cent from the recrystallized state. The total length of each specimen was approximately 1-3/8 inches, with a thickness of 1/8 inch through the center. The gage length was taken as 1 inch, which included the length of the reduced section plus the shoulder up to the threads on the 1/4-inch section.

Results and Discussion

Effect of Fabrication

Table 1 gives the room-temperature hardness of the Mo-3Th alloy after swaging at 1000 to 1100 F for reductions of 43, 55, 80, and 84 per cent. A comparison of the hardening effect of these various reductions in area with published data on arc-cast molybdenum(5) and Mo-0.5Ti(6) is shown in Figure 1.

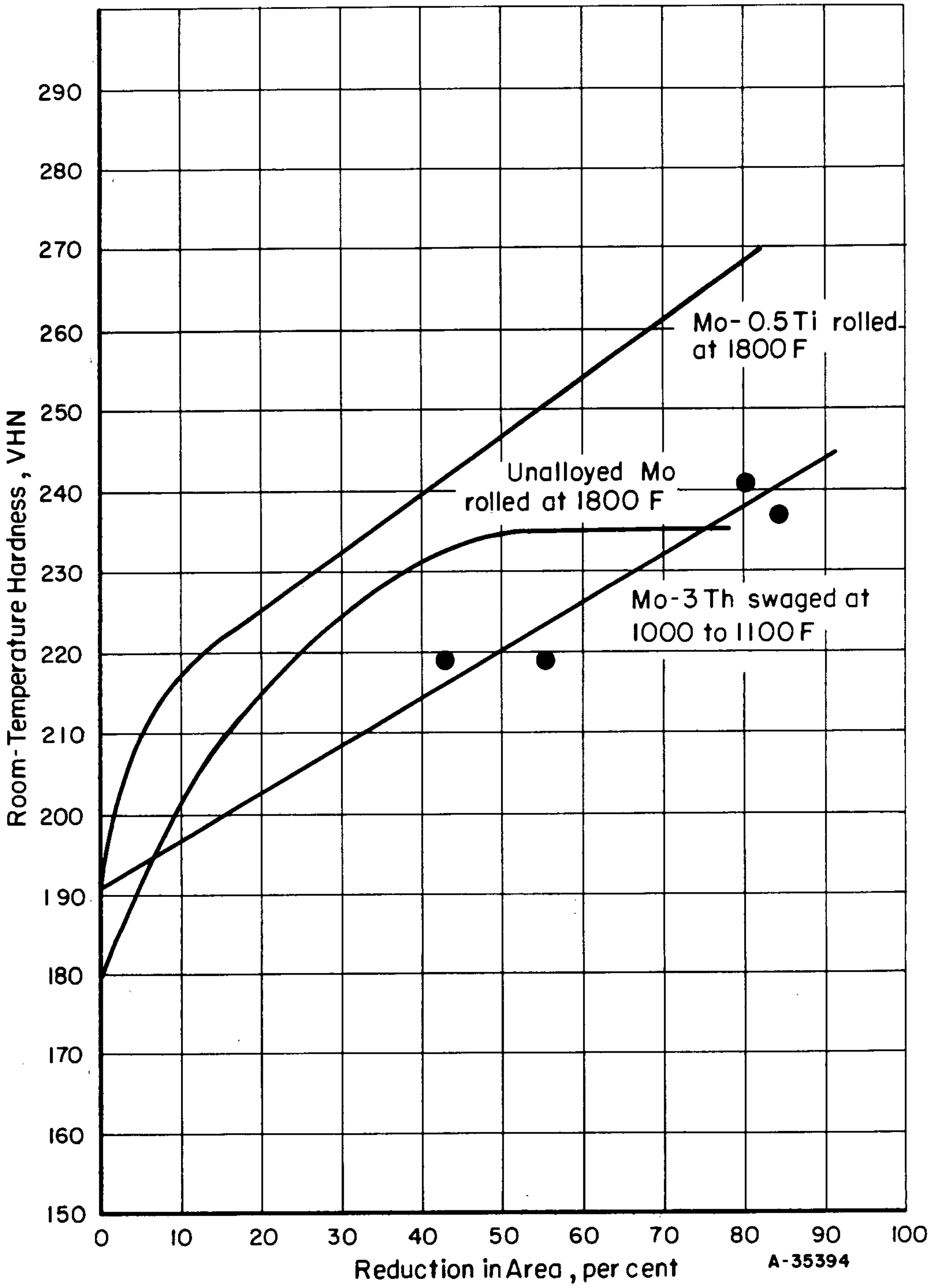

FIGURE 1. ROOM-TEMPERATURE HARDENING DUE TO FABRICATION OF Mo-3Th COMPARED WITH PUBLISHED DATA ON UNALLOYED ARC-CAST MOLYBDENUM(5) AND THE Mo-0.5Ti ALLOY(6)

TABLE 1. HARDNESS OF THE MOLYBDENUM-3 PER CENT THORIUM ALLOY AS SWAGED AND AFTER ANNEALING AT 2200 TO 2600 F

	Hardness, VHN			
Heat Treatment	Reduced 43 Per Cent	Reduced 55 Per Cent	Reduced 80 Per Cent	Reduced 84 Per Cent
As swaged[(a)]	219	219	241	237
2200 F 1/2 hr, air cool	205	205	216	231
2300 F 1/2 hr, air cool	204	203	216	224
2400 F 1/2 hr, air cool	201	201	205	210
2500 F 1/2 hr, air cool	199	185	187	195
2600 F 1/2 hr, air cool	184	180	174	179

(a) Before swaging, the alloy was rolled and swaged for a reduction of area of approximately 50 per cent. The hardness at that time was 226 VHN. It was then recrystallized by heating to 2600 F for 1/2 hr. Subsequent metallographic observation showed that recrystallization was not quite complete. The hardness after this treatment was 191 VHN.

The most striking difference between the Mo-3Th alloy and the Mo-0.5Ti alloy is that the thorium-containing alloy is so much softer at any given reduction. Both show a continuous increase in hardness with increasing amounts of work as contrasted with the unalloyed molybdenum. The latter reaches a peak hardness at about 50 per cent reduction, after which the hardness is not increased by additional working. A possible explanation for part of the difference is that the unalloyed molybdenum was being worked at a temperature within its recrystallization range, whereas neither of the alloys are recrystallized at their working temperature even after severe deformation.

An important point to keep in mind is that the Mo-3Th alloy was fabricated at 1000 to 1100 F, and that the results are compared with those for unalloyed molybdenum and Mo-0.5Ti fabricated at 1800 F. It is undoubtedly true that even the unalloyed molybdenum would have been much harder after all amounts of fabrication if it had been fabricated at such a low temperature.

Effect of Annealing Temperature

The room-temperature hardness values of the Mo-3Th specimens after annealing 1/2 hour at 2200, 2300, 2400, 2500, and 2600 F are given in Table 1. Also included are the previously discussed data on the effect of swaging on hardness. These data are plotted in Figure 2 to show the effect of amount of fabrication on softening as a result of annealing. Most of the points fall in logical sequence, with a lower amount of working resulting in a lower hardness up to 2400 F. At higher temperatures, where the greater amount of work should cause earlier recrystallization, some of the curves should and do cross.

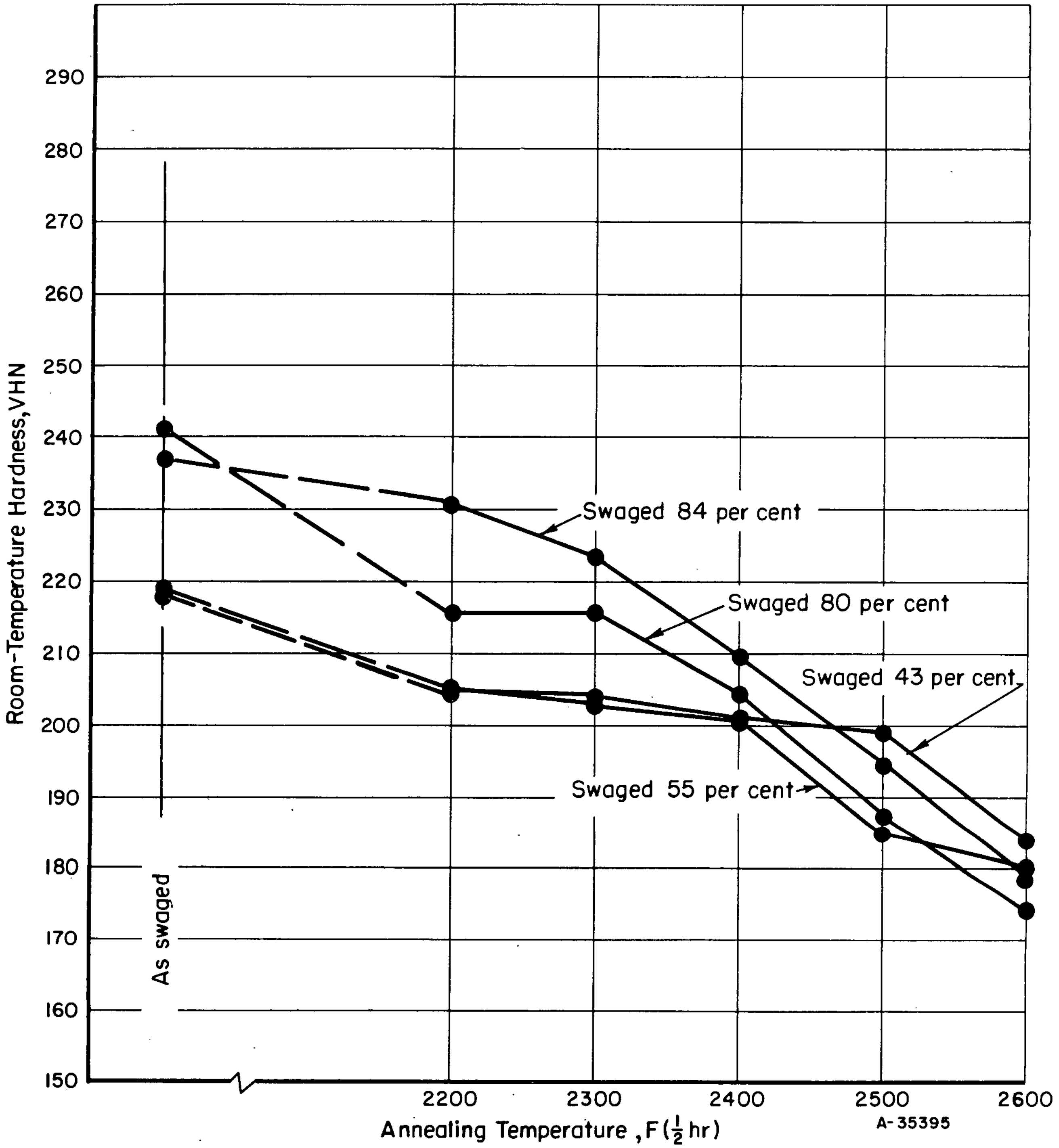

FIGURE 2. EFFECT OF ANNEALING 1/2 HOUR AT 2200 TO 2600 F ON THE HARDNESS OF Mo-3Th ALLOY SWAGED AT 1000 TO 1100 F TO VARIOUS REDUCTIONS IN AREA

There are a few inconsistent points on the set of curves, but the data are not believed to be precise enough to give more than a general pattern. More detailed explanations should await more complete studies to determine the true significance of the deviations observed.

Figure 3, wherein the data on the Mo-3Th alloy are compared with published data on unalloyed molybdenum and the Mo-0.5Ti alloy, is particularly important. These curves show that the unalloyed molybdenum is essentially fully annealed and recrystallized at 2100 F, a temperature which has little effect on either the Mo-3Th or the Mo-0.5Ti alloys.

Furthermore, these curves show that the high-strength Mo-0.5Ti alloy has lost most of its work-induced hardness at 2400 F, and that the Mo-3Th has suffered much less, comparatively, by treatment at that temperature. If this effect on hardness reflects the high-temperature strength, it appears that the Mo-3Th alloy would be superior at temperatures around 2300 to 2500 F. This is a possibility which would be well worth studying in more detail.

Temperature-Dependent Hot Hardness

The hardness of the Mo-3Th alloy which had been swaged 84 per cent was determined at room temperature, 1200 F, 1500 F, 1800 F, and 2000 F; the results are given in Table 2. These results are plotted in Figure 4 along with published data(7) for the as-rolled Mo-0.45Ti alloy and unalloyed molybdenum in both the as-rolled and annealed state. The fact that the fabricated Mo-3Th alloy up to at least 1600 F is appreciably softer than unalloyed molybdenum in a fabricated state is very apparent from these curves. The ability of the Mo-3Th alloy to be fabricated readily at temperatures around 1000 F is undoubtedly affected by this factor.

It is most probable that a hot-hardness plot extending to higher temperatures would show the curve for the as-rolled unalloyed molybdenum dropping below that of the Mo-3Th alloy somewhere between 1800 and 2100 F. It is also likely that the Mo-0.45Ti curve would drop slightly below the Mo-3Th curve somewhere around 2200 to 2400 F before they leveled off together at around 2600 F.

Time-Dependent Hot Hardness

The effect of time of indentation at 1800 and 2000 F on the apparent hardness of the Mo-3Th alloy is given in Table 2. As pointed out by Underwood(4), the time-dependent data can be used to extend the knowledge of high-temperature strength properties of an alloy into regions where ordinary hot-hardness data cannot be obtained. In particular, it substitutes time for temperature and thus, in effect, extends hardness data to temperatures above the maximum of the equipment. In addition, it allows time for recrystallization and other strength-changing phenomena to occur. The time-dependent hardness data bear the same relationship to normal short-time hardness data that stress-rupture data bear to hot-tensile-test data.

The data from the time-dependent hardness tests are used later in this report in discussions about high-temperature strength parameters.

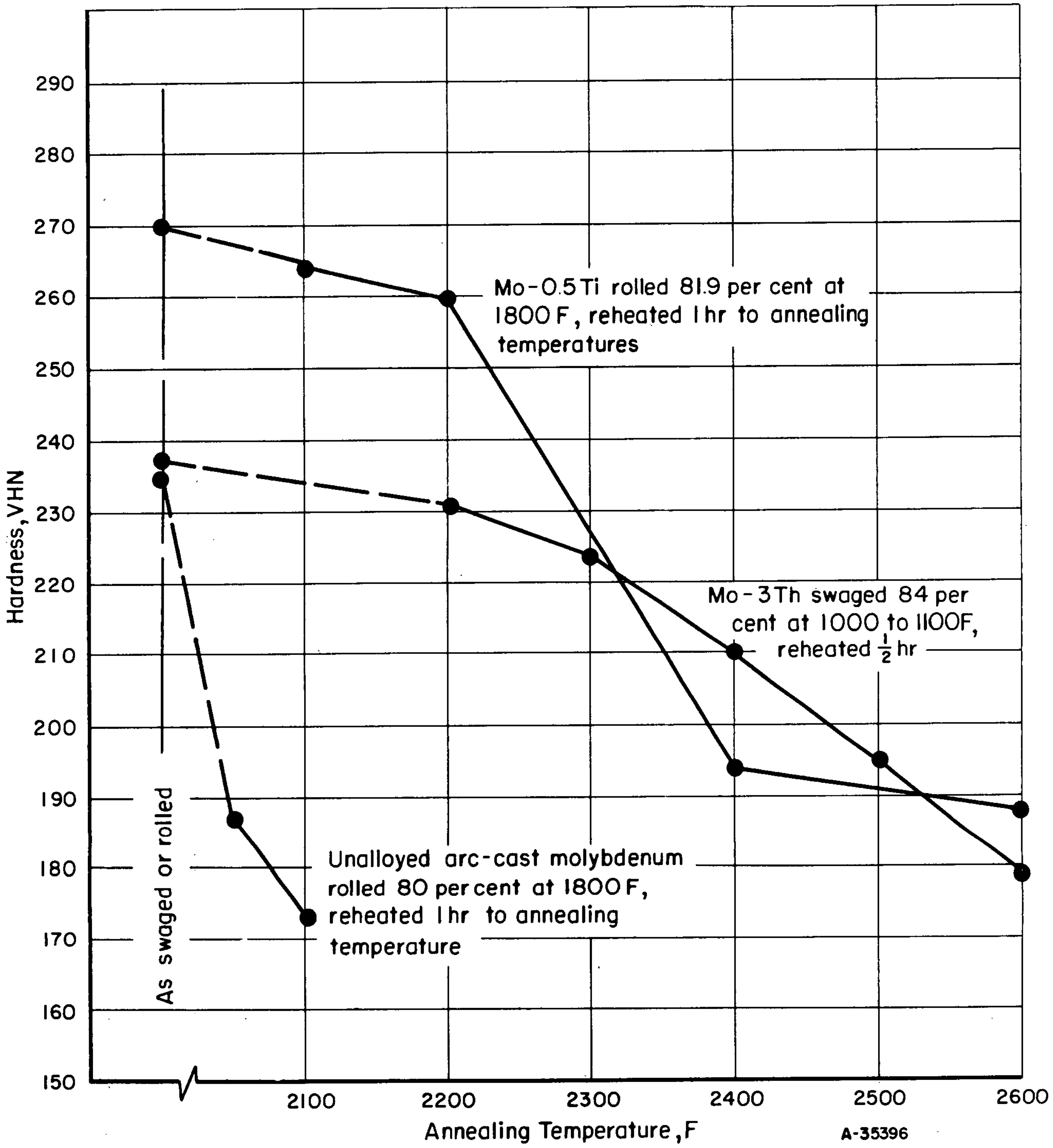

FIGURE 3. THE EFFECT OF ANNEALING TEMPERATURE ON THE HARDNESS OF A SWAGED Mo-3Th ALLOY COMPARED WITH PUBLISHED INFORMATION ON ROLLED UNALLOYED ARC-CAST MOLYBDENUM(5) AND ROLLED ARC-CAST Mo-0.5Ti ALLOY(6)

TABLE 2. HOT HARDNESS OF THE MOLYBDENUM-3 PER CENT THORIUM ALLOY AS FABRICATED

Test Temperature, F	Time of Indentation		Average Hardness, VHN
	Seconds	Hours	
1200	15	0.0042	107
1500	15	0.0042	90.3
1800	5	0.0014	80.5
	15	0.0042	81.0
	80	0.022	77.1
	500	0.14	67.6
	2000	0.56	64.5
2000	5	0.0014	68.1
	15	0.0042	69.1
	80	0.022	57.9
	500	0.14	51.9
	2000	0.56	46.5
Room Temperature (77 F)			
Before hot testing	15	0.0042	234
After testing at constant time (15 sec) up to 2000 F	15	0.0042	230
After time-dependent hardness testing at 1800 and 2000 F	15	0.0042	220

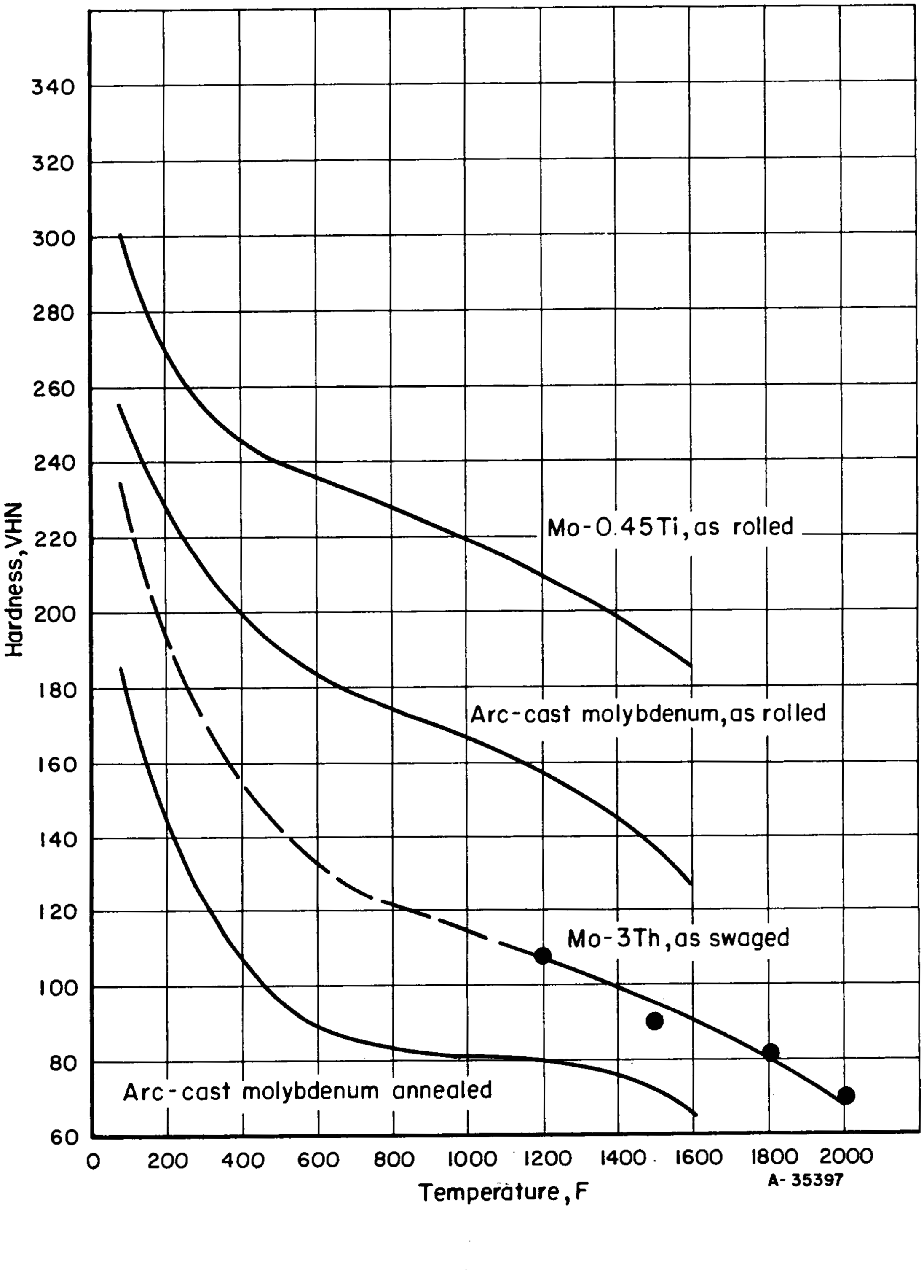

FIGURE 4. EFFECT OF TEMPERATURE ON THE HOT HARDNESS OF THE Mo-3Th ALLOY AS SWAGED COMPARED WITH PUBLISHED DATA(7) ON THE HOT HARDNESS OF ARC-CAST MOLYBDENUM AND Mo-0.45Ti ALLOY AS ROLLED AND ON ARC-CAST MOLYBDENUM IN THE ANNEALED STATE

Tensile and Stress-Rupture Properties

Table 3 gives the hot-tensile and stress-rupture properties of the Mo-3Th alloy. The elongations and reductions of area of the various specimens were generally comparable with those of other molybdenum alloys. The fact that they are on the low side of the general range of alloys may be a characteristic property of the alloy. More probably, it is the result of use of miniature specimens and the fact that the gage length which was used also included the thicker shoulders which did not deform during the test.

The strength properties of the alloy given in Table 3 are discussed in the following section of this report.

TABLE 3. TENSILE AND RUPTURE STRENGTH AND DUCTILITY OF THE MOLYBDENUM-3 PER CENT THORIUM ALLOY AS FABRICATED

Temperature, F	Stress to Rupture, psi	Time to Rupture, hours	Elongation, %	Reduction of Area, %
		Tensile Tests		
1800	49,700	~0.0014	8	72
1980	44,700	~0.0014	11.8	42
		Stress-Rupture Test		
2000	37,000	6.5	19.1	45.3

Table 4 gives the stress-rupture properties of the Mo-0.5Ti alloy which were selected from the literature(8,9) for comparison with those of the Mo-3Th alloy. Only data on specimens which actually failed in testing are given here. Data for specimens on which the test was discontinued before failure do not provide the time-temperature-stress relationships from which comparisons between the materials can be made. They are valuable, however, for estimating engineering properties of the alloys.

Stress (and Hardness)-Time-Temperature Relationships

A number of relationships have been proposed for relating the effects of time and temperature with the load-carrying ability of various materials. One of the more generally used of these relationships was that developed by Larson and Miller(10). They proposed the semiempirical relationship of:

$$P = T(C + \log t).$$

TABLE 4. PUBLISHED STRESS-RUPTURE DATA ON THE Mo-0.5 Ti ALLOY IN THE STRESS-RELIEVED CONDITION AND IN THE RECRYSTALLIZED CONDITION(8,9)

Temperature, F	Temperature, R	Stress, psi	Rupture Time, hr	P[(a)] (C = 14.3)
		Worked and Stress Relieved		
1400	1860	70,000	254.7	31,100
1600	2060	85,000	0.5	28,800
1600	2060	75,000	18.2	32,100
1600	2060	70,000	138.0	33,800
1600	2060	65,000	171.0	34,000
1800	2260	70,000	1.0	32,300
1800	2260	60,000	27.5	35,500
1800	2260	55,000	94.6	36,800
1800	2260	50,000	227.9	37,700
1800	2260	48,000	550.0	38,400
2000	2460	70,000	0.2	33,500
2000	2460	50,000	6.7	37,100
2000	2460	30,000	257.2	41,100
2000	2460	27,000	501.2	41,800
		Recrystallized Condition		
1600	2060	40,000	1.7	29,900
1600	2060	35,000	74.9	33,400
1600	2060	34,000	223.0	34,200
1800	2260	35,000	0.35	31,200
1800	2260	31,000	3.9	33,000
1800	2260	29,000	82.3	36,600
2000	2460	30,000	0.3	33,900
2000	2460	25,000	4.4	36,700
2000	2460	20,000	221.1	40,800
2400	2860	5,000	258.9	47,700

(a) $P = T(C + \log t)$.

In this relationship, P is the strength parameter, T is the absolute temperature which by convention is in degrees Rankine, C is a constant which Larson and Miller took to be about 20 but the value of which has been shown to be dependent upon the material. This strength parameter was applied to unalloyed molybdenum by Pugh(11). Recently Green, Smith, and Olson(12) have added data to that of Pugh.

It has long been known that a relationship existed between hot hardness and hot tensile properties of alloys. Underwood(4) showed that the Larson-Miller relationship held for the time-temperature dependence of hot hardness as well as the time-temperature dependence of hot strength. He also showed that it was possible to compare the readily obtained time-temperature dependence curve for hot hardness with at least two points for hot strength, and from such information, to plot a reasonably good curve for the range of hot-strength properties. This was the approach used in this study.

Pugh(11) in plotting his data determined the value of C for unalloyed molybdenum to be 13.9. Green, Smith, and Olson(12) obtained a value for C of 15.8 as the best fit for their own higher temperature data and determined that a value of 14.3 best fit the combined data of the two investigations. Actually, the scatter of the various points would allow any of these values to be used without much question. The intermediate value of 14.3 has therefore been taken as reasonable for comparison purposes.

Figure 5 shows the strength versus strength parameter (P) line for unalloyed molybdenum for C = 14.3. Also plotted are the data for (1) Mo-0.5Ti in the worked and stress-relieved condition as given in Table 4, (2) Mo-0.5Ti in the recrystallized condition as given in Table 4, and (3) Mo-3Th in the as-swaged condition as given in Table 3.

These data show a definite break in the curve showing the properties of the Mo-0.5Ti alloy at about P = 38,000 to 42,000 in both the stress-relieved (fabricated) and the recrystallized conditions. This break might be associated with recrystallization, although it occurs before recrystallization is observed. If, as is generally believed, the high strength of this alloy is the result of a dispersion (precipitation hardening) effect, it is possible that the change in slope is the result of a beginning of solution of the precipitate. Recrystallization might then occur when solution is essentially complete.

The fact that the slope of the strength curve for the Mo-3Th alloy is considerably different from both those of unalloyed molybdenum and the Mo-0.5Ti alloy in either fabricated state is of importance. The Mo-3Th alloy does not lose strength with an increase in temperature or time nearly as fast as either of the latter two commercial materials.

The location of a break in the curve for the Mo-3Th alloy is of considerable importance in evaluating its properties, as is the slope of the curve after the break. The fact that recrystallization effects apparently occurred at a higher temperature (Figure 3) would make it appear that the drop in strength properties would also take place at a higher temperature. The fact that the drop in hardness was more gradual with increased annealing temperature indicates that the slope of the curve after the break would be more gradual. Both of these effects, if they actually exist, would indicate that the Mo-3Th alloy exhibits better strength properties than the Mo-0.5Ti alloy at temperatures above 2000 F, or at rupture times longer than 5 to 10 hours at 2000 F.

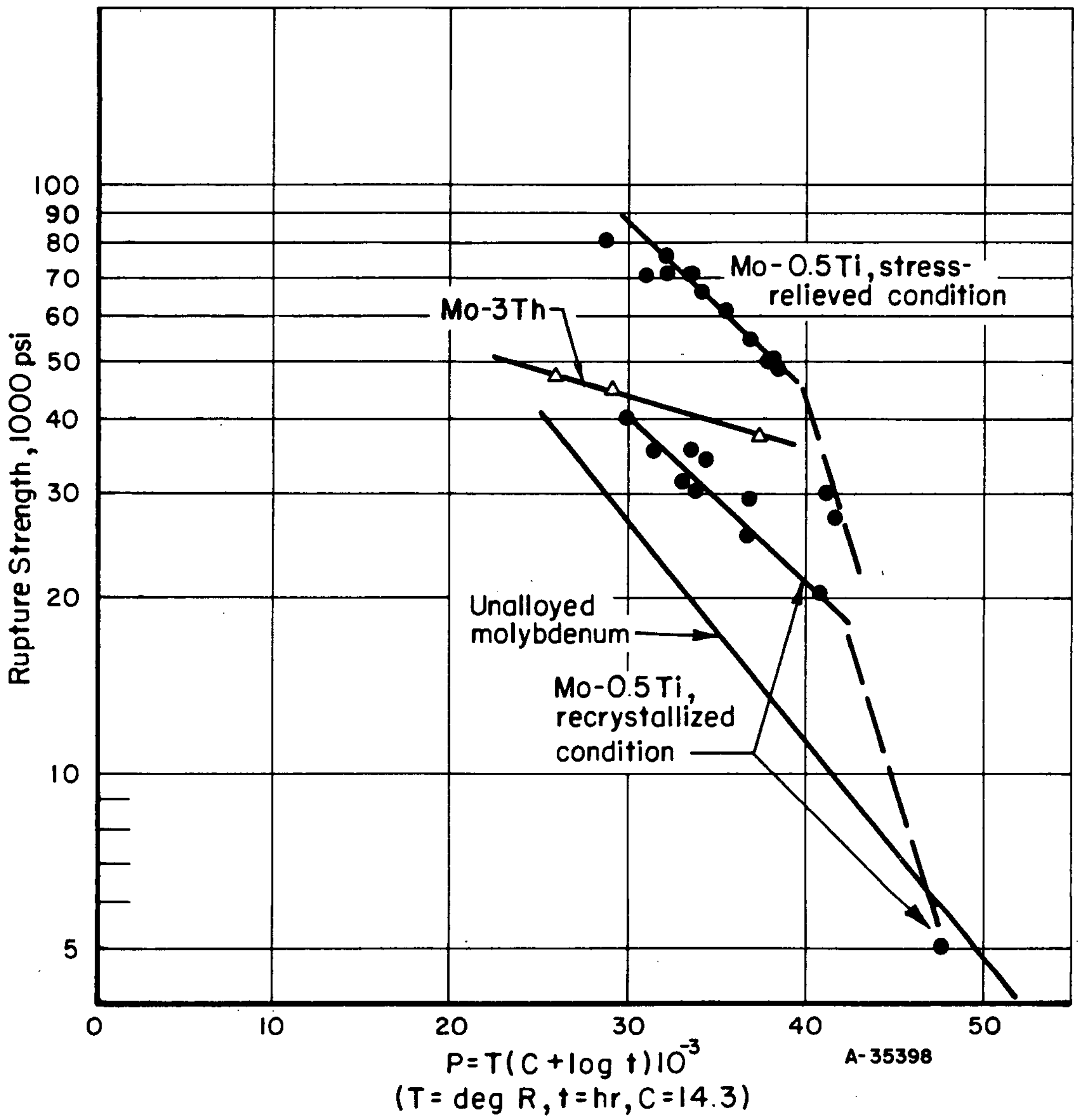

FIGURE 5. RUPTURE STRENGTH VERSUS STRENGTH PARAMETER FOR UNALLOYED MOLYBDENUM(11,12), THE Mo-0.5Ti ALLOY(8,9), AND THE Mo-3Th ALLOY

Using both the temperature-dependent and time-dependent hot-hardness data for the Mo-3Th alloy which were given in Table 2, the curve shown in Figure 6 is obtained for an assumed C value of 14.3. This shows a break in the hardness curve at a value of P of 32,000. As shown in Figure 5 and again in Figure 6, this break does not appear in the curve for the strength properties of the alloy. As discussed above, there is reason not to expect the break to occur at this point.

As shown in Figure 7, if the C for hardness is taken as a different value than it is for strength, and if the break is assumed to occur at the same P value, then the discrepancy between the hardness and rupture properties is eliminated. The C value of 22.15 used for Figure 7 was determined as the best fit for the hardness data alone. The fit was obtained largely on the basis of the time-dependent hot-hardness data at 1800 and 2000 F.

On the basis of experimental difficulties, two other possible explanations are advanced for the differences between the conclusions reached from the hardness and the strength data. Heating to 2000 F in the evacuated hardness tester might have contaminated the surface of the specimens in a manner which would give apparent softening without greatly affecting over-all strength. This possibility is substantiated by the fact that the room-temperature hardness dropped only from 234 to 230 after the temperature-hardness tests which involved only a short time at 2000 F, but dropped an additional 10 points to 220 after the longer time at 2000 F in the time-dependent tests. The other obvious possibility, i.e., that the stress-rupture life of 6.5 hours at 2000 F under a load of 37,000 psi is erroneously high, is less likely. Although factors can cause a single stress-rupture test to be too low, few cause it to be too high.

Stress-Rupture Properties

The stress-parameter curves in Figure 5 were used to plot the time versus rupture strength curves shown in Figure 8. The curves showing strength of the Mo-0.5Ti alloy at 1800 and 2000 F can be plotted directly from experimental data at these temperatures, and the experimental points are included in the figure. These two curves have essentially the same slope as the curves published by Freeman(7), and it is probable that he was also using the experimental data given in Table 4.

The stress-rupture curves for the Mo-0.5Ti alloy at 2200 F and for the Mo-3Th alloy at 1800, 2000, and 2200 F were all taken only from the stress-parameter curve. If they are correct, however, they show that:

(1) At 1800 F, the Mo-0.5Ti alloy is stronger than the Mo-3Th alloy at least for loads which cause it to fail in less than several thousand hours.

(2) At 2000 F, the Mo-0.5Ti is able to withstand greater loads than the Mo-3Th alloy for periods up to 100 hours or more. The thorium-containing alloy appears to have greater strength if the load is to be applied for longer periods.

(3) At 2200 F, the Mo-0.5Ti will resist failure under greater loads than the Mo-3Th alloy for periods of only up to 10 hours.

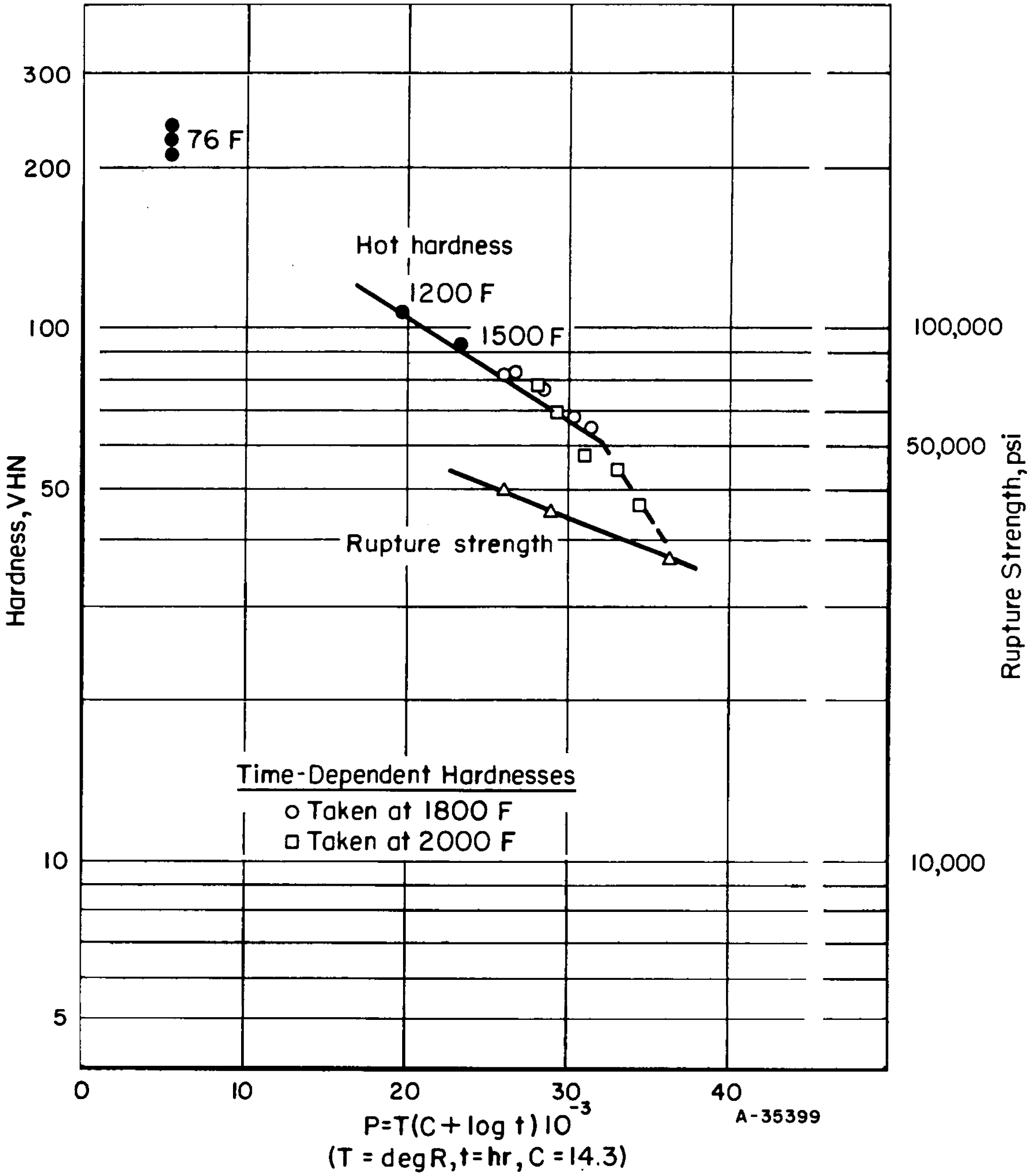

FIGURE 6. HOT HARDNESS (TIME AND TEMPERATURE DEPENDENT) AND RUPTURE STRENGTH OF THE Mo-3Th ALLOY AS A FUNCTION OF STRENGTH PARAMETER FOR C = 14. 3

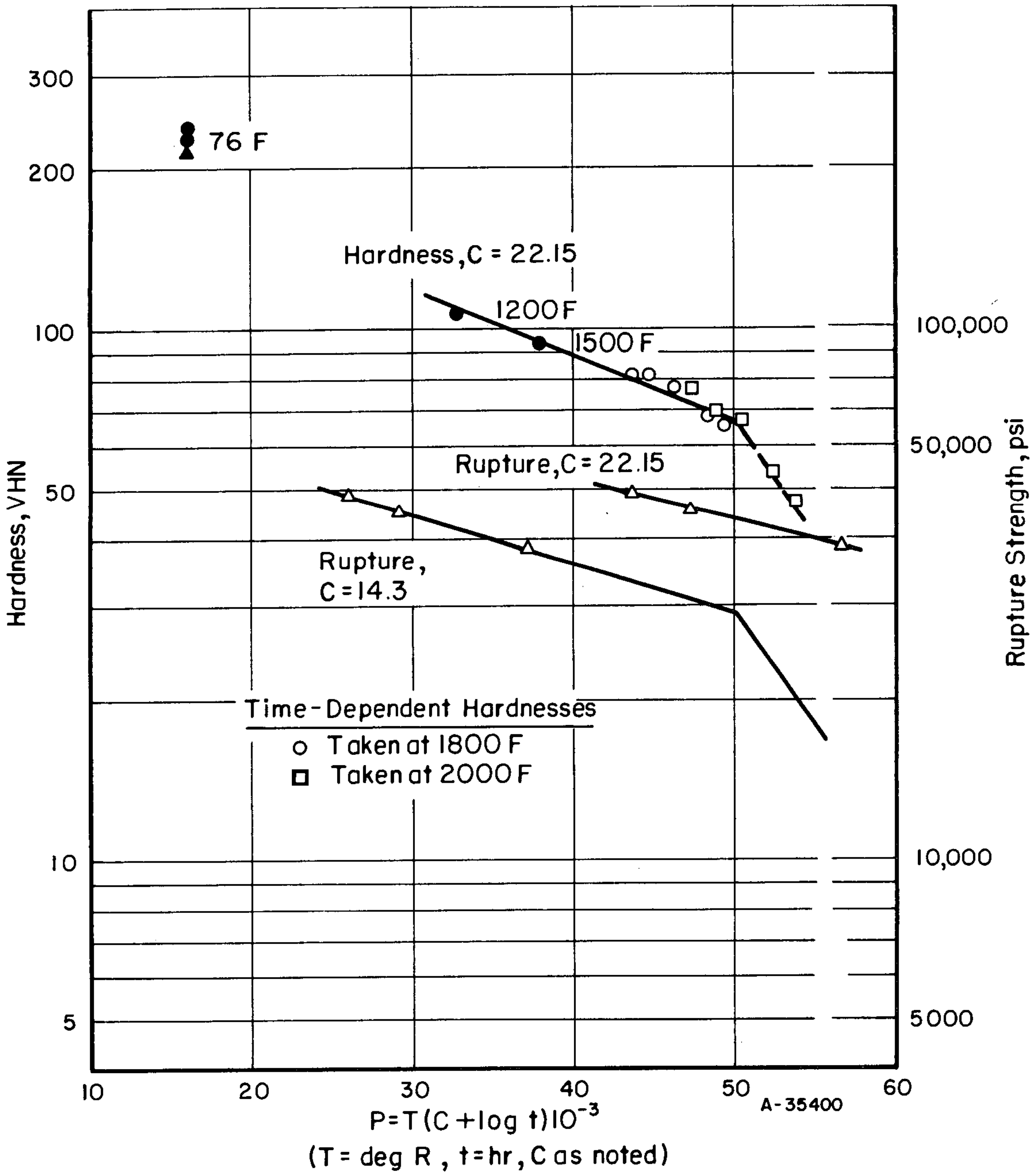

FIGURE 7. HARDNESS VERSUS STRENGTH PARAMETER FOR THE Mo-3Th ALLOY FOR C = 22.15 (BEST FIT) AND RUPTURE STRENGTH VERSUS STRENGTH PARAMETER FOR C = 22.15 AND C = 14.3

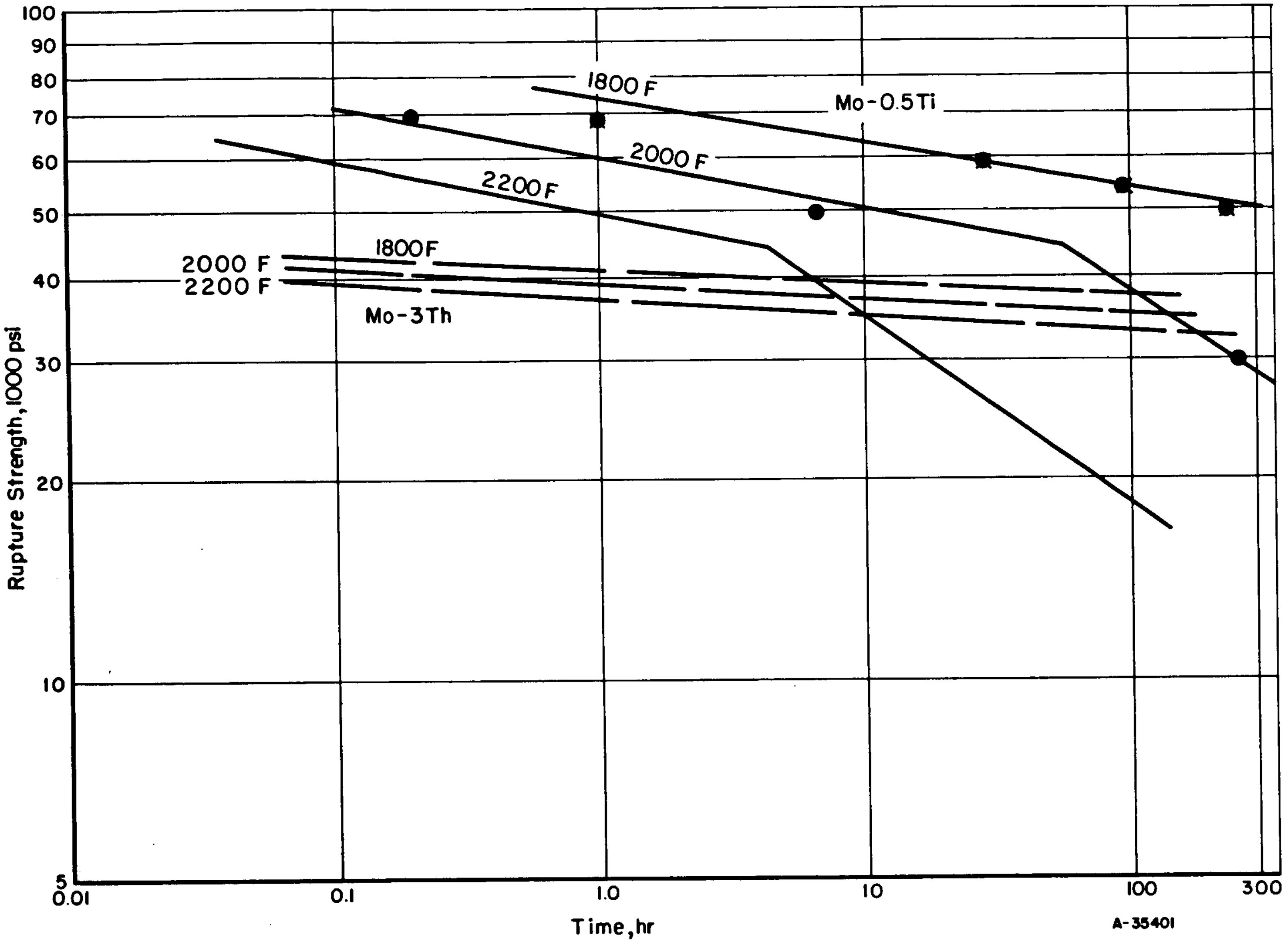

FIGURE 8. STRESS-RUPTURE CURVES AT 1800, 2000, AND 2200 F FOR Mo-0.5Ti AND Mo-3Th ALLOYS AS PLOTTED FROM THE STRENGTH PARAMETER CURVES OF FIGURE 5

Also plotted are experimental points for the Mo-0.5Ti alloy at 1800 and 2000 F from Table 4.

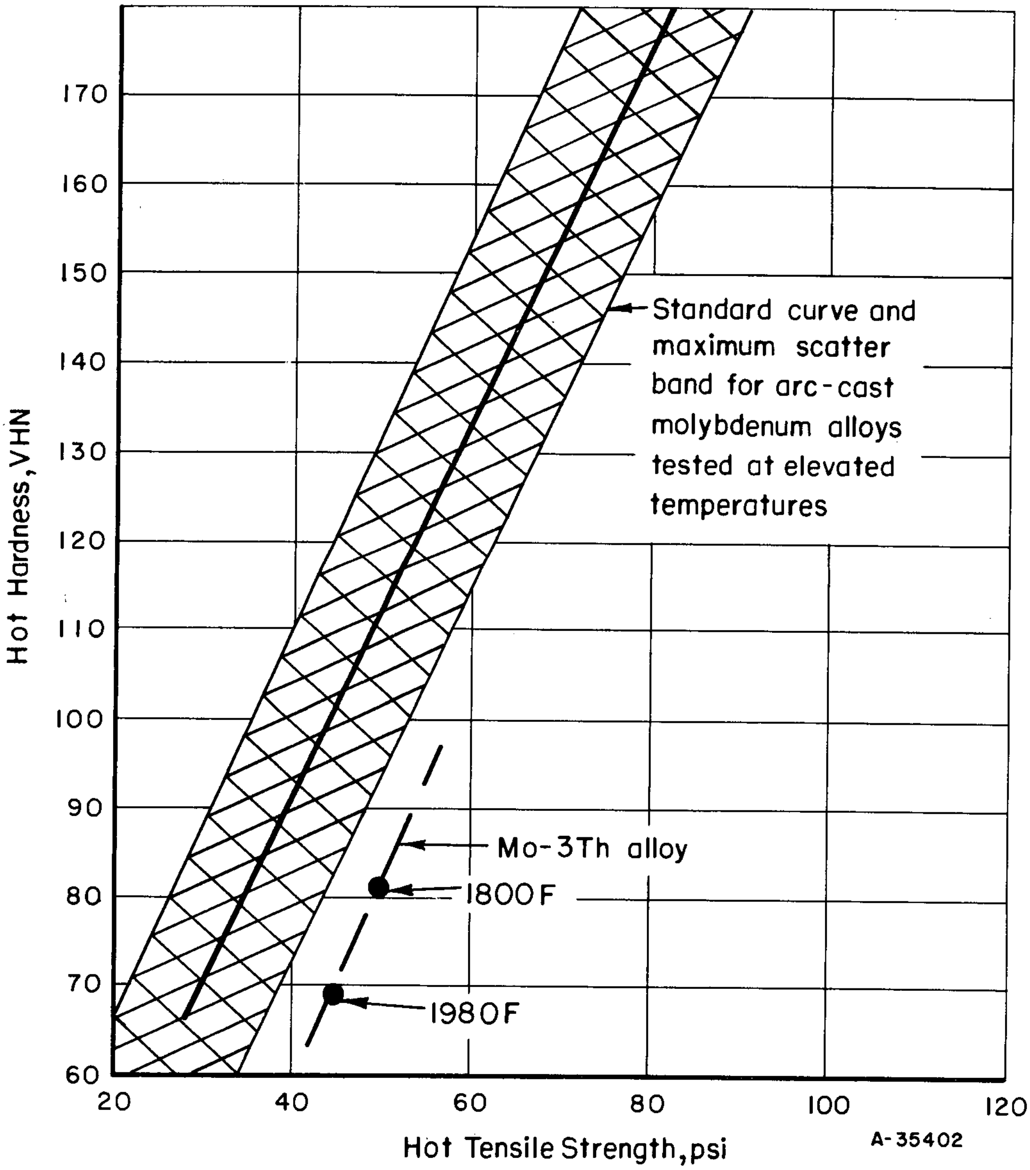

FIGURE 9. TENSILE STRENGTH VERSUS HOT HARDNESS OF THE Mo-3Th ALLOY COMPARED WITH A LARGE NUMBER OF EXPERIMENTAL MOLYBDENUM ALLOYS(13)

The experimental alloys had been rolled to bars 1/2 and 5/8 inch in diameter. In each case the tensile strength and hardness were determined at the same temperature.

Relationship of Hardness and Tensile Strength

Semchyshen(13) studied the relationship of strength and hardness of several dozen fabricated arc-cast molybdenum alloys and showed that, at elevated temperatures, the relationship shown in Figure 9 could be obtained. In the figure, a shaded band is given which includes all of his alloys. Most of these had a strength versus hardness relationship which was very close to the base line.

The two plotted points for the Mo-3Th alloy show that thorium imparts a relationship of hardness versus strength which is considerably different from that of other molybdenum alloys, i.e., the Mo-3Th is much softer at equivalent strengths.

CONCLUSIONS

The data presented in this report show that thorium should be studied more intensively as an alloying addition for molybdenum.

The low hardness, and the comparatively small amount of work hardening appear to recommend it particularly for service for rivets and other fasteners for high-temperature service. It has reasonably high strength at 1800 and 2000 F and it may have outstanding strength at higher temperatures. It resists recrystallization at high temperatures. It should therefore be possible to produce fasteners from a fabricated wire or rod having high strength at high temperature. The base material, being comparatively soft and ductile, might be further deformed by heading and roll threading to form a fastener. The resulting material should then retain strength in high-temperature service.

The evidence presented in this report suggests that the Mo-3Th alloy will have greater strength than the Mo-0.5Ti alloy at temperatures in the range of 2200 to 2500 F depending on the time that the load must be held. This probability requires confirmation, but if true, introduces the possibility that molybdenum-thorium will be useful for some applications requiring maximum load-carrying abilities in the upper temperature range where molybdenum can now carry a sustained load.

In the studies made with molybdenum-thorium alloys, all tests have been made with pure binary alloys. It is probable that a second addition such as carbon or a metal could be used to enhance the effect of thorium and result in a truly outstanding alloy.

The difficulties in arc-melting thorium-containing alloys and the need to start with an oxygen-free alloy to prevent entrapment of slag layers pose difficulties in preparing the alloys. This problem must be overcome before the alloys can be made commercially useful. It appears, however, that special melting procedures can be devised, and a study of some of the possibilities should be included in any research program for developing the alloys.

The use of a temperature of 1000 to 1200 F for breakdown rolling or swaging of the as-cast alloys was based on meager and inconclusive studies. Further research should include at least a preliminary investigation of other fabrication procedures including extrusion at various temperatures.

In considering possible additions for improving the ductility and/or strength of molybdenum, the comparatively low cost and high availability of thorium should be considered. In comparison with rhenium and some of the platinum metals which also impart ductility and strength, thorium at $20 to $40 per pound is cheap and is a plentiful (surplus) metal.

PART 2. EVALUATION OF A COLUMBIUM-ZIRCONIUM-TITANIUM CLADDING ALLOY

by

G. S. Root and F. C. Holden

INTRODUCTION

In work done at The Ohio State University under an ONR contract, an oxidation-resistant alloy of columbium was developed. The optimum composition was reported as Cb-55Zr-5Ti (atomic per cent). Because of its promise as a potential cladding material for refractory metals and alloys, a program was established at Battelle to evaluate further the mechanical properties and oxidation behavior of this material. Two commercially produced structural alloys, Mo-0.5Ti and Cb-33Ta-0.7Zr (Fansteel 82 alloy) were selected as suitable cores for cladding experiments. The program objectives included (1) a check of the previously reported oxidation behavior, (2) a determination of mechanical properties at elevated temperatures, and (3) an evaluation of the cladding properties of the alloy. The results of experiments intended to accomplish these objectives are summarized in the following sections of this report.

PREPARATION OF MATERIAL

Melting

To provide sufficient material for mechanical-property evaluation, oxidation testing, and cladding experiments, a 3-pound ingot was prepared. A consumable electrode was made by welding together rods of electron-beam-melted columbium, iodide-refined titanium in the proper proportions. After arc melting, the resulting ingot was quartered, welded to form another consumable electrode, and arc melted a second time to insure homogeneity. The final ingot was approximately 3 inches long and 2 inches in diameter.

At a later stage in the work, additional material was arc melted using a non-consumable electrode to produce small buttons of the Cb-55Zr-5Ti alloy. These were used in some of the later cladding experiments.

Fabrication

The most critical stage in the fabrication of a heat-resistant alloy usually is the initial breakdown of the cast structure. To avoid possible failure during forging, the 3-pound ingot was cut into two rectangular slabs, which then were encased in stainless steel packs and rolled directly to sheet. In this way, the packs provided constraint to aid in the fabrication as well as protection from the atmosphere during hot working. The packs were rolled at 1800 F to provide a final alloy sheet approximately 0.080-inch thick. The packs then were stripped and the sheet was surface conditioned and cleaned. After cutting specimen blanks from the sheet, the pieces were annealed 1 hour in a vacuum at 2010 F.

MECHANICAL PROPERTIES

Specimens of the Cb-55Zr-5Ti alloy were tested in tension at room temperature, 1500 F, and 1800 F. Bend ductility was evaluated at 70, -105, and -320 F. These test results are listed in Table 5. Included for comparison are tensile data obtained for a similar alloy (Cb-45Zr-5Ti).

The Cb-55Zr-5Ti alloy exhibits moderate strength at room temperature, combined with adequate ductility. Tensile strengths are reduced markedly at 1500 and 1800 F, while ductilities are increased. In comparison with the Cb-45Zr-5Ti alloy, the alloy containing more zirconium is less strong and more ductile. This effect may be expected to be more pronounced at higher temperatures due to the less refractory nature of zirconium. If the available data are plotted as functions of the Larson-Miller parameter (C = 20), as shown in Figure 10, the two alloys are seen to have similar strength behaviors up to at least 1200 F. The break in the rupture strength curve appears at about 1500 F for the Cb-55Zr-5Ti alloy.

The bend-test data, shown in Table 5, indicate excellent ductility at temperatures down to -320 F. Thus, this alloy exhibits excellent ductility in bending and in tension, combined with moderate strength. Its mechanical properties alone, however, are not outstanding, so that the reason for its use would be oxidation resistance rather than strength.

OXIDATION BEHAVIOR

The oxidation behavior of the Cb-55Zr-5Ti alloy was evaluated by exposing samples 1.25 x 1 x 0.050 inch thick to flowing dry air at 1470, 1830, 2190, and 2550 F. The weight gains were measured by means of a continuously recording balance, and tests were conducted for exposures up to 5 hours. The results are summarized in Table 6.

At 1470 F, a transition from parabolic to linear behavior was observed after about 200 minutes, whereas at 2550 F, a high linear rate was observed. At 1830 and 2190 F, the behavior was neither parabolic nor linear. The weight gain data at 1830 F are similar to those reported for the Cb-50Zr-5Ti alloy (see Table 6) for which a quartic rate was proposed.

At 1830 F, the weight-gain data indicate that the two alloys are very similar, and afford reasonable oxidation protection. The rate is increased at 2190 F, and becomes

TABLE 5. TENSILE AND BEND PROPERTIES OF Cb-Zr-Ti ALLOYS

			Tensile Properties					
Composition, atomic per cent	Test Temperature, F	Proportional Limit, psi	0.1 % Offset Yield Strength, psi	0.2 % Offset Yield Strength, psi	Ultimate Strength, psi	Elongation in 1 Inch, per cent	Reduction in Area, per cent	Hardness (5 Kg Load), VHN
Cb-55Zr-5Ti	70	91,000	102,000	104,000	108,000	17	47	253
Cb-55Zr-5Ti	1500	--	--	45,600	48,100	16	(a)	--
Cb-55Zr-5Ti	1800	--	--	--	13,600	100(b)	--	--
Cb-45Zr-5Ti	70(c)	--	--	124,000	128,000	8	--	--
Cb-45Zr-5Ti	70(c)	--	--	--	78,000	3	--	--

Bend Properties

Composition, atomic per cent	Test Temperature, F	Minimum Bend Radius, T(d)
Cb-55Zr-5Ti	70	0
Cb-55Zr-5Ti	-105	0
Cb-55Zr-5Ti	-320	0.3

(a) Specimen broke in shoulder.

(b) Specimen reached maximum load but did not break. Test was stopped after 100 per cent elongation.

(c) Data from Reference (14).

(d) Bend ductility is expressed in the T unit which is minimum bend radius divided by specimen thickness.

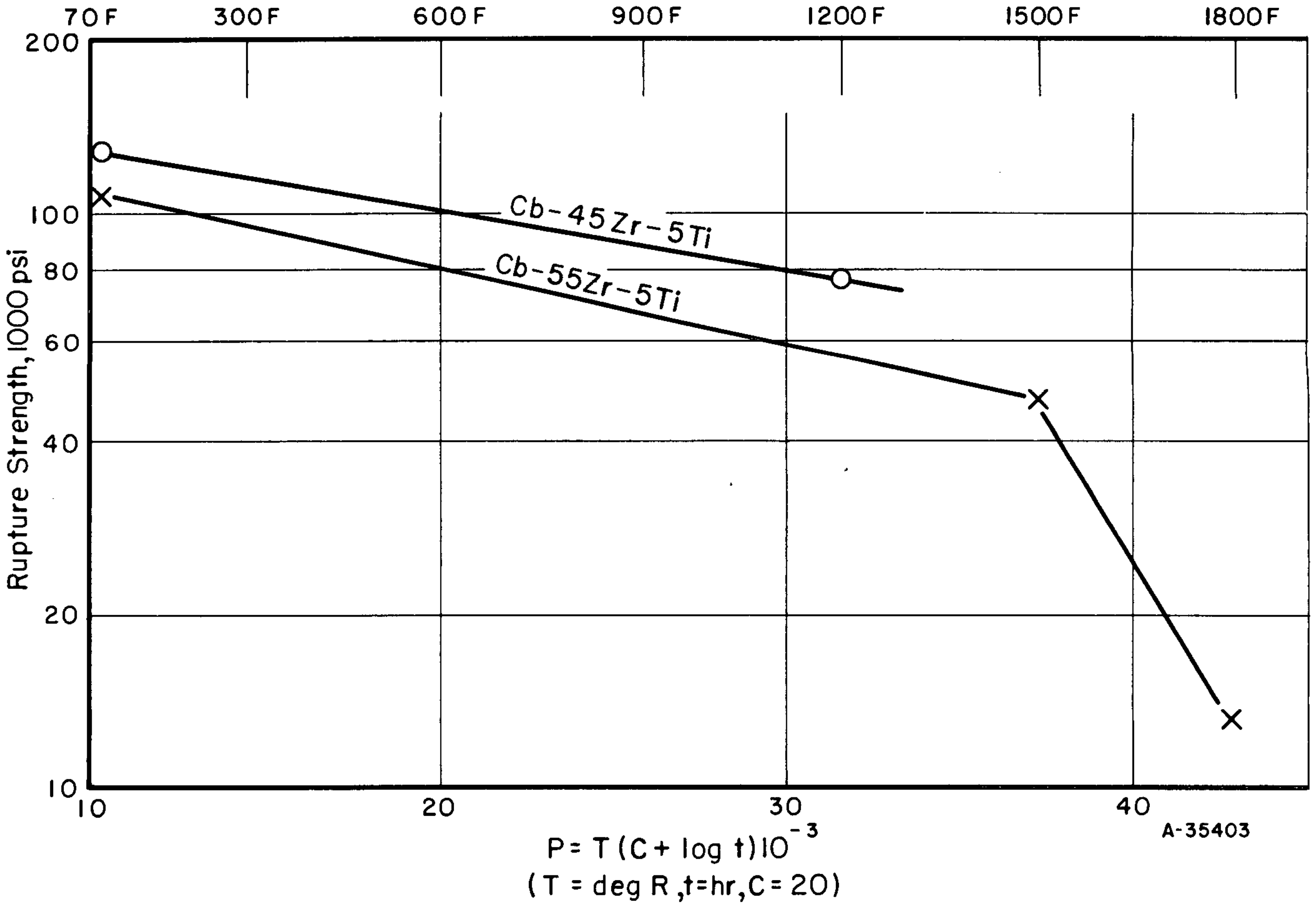

FIGURE 10. RUPTURE STRENGTH (0.1 HOUR) AS A FUNCTION OF THE LARSON-MILLER PARAMETER (C = 20) FOR A Cb-55Zr-5Ti ALLOY AND A Cb-45Zr-5Ti ALLOY

TABLE 6. OXIDATION PROPERTIES OF Cb-Zr-Ti ALLOYS AT 1470, 1830, 2190, AND 2550 F

Composition, atomic per cent	Exposure Temperature, F	Parabolic Rate Constant, $(mg/cm^2)^{-2}$/hr	Transition to Linear Behavior, minutes	Linear Rate Constant, mg/cm^2/hr	Weight Gain, mg/cm, After Indicated Exposure, hours				
					1	2	3	4	5
Cb-55Zr-5Ti	1470	288	200	4.4	16.3	23.5	29	34.8	40
Cb-55Zr-5Ti	1830	--	--	--	26.3	31	34	36.5	38.2
Cb-55Zr-5Ti	2190	--	--	--	50	65	75	83	94
Cb-55Zr-5Ti	2550	--	--	--	68.5	--	--	--	--
Cb-50Zr-5Ti(a)	1830	--	--	--	19	24	27	28	30

(a) Data from Reference (15).

very rapid at 2550 F. Thus, the alloy may be considered nonspalling and fairly oxidation resistant at temperatures up to about 2000 F. The optimum zirconium composition for oxidation resistance appears to be about 50 atomic per cent.

CLADDING EXPERIMENTS

Because the Cb-55Zr-5Ti alloy does not provide exceptionally good high-temperature strength, it was considered as a possible cladding material for stronger and less oxidation-resistant alloys. Two of these were selected for cladding experiments, Mo-0.5Ti and Cb-33Ta-0.7Zr (Fansteel 82 alloy). Provided that sections of these alloys could be clad satisfactorily, it was intended to use samples of these for oxidation and mechanical tests.

Roll-bonding experiments were conducted on both core materials at 1650, 1800, and 2190 F. The cores were sandwiched between two sheets of the Cb-55Zr-5Ti cladding alloy, and the assembly was enclosed in a stainless steel pack. The packs were welded, then evacuated and sealed before hot rolling. In all experiments, an initial reduction of 20 to 25 per cent was made on the first pass; this was followed by 10 per cent reductions until the final thickness was reached. In one experiment (1800 F), a parting compound of Cr_2O_3 and sodium silicate was used between the cladding alloy and the stainless steel pack.

It was found that successful bonds between the base metal (Mo-0.5Ti or Cb-33Ta-0.7Zr) and the cladding (Cb-55Zr-5Ti) were not formed at any of the three temperatures. In all instances, the cladding could be peeled away from the core very easily. In addition, a low-melting eutectic (1715 F) in the iron-zirconium system resulted in melting at the interface between the stainless steel cover plates and the cladding alloy in the experiments at the higher temperatures. Thus, no successfully bonded samples were available for further testing.

It appears that successful roll cladding would require temperatures in excess of 2190 F. The cladding would have to be applied either without the protection of the stainless steel pack or with a barrier, such as molybdenum, between the Cb-55Zr-5Ti alloy and the steel. The latter alternative probably would be more desirable in view of the oxidation problem, although this would be more expensive.

CONCLUSIONS

The data obtained on the Cb-55Zr-5Ti alloy show moderate strength, good ductility, and good oxidation resistance at temperatures up to about 2000 F. It seems probable that other columbium-base alloys with equally good oxidation resistance and better strength will be developed. There does not seem to be a large potential for this material as a cladding for other stronger and less oxidation-resistant materials.

* * * * * * *

Experimental work performed may be found in Battelle Laboratory Record Book No. 15824, pp 1 through 20.

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