CLIMAX MOLYBDENUM CO.
OF MICHIGAN

Detroit, Michigan

a subsidiary of AMERICAN METAL CLIMAX, INC.

INVESTIGATION OF MOLYBDENUM- AND
TUNGSTEN-BASE ALLOY SHEET MATERIALS

Prepared under Bureau of Naval Weapons
Contract No. NOw 61-0581-d
Third Quarterly Report

25 November 1961 to 24 February 1962

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ABSTRACT

Room temperature tensile tests and bend transition temperature determinations have been conducted on stress-relieved and recrystallized specimens of several high strength molybdenum-base and tungsten-base alloy rolled sheets. The 50-mil thick sheet stock had been rolled in air on a conventional sheet rolling mill.

The preparation and rolling of additional sheet bars of the same alloys in the InFab facility is also described.

INTRODUCTION

The objective of Contract NOw 61-0581-d is to produce and evaluate several molybdenum-base and tungsten-base alloy sheet materials in compositions that have demonstrated, in the form of round bar stock, attractive mechanical properties.

During the first half of the contractual year six vacuum-arc-cast alloy ingots were produced for the program. Extruded sheet bars in the following compositions were successfully obtained from five ingots:

Mo + 1.35% Cb + 0.028% C
Mo + 1.17% Ti + 0.27% Zr + 0.17% C
Mo + 25.4% W + 0.10% Zr + 0.053% C
Mo + 49.1% W + 0.014% C
W + 3.5% Mo + 0.015% C

Two sheet bars of each composition were rolled to 50-mil thick sheet on conventional mill equipment (in air) using two different rolling schedules for each alloy (fabrication details were given in Quarterly Report No. 2).

Studies conducted on the rolled sheets during the third quarter, included the determination of recrystallized grain size, establishing the presence and amount of surface contaminated layers, determining the bend transition temperatures and also the room temperature tensile strengths for various structural conditions and orientations.

Additional sheet bars were prepared and rolled to sheet at the Navy "InFab" facility operated by Universal-Cyclops Steel Corporation personnel.

Metallographic Studies

The rolled alloy sheet stock, as-received from the rolling mill, was in the cropped and cleaned condition. The cleaning operation consisted of immersing the sheets in a molten caustic bath to remove adherent oxide scale followed by a light etch in dilute sulfuric acid to remove any traces of iron particles picked up and rolled into the sheets' surfaces. Samples of the sheets were obtained both before and after cleaning. Samples cut from the sheet materials were annealed for 15 minutes in hydrogen at the minimum temperatures which would fully recrystallize their "core areas". It has been found that following recrystallization anneals of conventionally rolled molybdenum-base alloy sheets in hydrogen there almost invariably remains unrecrystallized surface layers, the exact nature of which has not yet been fully established. It is known, however, that their existence and depth is primarily dependent upon alloy composition and processing environment.

The thickness of the contaminated layers and the average grain diameters (i.e., grain size) of the various sheets were measured on metallographically prepared specimens cut from the samples annealed at the minimum recrystallization temperature. The results obtained are shown in Table 1.

TABLE 1

Grain Size and Contaminated Layer Measurements of Molybdenum-Base and Tungsten-Base Rolled Alloy Sheets in the Fully Recrystallized Condition

Sheet No.	Analysis, %	Recryst. Temp., F (15 min)	Depth of Contaminated Surface Layers, mil		Average Recryst. Grain Size Dia., mm
			As-Rolled	After Cleaning	
4051-3	Mo+1.35Cb+0.028C	2300	1.00	0.85	0.012
4051-4		2300	1.00	0.80	0.011
4053-2	Mo+1.17Ti+0.27Zr+0.17C	2900	1.00	0.80	0.017
4053-3		2900	0.50	0.50	0.017
4052-4	Mo+25.4W+0.10Zr+0.053C	2750	1.25	1.00	0.013
4052-5		2750	1.25	1.20	0.012
4056-2	Mo+49.1W+0.014C	2800	N.A.*	0.50	0.017
4054-3	W+3.5Mo+0.015C	3000	0.15	0	0.014
4054-4		3000	0.15	0	0.013

* N.A. - Not available

Tensile Strength

Room temperature tensile tests were conducted on sheet specimens prepared from three of the five alloy compositions, namely, sheets 4051 (Mo + 1.35% Cb + 0.028% C), 4053 (Mo + 1.17% Ti + 0.27% Zr + 0.17% C) and 4052 (Mo + 25.4% W + 0.10% Zr + 0.053% C).

The structural conditions evaluated were stress-relieved (i.e., annealed for 15 minutes in hydrogen 50 F to 100 F below the temperature causing the onset of recrystallization) and fully recrystallized. The temperatures employed for these thermal treatments are listed in Table 2. Part of the tensile test specimens were chem-milled prior to testing, the remainder retained their as-received surface. The chem-milling operation was carried out to remove completely any vestiges of contaminated surface layers present on the as-received sheets. The chem-milling was accomplished in a HNO_3:HF solution. A total reduction in gage of 3 mils was achieved during the chem-milling, which was more than adequate to insure complete removal of the contaminated surface layer.

TABLE 2

Annealing Temperatures for Test Specimens

Sheet No.	Analysis, %	Stress Relief Temp., F (15 min. Anneal)	Recryst. Temp., F (15 min. Anneal)
4051-3	Mo+1.35Cb+0.028C	2000	2300
4051-4		2000	2300
4053-2	Mo+1.17Ti+0.27Zr+0.17C	2350	2900
4053-3		2350	2900
4052-4	Mo+25.4W+0.10Zr+0.053C	2400	2750
4052-5		2400	2750

Specimens were prepared with (a) axes parallel to the final direction of rolling and (b) axes transverse to the direction of rolling. Reduced gage dimensions were 0.25 in. wide by 1-1/4 in. long by the sheet thickness. The over-all length of the tensile specimen was 4-1/2 in.

Steel pins, 5/16" diameter, located through yokes and holes at each end of the specimen were used to transmit the load during test.

During the tensile test, strain rates of 0.005"/"/min. in the elastic range and 0.05"/"/min. thereafter were employed.

Strain measurements were made with a microformer-type gage and monitored by a strain pacer. A stress-strain curve was autographically recorded for each test.

The 0.1% and 0.2% offset yield strengths were calculated from the stress-strain records for all specimens not exhibiting a drop in load at the yield point.

The tensile test results are listed in Table 3.

Room temperature strength properties were fairly consistently proportional to the corresponding room temperature hardness values. This is illustrated in Figure 1, a plot of hardness against room temperature tensile strength for stress-relieved and recrystallized specimens. All of the strengths for both parallel and normal rolling directions fall into a fairly narrow band. The dotted line in Figure 1 represents the average tensile strength vs hardness relationship which was established for molybdenum-base alloy bar stock in earlier research programs.

TABLE 3

Room Temperature Tensile Test Results for 50 mil Gage Molybdenum-Base Alloy Sheet Materials

Sheet No.	Analysis, %	Condition*	Orientation**	Test Temp., F	0.1% Offset Yield Str., psi x 10^{-3}	0.2% Offset Yield Str., psi x 10^{-3}	Tensile Strength psi x 10^{-3}	El., %
4051-3	Mo+1.35Cb+0.028 C	S.R. (303)	P	76	106.9	114.3	135.3	10
		S.R.-C.M.	P	75	108.1	114.5	133.5	10
		S.R.	N	76	120.0	129.8	145.5	6
		S.R.-C.M.	N	75	117.0	127.8	148.8	5
		Rec. (193)	P	75	81.7***	-	92.7	29
		Rec.-C.M.	P	75	78.3***	-	92.9	30
		Rec.	N	75	81.6***	-	99.2	26
		Rec.-C.M.	N	75	83.3***	-	94.9	31
4051-4	Mo+1.35Cb+0.028 C	S.R. (304)	P	76	109.4	120.9	140.6	10
		S.R.	N	75	122.1	131.9	147.7	7
		Rec. (191)	P	75	83.7***	-	91.7	38
		Rec.	N	75	81.6	81.8	95.5	23
4052-4	Mo+25.4W+0.10Zr+0.053C	S.R. (317)	P	76	116.0	116.0	133.9	11
		S.R.-C.M.	P	76	114.1	114.1	134.3	11
		S.R.	N	76	127.9	132.6	144.6	10
		S.R.-C.M.	N	75	133.8	136.9	145.2	8
		Rec. (216)	P	75	82.0***	-	99.6	36
		Rec.-C.M.	P	75	75.4***	-	97.5	23
		Rec.	N	75	83.3***	-	101.2	23
		Rec.-C.M.	N	75	78.6***	-	99.6	22
4052-5	Mo+25.4W+0.10Zr+0.053C	S.R. (320)	P	75	125.8	125.8	145.0	8
		S.R.	N	76	137.2	140.0	151.9	10
		Rec. (220)	P	76	86.3***	-	100.4	40
		Rec.	N	75	81.3***	-	101.1	36

TABLE 3 (continued)

Room Temperature Tensile Test Results for 50 mil Gage Molybdenum-Base Alloy Sheet Materials

Sheet No.	Analysis, %	Condition*	Orientation**	Test Temp., F	0.1% Offset Yield Str., psi x 10^{-3}	0.2% Offset Yield Str., psi x 10^{-3}	Tensile Strength psi x 10^{-3}	El., %
4053-2	Mo+1.17Ti+0.27Zr+0.17C	S.R. (322)	P	74	96.2	106.7	133.3	14
		S.R.-C.M.	P	75	99.3	108.2	137.7	15
		S.R.	N	75	117.9	126.3	143.0	10
		S.R.-C.M.	N	74	119.5	127.2	140.6	5
		Rec. (213)	P	75	64.2***	-	95.7	35
		Rec.-C.M.	P	74	64.1***	-	95.0	28
		Rec.	N	75	68.4***	-	99.2	21
		Rec.-C.M.	N	75	63.9***	-	98.8	28
4053-3	Mo+1.17Ti+0.27Zr+0.17C	S.R. (331)	P	76	103.2	115.0	143.6	14
		S.R.	N	76	125.8	134.9	150.4	9
		Rec. (212)	P	75	63.2	65.4	96.3	29
		Rec.	N	75	69.4***	-	99.6	29

* S.R. - Stress Relieved.
S.R.-C.M. - Stress Relieved and Chemically Milled.
Rec. - Recrystallized.
Rec.-C.M. - Recrystallized and Chemically Milled.
Parenthetical numbers indicate Diamond Pyramid Hardness.

** P - Tension axis parallel to the final rolling direction.
N - Tension axis normal to the final rolling direction.

*** Drop in load yield strength.

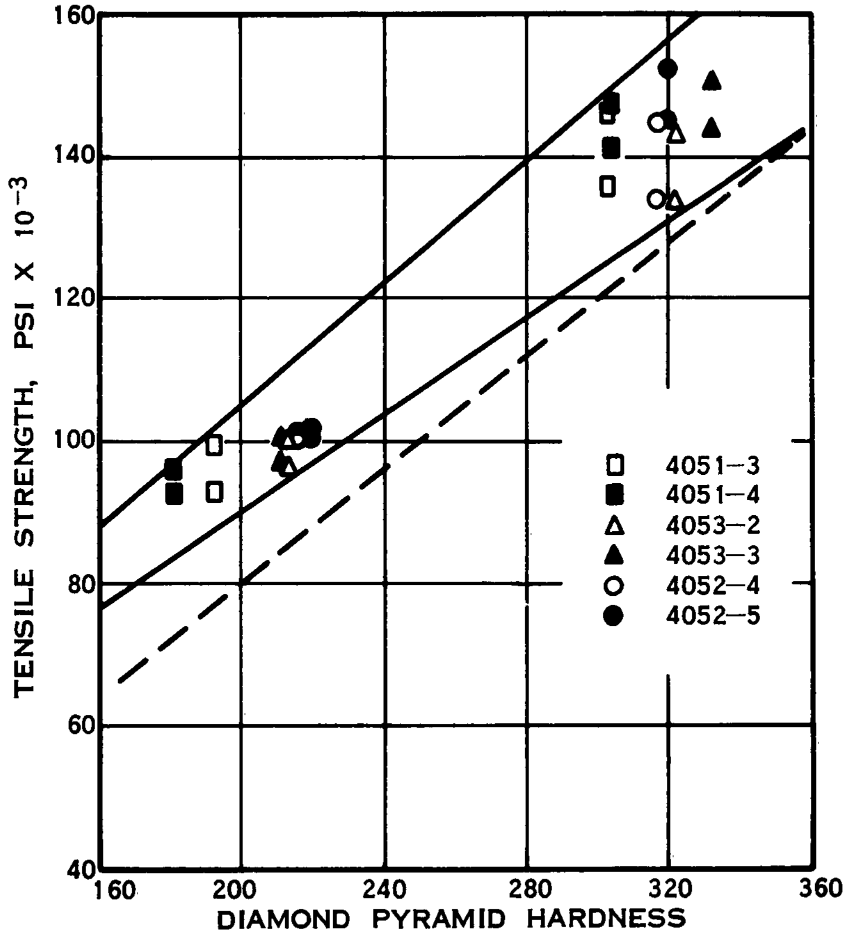

FIGURE 1 — HARDNESS VERSUS ROOM TEMPERATURE TENSILE STRENGTH FOR 50-MIL-GAGE MOLYBDENUM-BASE ALLOY SHEET MATERIALS (STRESS-RELIEVED AND RECRYSTALLIZED). STRENGTHS PARALLEL AND NORMAL TO THE FINAL ROLLING DIRECTION ARE PLOTTED.

The position of the current data above the average line established for bar stock probably reflects specimen geometry and specimen surface to volume ratio in sheet materials.

It will be noted that the tensile strengths are higher and elongation values lower for the transverse specimens for each sheet composition than those obtained for the parallel specimens. This is attributed to the fact that 80-85% reductions in thickness, during rolling, were made transverse to the final rolling direction while 55-65% reductions were sustained by the sheets in final rolling.

Two sheets were rolled of each alloy, the second (as listed in Table 3) at somewhat lower temperatures than the first. The increased strain-hardening raised the tensile strength but did not materially affect the ductility.

The tensile test results obtained on chemically milled specimens when compared with those not chem-milled, showed no consistent trend as to the effectiveness of the chem-milling operation.

Bend Test Results

From each of the six sheets, stress-relieved and fully recrystallized bend test coupons (0.50 in. wide by 1 in. long by sheet thickness) were prepared either with their major axes (a) parallel to the final rolling direction, or (b) normal to the final rolling direction.

The edges of the coupons were fine surface ground and hand polished. The bend testing was conducted on a "Beam Bending Jig" which permitted a maximum bend angle of 140° for the 50 mil gage sheets. The specimens were loaded at the center of a 5/8 in. span using a deflection rate of 10 in. per minute. Bearing surfaces of the jig were 1/8 in. diameter hardened drill rod and the bend radius was 2T. The maximum bend angle sustained before fracture on those specimens not exhibiting maximum ductility was determined by measuring the angles resolved by the reassembled pieces of the broken test specimens. Test temperatures were maintained throughout each test to $\pm$ 2 F by means of a controlled temperature bath. Specimens were allowed to reach equilibrium conditions by holding them at test temperatures a minimum of five minutes before applying a bending load.

As yet, no chemically milled specimens have been tested.

The bend test data obtained will be reported in detail, with appropriate illustrations, in the final report for the program. The results are summarized, however, in Table 4 which lists the bend transition temperatures (i.e., the lowest temperature at which a 140° bend angle was obtained without fracture) of each sheet for the various structural conditions.

TABLE 4

Bend Transition Data

Sheet No.	Analysis, %	Minimum Temperature at Which a 140° Bend was Obtained Without Fracture			
		S.R. (Parallel)	S.R. (Normal)	Rec. (Parallel)	Rec. (Normal)
4051-3	Mo+1.35Cb+0.028C	40	65	60	70
4051-4		30	65	40	70
4053-2	Mo+1.17Ti+0.27Zr+0.17C	-10	30	80	90
4053-3		30	60	90	100
4052-4	Mo+25.4W+0.10Zr+0.053C	40	50	90	100
4052-5		20	60	70	70
4056-2	Mo+49.1W+0.014C	175	225	400	500
4054-3	W+3.5Mo+0.015C	350	350	700	925
4054-4		325	350	775	950

"InFab" Rolling of Sheet

Extruded sheet bars from Heats 4051, 4052, 4053, 4054 and 4056 were selected for conversion to sheet in the Navy's "InFab" facility.

Since the available heating equipment at this laboratory was limited to a maximum temperature of 3150 F and as the recrystallization temperatures of the sheet bars were higher than 3150 F, annealing times of up to three hours were used to effect maximum reductions in hardness of the sheet bars.

The annealed bars were ground to remove surface defects prior to rolling. The size and weight of the sheet bars submitted for rolling are listed in Table 5.

The rolling schedules employed for the "breakdown" of the sheet bars varied considerably and were based on experience gained from the rolling of the same alloys in air.

Some difficulties were encountered during rolling in InFab, however, despite the limitations of the equipment available for the type of rolling desired for materials of this investigation the operating and engineering personnel are to be highly commended for their spirit of cooperation and for the degree of success that was achieved. The final gage thicknesses of the rolled sheets are listed in Table 5.

The Mo + 1.35% Cb + 0.028% C alloy was broad-rolled at 2400 F for six passes, cropped, cross-rolled at 1500 F for five passes, cropped, and then finish pack-rolled at the same temperature. All cropping was conducted by sawing or the use of cut-off wheels at room temperature outside the InFab unit.

The Mo + 25.4% W + 0.10% Zr + 0.053% C alloy bars were broad-rolled for seven passes at 2600 F, cropped, and cross-rolled to 0.135 in. thick at 2200 F. The two sheets were submitted for cropping to matched sizes in anticipation of finish pack rolling but inadvertently both sheets were extensively cracked by mishandling.

A third piece of the Mo + 25.4% W + 0.10% Zr + 0.053% C alloy sheet bar was successfully rolled to 50 mil gage sheet without mishap by the same schedule.

The TZC (Mo + 1.17% Ti + 0.27% Zr + 0.17% C) sheet bars were processed to sheet without difficulty by broad-rolling for six passes at 2800 F. The broad-rolled material was cropped, cross-rolled at 2500 F for five passes, sized for pack-rolling, then finish-rolled by six passes at 2400 F.

The W + 3.5% Mo + 0.015% C alloy sheet bar cracked up after seven passes at 2800 F. Unfortunately, no additional stock was available for a re-run.

The two Mo + 49.1% W + 0.014% C bars were severely cracked after one pass at 2800 F. A third bar of this composition was broad-rolled at 2400 F for seven passes, cropped, pack-rolled for three passes at 2200 F, cropped and finish pack-cross-rolled at 2400 F.

The sizes and weights of the sheet bars submitted for rolling and the recovery data are listed in Table 5.

TABLE 5

Sizes, Weights and Recovery Data for Molybdenum-Base and Tungsten-Base Alloy Sheet Bars Submitted to "InFab" for Rolling to Sheet

		Sheet Bar		Sheet		
Bar No.	Analysis, %	Size, In.	Wt., Lb.	Gage, Mil	Cropped Weight, Lbs.	Rolling Recovery, %
4051-2-1	Mo+1.35Cb+0.028C	7/8x1-7/8x7	4.22	50-54	2.80	66.4
4051-2-2		7/8x1-7/8x7	4.22	56-59	2.50	59.2
4052-1-1	Mo+25.4W+0.10Zr+0.053C	9/16x1-7/8x7-1/16	2.95	58-64	1.85	62.7
4052-3-1		7/8x1-7/8x7	4.77	-	0	0
4052-3-2		7/8x1-7/8x7	4.75	-	0	0
4053-4-1	Mo+1.17Ti+0.27Zr+0.17C	7/8x1-7/8x7	4.20	54-58	2.62	62.4
4053-4-2		7/8x1-7/8x7	4.22	53-57	2.60	61.6
4054-5-2	W+3.5Mo+0.015C	7/8x2x7	7.77	-	0	0
4056-4-1	Mo+49.1W+0.014C	7/8x1-15/16x7	5.81	-	0	0
4056-4-2		7/8x1-15/16x7	5.83	-	0	0
4056-5-1		9/16x1-13/16x7	3.39	44-48	1.30	38.3

FUTURE WORK

Elevated temperature tensile tests, and creep rupture tests are proceeding on all of the alloy sheet stock produced by conventional methods.

Recrystallization data, surface contaminated layer measurements and bend transition temperature determinations have been initiated for the InFab-rolled sheet stock. Spot checks will be made on the tensile and creep rupture strengths of these alloys where stock permits.