4. PHYSICAL METALLURGY OF FAST BREEDER REACTOR CLADDING MATERIALS AND REFRACTORY METALS

(1177)

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The objective of this program is to define heat treatment, composition, and microstructures that result in optimum creep ductility of selected fuel cladding alloys. This objective represents a redirection of this task as of January 1968 toward emphasis on fast breeder reactor fuel cladding materials. During 1967, the task was concerned with the physical metallurgy of refractory metals, specifically W-Re-Mo alloys and molybdenum, in support of the alloy research and development efforts under task 1115. Work on refractory metals, particularly molybdenum, will continue through the remainder of the current fiscal year, with the major effort henceforth devoted to stainless steels and other selected fuel cladding alloys noted subsequently.

4.1 TUNGSTEN-RHENIUM-MOLYBDENUM ALLOYS

Studies of the W – 25Re – 30Mo and W – 30Re – 30Mo (at. %) alloys were concerned with recrystallization, ductility, hardness, and aging characteristics of original process and specially purified powder metallurgy materials. Specific objectives were to improve production procedures and properties of the sheet product.

FABRICATION

Fabrication studies centered on means of incorporating purification procedures without impairing yields or properties. As indicated in Figure 4.1, the original fabrication process for sheet material of the two alloys involved hot rolling at 1400°C to about 1-mm thickness with subsequent 5 percent reduction steps obtained in multiple passes at 200°C to final thickness. Intermediate anneals of about 15 minutes at 1400°C were made after each reduction step. Subsequently, special purification steps outlined in Figure 4.1 were incorporated in the procedure to improve weldability. Unfortunately, the temperatures initially utilized in the final purification treatment after hot rolling caused poor yields in working and limited room-temperature ductility in both alloys.

W – 25Re – 30Mo

Simpler production procedures were established for W – 25Re – 30Mo using the modified procedures indicated in Figure 4.1. Since this alloy exhibits the brittleness typical of refractory metals in the recrystallized condition, the wrought structure necessary for cold working could be retained by the following modifications: (1) carrying out the final purification treatment at temperatures below that at which recrystallization occurred, (2) omission of this final treatment, or (3) carrying out the purification treatment prior to the final hot rolling step. With a sufficiently wrought structure, it was possible to achieve reductions of 10 percent per pass at room temperature and total reductions of up to 80 percent without annealing or stress-relief treatments. With modifications No. 1

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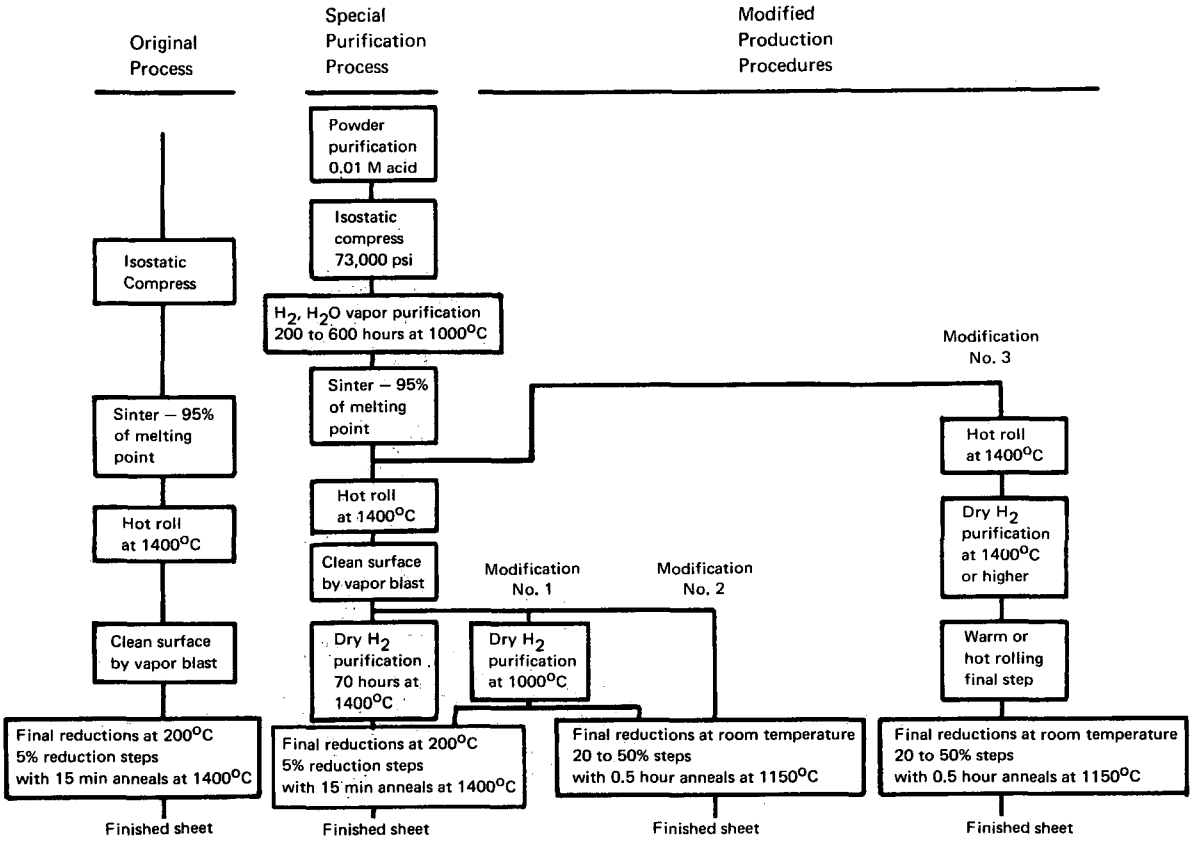

Fig. 4.1 – Production procedures for W-Re-Mo alloys

and 2 (Figure 4.1), improved yields were obtained in the processing of sheet and the final stress-relieved material possessed excellent room-temperature ductility. Present analytical data do not indicate whether the concentration of interstitial impurities, particularly oxygen, differs appreciably in sheet produced by modifications No. 1 and 2, i.e., when the final purification treatment is omitted. Weld porosity was not adversely affected by the latter procedure, however. Pending clarification of this point, studies of modification No. 3 have not been pursued.

W – 30Re – 30Mo

Similar modifications in sheet fabrication were successfully applied to the W–30Re–30Mo alloy with improvements in yield and ductility. This alloy is ductile in the recrystallized condition, although relatively poor ductility properties can arise from precipitation of a sigma phase which forms at temperatures below approximately 1700°C. Material recrystallized above the sigma solution temperatures was definitely more ductile than that recrystallized at temperatures at which sigma precipitated, even though interstitial impurities may also be involved in the ductility. Modifications in the production process therefore involved reduction and stress-relieving treatments identical to those described for the W – 25Re – 30Mo alloy (see Figure 4.1), and a final recrystallization anneal at 1700°C or higher to obtain a ductile-to-brittle bend transition temperature below -70°C. The final anneal also served as a further deoxidation treatment.

RECRYSTALLIZATION

Recrystallization studies to aid fabrication development were conducted on both W-Re-Mo alloys after cold reduction of sheet from the as-processed condition (produced by the original procedure outlined in Figure 4.1) and from the annealed (2000°C, 2 hr) condition. Also

included were W – 30Re – 30Mo specimens processed using special purification procedures. All materials were cold rolled at room temperature to reductions ranging from about 10 to 75 percent without intermediate anneals. A summary of the specimens prepared for this recrystallization study appears in Table 4.1.

In general, the two alloys exhibited typical recrystallization behavior; a pronounced decrease of grain size on recrystallization occurred at reductions greater than 15 to 30 percent. Data established that the final purification treatment at 1400°C for 70 hours after hot rolling amounted to a recrystallization anneal, and that the purification treatment should be 1200°C or lower if recrystallization is to be avoided.

W – 25Re – 30Mo

In the as-reduced condition, pre-annealed specimens retained the large equiaxed grain structure up to about 13.5 percent cold reduction, at which point a wrought structure became apparent. Grain sizes decreased with increasing amounts of reduction as shown in Figure 4.2, the largest decrease occurring at reductions in the range of 15 to 30 percent. Grain size in this instance refers to grain height measured in the thickness direction of the material.

TABLE 4.1

RECRYSTALLIZATION AND AGING SPECIMENS BEFORE TESTING

Specimen No.	Pre-Rolling Treatment[a]	Reduction, %	Final Sheet Thickness, cm	Hardness, DPH[b]	Grain Size, microns[c] Width	Height
W – 25Re – 30Mo						
1	A	13.5	0.046	508	62.3	62
2	A	24.6	0.039	525	49.4[d]	30
3	A	39.8	0.030	560	50.4[d]	24.8
4	A	45.5	0.027	560	51[d]	28.5
5	A	54.0	0.023	588	49.4[d]	19
6	A	59.1	0.019	595	55.7[d,e]	17.2
7	B	33.5	0.036	575	32.2[d,e]	10.5
8	B	43.3	0.031	610	31.2[d,e]	9.5
9	B	51.2	0.027	610	30.8[d,e]	9.0
10	B	65.1	0.019	615	34.3[d,e]	8.3
11	B	56.9	0.047	583	35.1[d,e]	7.3
12	B	76.2	0.026	625	32[d,e]	6.8
W – 30Re – 30Mo						
1	C	19.4	0.042	525	94.8	95
2	C	32.7	0.034	553	33.8	16.5
3	C	43.1	0.029	573	32.5[d]	13.9
4	C	55.8	0.022	578	31.8[d,e]	14.2
5	C	66.8	0.015	583	39.5[d,e]	9.7
6	D	18	0.043	554	54.5	55
7	D	35.1	0.033	563	42.7[d]	15.1
8	D	45.7	0.027	573	57.4[d]	23.4
9	D	54.8	0.022	580	33.8[d]	11.3
10	B	31.2	0.036	600	115.6[d]	19.3
11	B	41.5	0.030	630	105.3[d,e]	17.9
12	B	49.8	0.026	635	105.3[d,e]	13.9
13	B	68.3	0.019	638	131.6[d,e]	14

[a]A – Annealed 2 hours at 2000°C.
B – Stress relieved at 1400°C.
C – Purified, solution annealed for 2 hours at 2000°C.
D – Solution annealed 2 hours at 2000°C.

[b]Average of 3 to 5 indentations with 2.5-kg load using microhardness tester: usual spread of values ± 10 DPH.

[c]Grain sizes were determined by the linear intercept method on transverse sections.

[d]Individual grains elongated.

[e]Microstructure heavily worked, wrought.

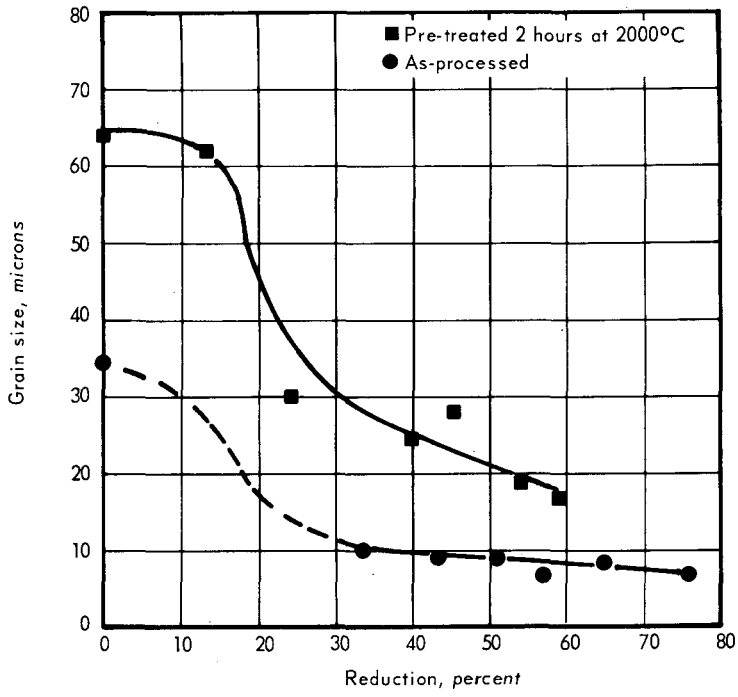

Fig. 4.2 – Influence of pre-treatment (2 hours at 2000°C) and amount of reduction in thickness by cold rolling on W – 25Re – 30Mo grain size

Isochronal anneals of 0.5 hour at 1200°, 1300°, 1400°, 1600°, 1800°, and 2000°C for both the as-processed and pre-annealed materials produced complete recrystallization at 1800°C and 2000°C regardless of the amount of reduction; at 1600°C for reductions of 40 percent or more, and at 1400°C for a reduction of 90 percent. Grain sizes after recrystallization decreased markedly at reductions of 20 to 30 percent with relatively small additional decreases for the larger amounts of reduction. Data for recrystallization at 1800°C shown in Figure 4.3 are representative of other temperatures.

Isothermal anneals for various times of material reduced 60 percent (a region of particular interest in fabrication) indicated essentially complete recrystallization at 1400°C in 8 to 9 hours, at 1300°C in approximately 100 hours, and at 1200°C in about 1000 hours. Measurements of the amount of recrystallization at various temperatures indicated that the activation energy for recrystallization was approximately 100 kcal.

W – 30Re – 30Mo

The recrystallization behavior of the W – 30Re – 30Mo alloy in the different purities and conditions examined was similar to that of the W – 25Re –30Mo alloy. In grain sizes obtained in 0.5-hour anneals at 1800°C (Figure 4.4) the decrease in the recrystallized grain size after 10 to 30 percent reduction is similar to that of the W – 25Re – 30Mo alloy. Although the different starting conditions led to differences at low reductions, the grain size after annealing was roughly equal at reductions greater than 30 percent; hence the recrystallization behavior was not markedly influenced by purification or solution treatments or by the presence of some sigma phase. For reductions greater than 30 percent, recrystallization was complete after 0.5 hour anneals at 1600°C or above and after 2 hours at 1400°C.

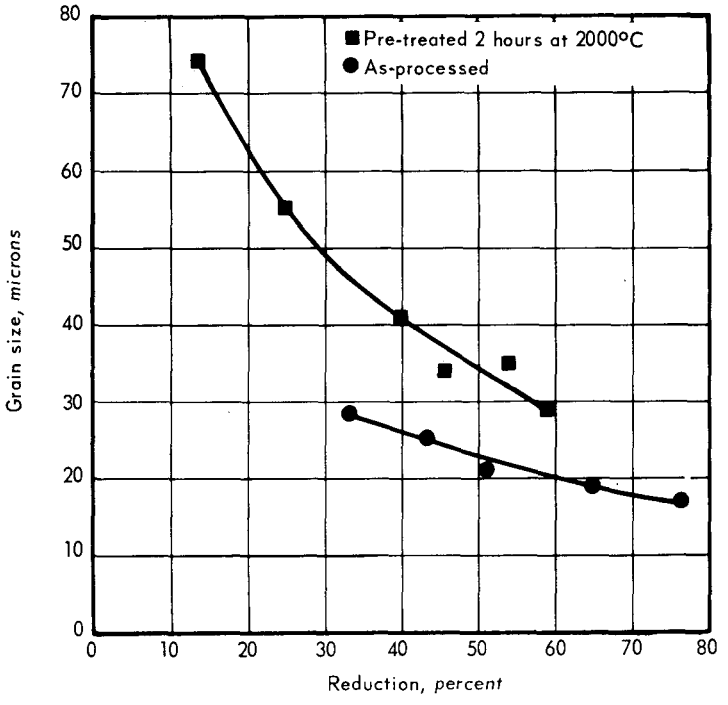

Fig. 4.3 – Grain size of W – 25Re – 30Mo as a function of reduction in thickness after 0.5 hour at 1800°C recrystallization anneal

Hardness

The hardness of the two alloys increased rapidly with increasing amounts of reduction, as indicated in Figures 4.5 and 4.6, but reductions greater than 40 percent produced little additional change. Relatively little effect of the 2-hour pre-anneal at 2000°C remained after about 20 percent cold work. In the W – 30Re – 30Mo alloy, the as-processed material attained a higher hardness with reduction than the annealed materials; this behavior is attributed to a rhenium-rich sigma phase present in this alloy in the as-processed condition. Hardness changes due to annealing and aging are noted subsequently.

AGING

Aging studies of the W – 25Re – 30Mo and W – 30Re – 30Mo alloys were conducted to assess grain growth and hardness changes of the original process materials and specially purified W – 30Re – 30Mo. Specimens were in the same pre-annealed, as-processed, and cold-worked conditions utilized in the recrystallization studies (Table 4.1). Measurements were completed on the two alloys after aging to 1000 hours at 1400°, 1600°, and 1800°C, and to 500 hours at 2000°C in helium.

Grain Growth

In general, the grain growth behavior of the two alloys was comparable. The major difference noted for the different purities and structures was that the materials pre-annealed two hours at 2000°C prior to reduction were less susceptible to secondary recrystallization.

In the W – 25Re – 30Mo alloy, the pre-annealed material exhibited good grain size stability at all aging temperatures and times, except for one specimen reduced only 5 percent which exhibited secondary recrystallization after 500 hours at 2000°C. Fairly typical results for these specimens are shown in Figure 4.7 for aging at 1800°C. The maximum grain size attained in aged specimens that had been reduced 40 percent or more was in

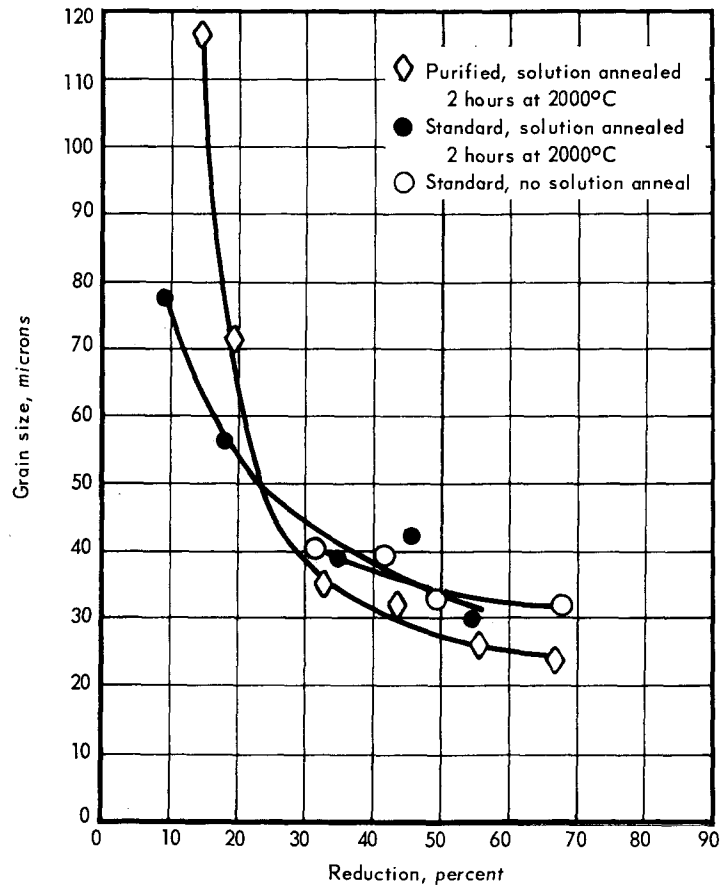

Fig. 4.4 – Grain size of W – 30Re – 30Mo as a function of reduction in thickness after 0.5-hour recrystallization anneal at 1800°C

the range of 40 to 50 microns. The lightly reduced specimens attained maximum grain sizes ranging up to 100 microns.

In contrast, the W – 25Re – 30Mo specimens in the as-processed condition, i.e., those with a wrought structure obtained by 5 percent reductions with anneals at 1400°C, exhibited secondary recrystallization in amounts roughly proportional to the amount of reduction. At 1600°C, only the specimens reduced 51 and 65 percent were affected. At 1800°C all specimens were affected, although the amount of secondary recrystallization in the two smallest reductions was not large. The 1800°C results are shown in Figure 4.8.

The overall behavior of the W – 30Re – 30Mo alloy including the specially purified material was essentially the same as that described for the W – 25Re – 30Mo alloy. As indicated in Figures 4.9 and 4.10, one specimen of the standard process material exhibited secondary recrystallization, whereas none was observed in the specially purified material. Secondary recrystallization occurred at 1800°C in the as-processed W – 30Re – 30Mo in all specimens reduced more than approximately 30 percent.

Secondary Recrystallization

Secondary recrystallization is a fairly common problem in both powder-metallurgy and arc-melted refractory metals. Its occurrence can cause loss of ductility and changes in other mechanical and physical properties. As with ordinary grain growth, the driving force for the process is the surface energy of grain boundaries. Although the causes are not well

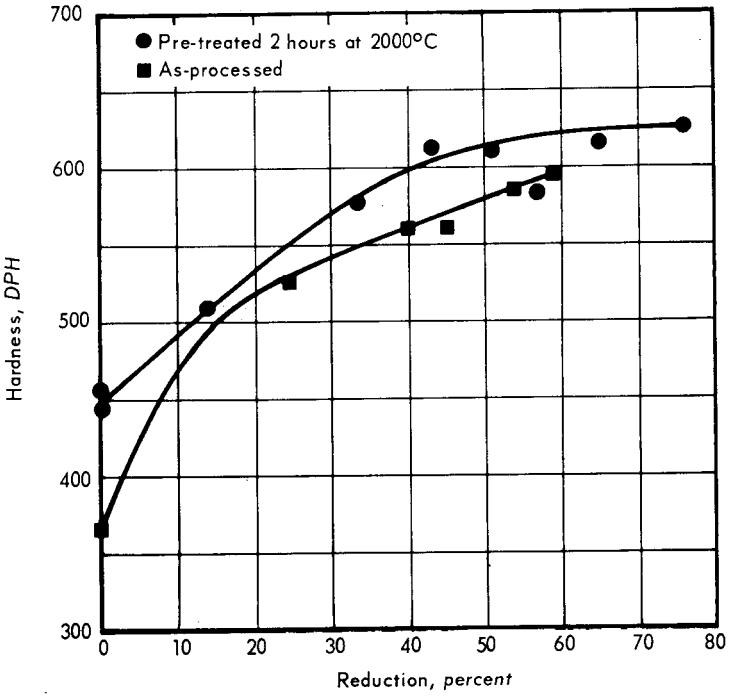

Fig. 4.5 — Hardness changes of W — 25Re — 30Mo alloy as a function of reduction in thickness by cold rolling

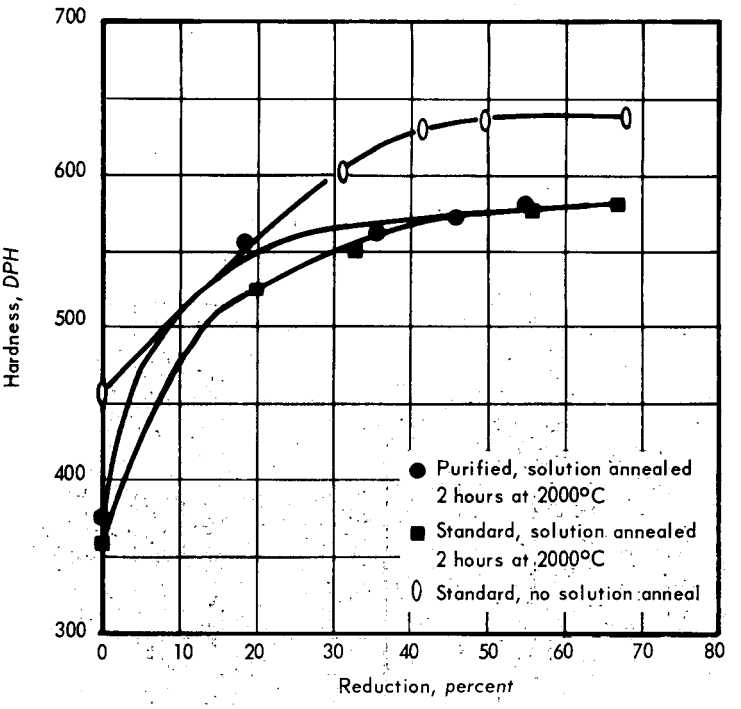

Fig. 4.6 — Hardness changes of W — 30Re — 30Mo alloy as a function of reduction in thickness by cold rolling

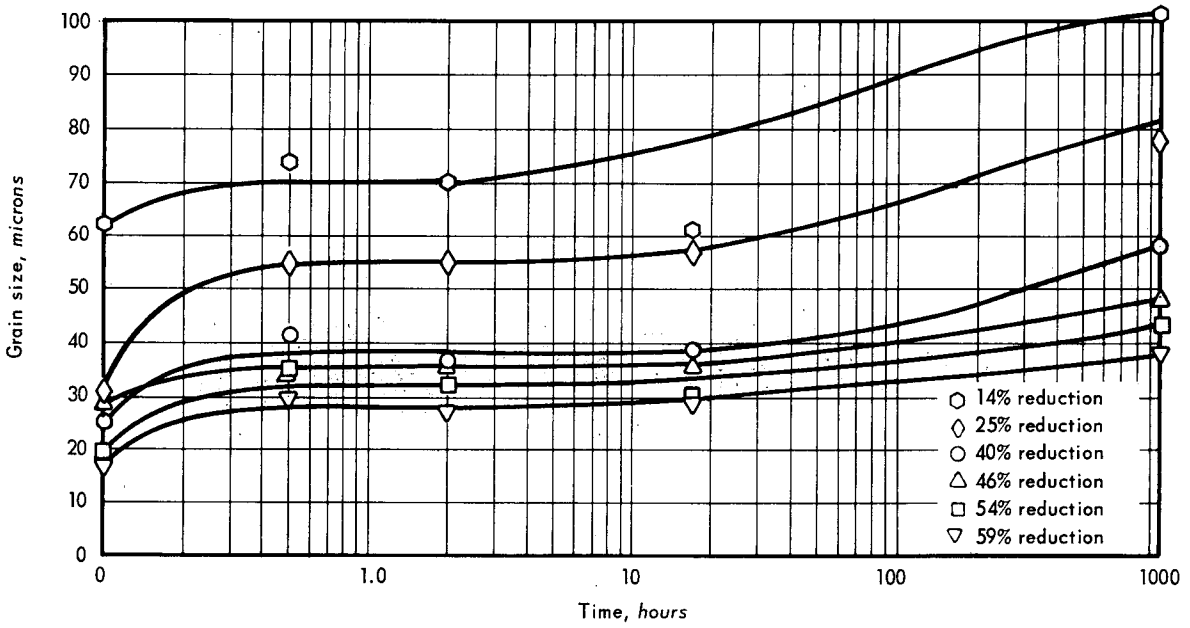

Fig. 4.7 – Grain size changes as a function of time at 1800°C for W–25Re–30Mo alloy pre-treated for 2 hours at 2000°C in H_2 before cold rolling and recrystallization anneals

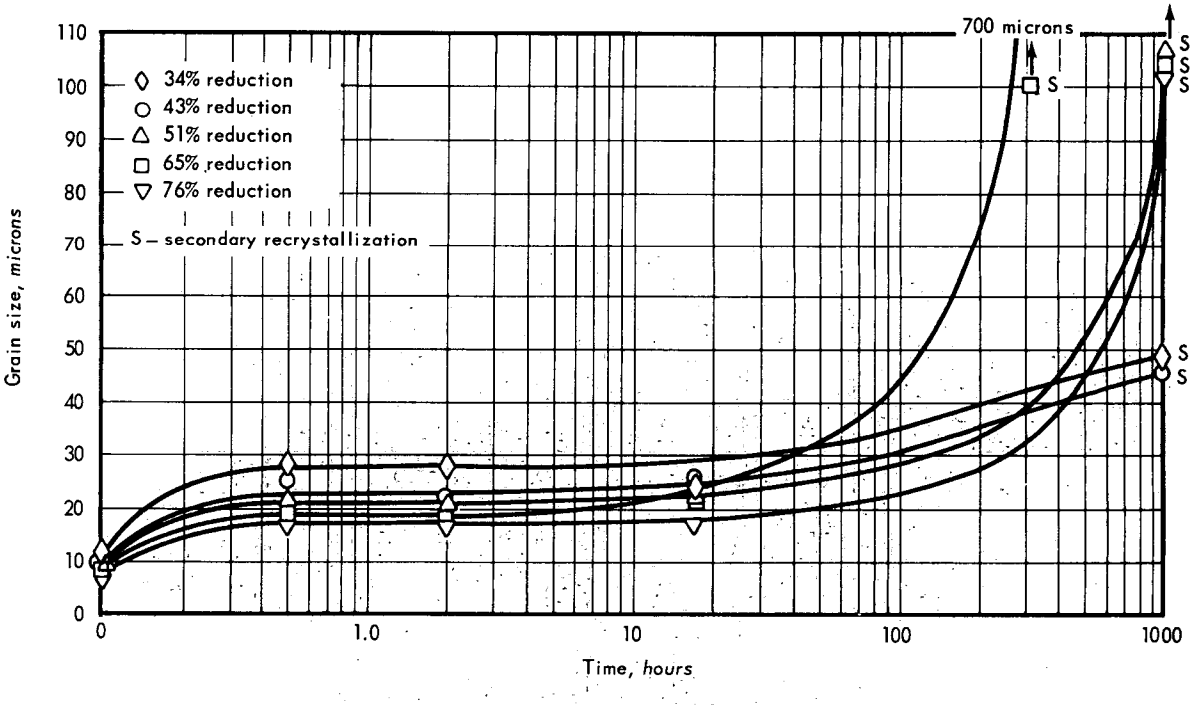

Fig. 4.8 – Grain size changes as a function of time at 1800°C for W–25Re–30Mo alloy. Samples were original process material cold-rolled from the as-fabricated condition.

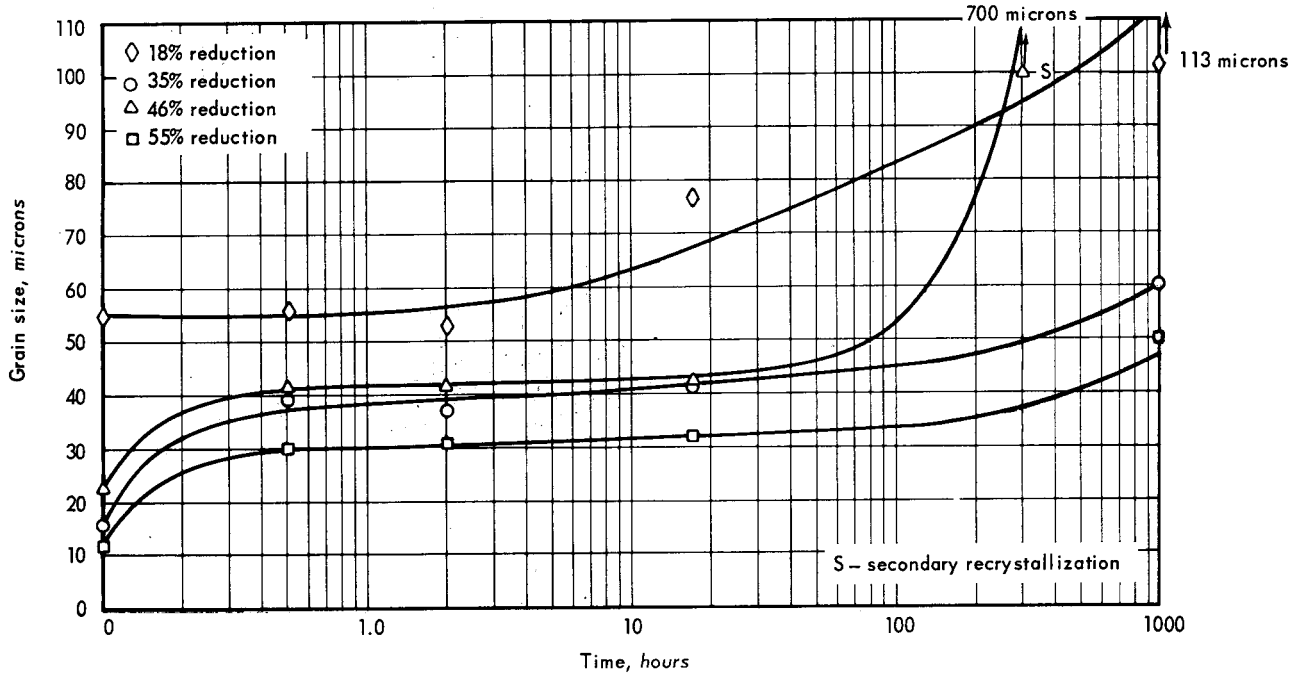

Fig. 4.9 – Grain size changes as a function of time at 1800°C for standard process W – 30Re – 30Mo solution annealed for 2 hours at 2000°C before cold rolling and recrystallization anneals

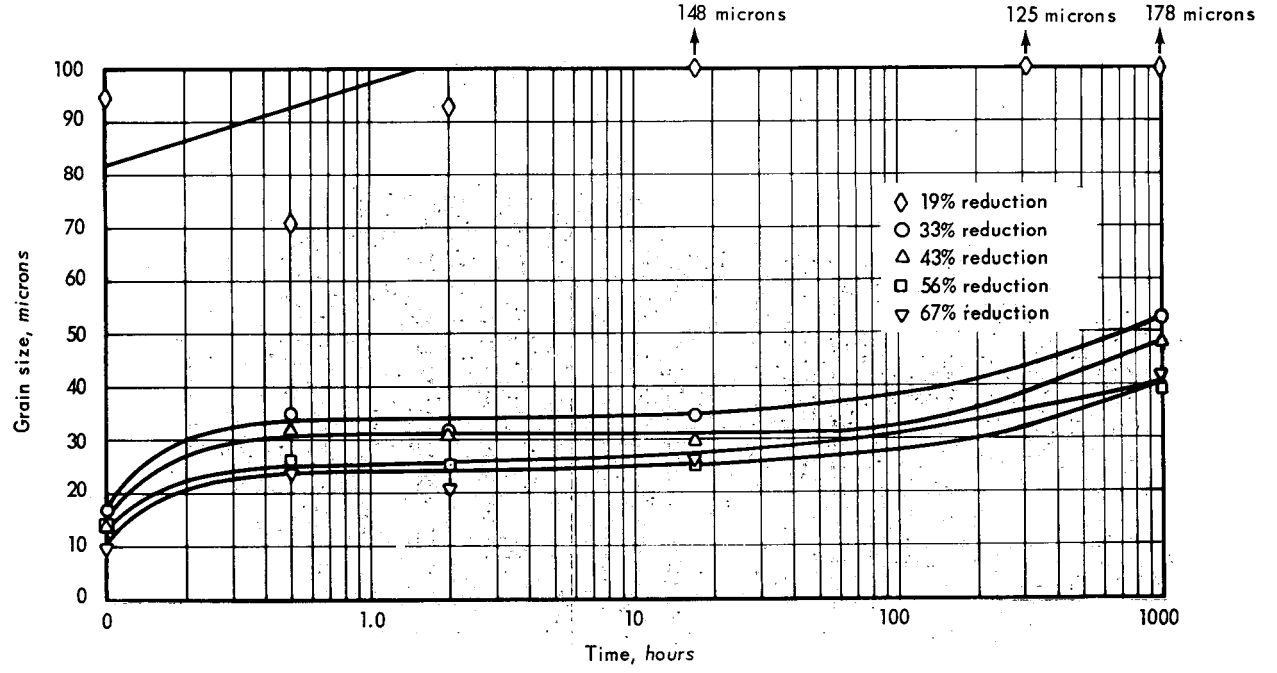

Fig. 4.10 – Grain size changes as a function of time at 1800°C for purified W–30Re–30Mo alloy solution annealed for 2 hours at 2000°C before cold rolling and recrystallization anneals

defined, purity, preferred orientation, and deformation are known to influence the phenomenon.

As noted in the preceding paragraphs, several specimens of both W-Re-Mo alloys exhibited areas of secondary recrystallization after aging at 1600°C or higher. Further investigation indicated that this occurred in about half the production sheets and confirmed the aging studies which indicated that it was related to amount of reduction and to purity. No definitive cause or complete solution to the problem was found.

In examinations of recent production lots of sheet materials of the two alloys, secondary recrystallization occurred in five of ten sheets produced by the original rolling procedure (small cold reductions with intermediate stress-relief anneals at 1400°C). Secondary recrystallization areas were found in four specimens after 17 hours at 2000°C in hydrogen and in a fifth specimen after an induction period of about 60 hours at 2000°C. In those materials susceptible to the phenomenon, there appeared to be a direct relationship between the amount of cold working and the occurrence of secondary recrystallization, as in the grain growth measurements described previously. This relationship was particularly apparent upon aging specimens that were cold rolled from 5 to 75 percent with no intermediate anneals, and is probably caused by strain-induced grain growth since secondary recrystallization is enhanced by both light and heavy plastic deformations.[1,2] It is not solely a function of the amount of deformation, however. Some W-Re-Mo specimens have been cold reduced 50 to 75 percent without secondary recrystallization occurring on subsequent aging treatments, whether with or without anneals during reduction.

The possibility that the impurity concentration or inclusions – or rather the lack of these – is a factor in secondary recrystallization was investigated with some success. Indirect evidence is the fact that materials produced some time ago, with a reportedly higher impurity concentration,[3] showed no secondary recrystallization in aging studies.[4] Furthermore, although there is no statistical sampling, secondary recrystallization has only recently been observed in work under various other tasks using these materials.[5] Direct evidence was obtained when specimens from a large sheet of W – 30Re – 30Mo, known to undergo extensive secondary recrystallization, were heated in a nitrogen atmosphere at temperatures ranging from 1000° to 1200°C and times from 3 minutes to 3 hours, annealed in argon at 2000°C for 2 hours, then cold rolled to 60 percent reduction in thickness. These specimens did not form secondary growth when aged for 100 hours at 2000°C even though some were strained by bending. In contrast, the control specimen without the nitrogen treatment formed extensive secondary growth within 17 hours at 2000°C in the same test. Chemical analyses failed to establish clearly that the nitrogen content was changed; both the nitrided and control samples indicated 10 to 20 ppm nitrogen. Considering that not all production materials exhibited secondary recrystallization, these data suggest the existence of a critical concentration of impurities which may prevent the phenomenon. For example, Fiedler[6] found that nitrogen concentrations in excess of 0.0184 percent inhibited secondary recrystallization in silicon-iron.

[1] C. D. Calhoon, "Exaggerated Grain Growth in Reactor-Grade Hafnium After Small Deformations," KAPL-3193, September 2, 1966.

[2] K. T. Aust, "Crystal Growth from the Solid State," General Electric Research and Development Center, Report No. 66-C-294, September 1966, p. 11.

[3] "AEC Fuels and Materials Development Program Progress Report No. 67," GE-NMPO, GEMP-67, June 30, 1967, p. 65.

[4] "Sixth Annual Report – High-Temperature Materials Program, Part A," GE-NMPO, GEMP-475A, March 31, 1967, pp. 133–135.

[5] "710 Reactor Program Progress Report No. 24," GE-NMPO, GEMP-529 (Conf.), July 31, 1967, pp. 37–42.

[6] H. C. Fiedler, "The Behavior of Nitrogen in 3.1% Silicon-Iron," General Electric Research and Development Center, Report No. 67-C-225, June 1967.

Efforts to relate the secondary recrystallization to local inhomogeneities or to preferred orientation were not successful. Local inhomogeneities of the order of 1 percent concentration variations can be detected in the materials by X-ray fluorescence techniques. These areas probably extend only to thicknesses of a few grains in diameter since both etching and polishing resulted in variations of the composition of the same spot of 3- to 6-mm diameter. Although the measurements may not be conclusive, no correlation between these inhomogeneities and the secondary recrystallization was obtained comparing sheets known to be susceptible to it and free of it. Similar negative results were obtained in X-ray diffraction analyses of preferred orientation. At present there is no way of detecting susceptibility to the phenomenon other than actual aging tests.

Hardness Changes

The general trend of the hardness changes of the purified W – 25Re – 30Mo and W – 30Re – 30Mo alloys was almost identical to that in material not specially purified, although the purified alloys were about 20 VPH units higher (400 versus 380) than the normal material for the softest condition. Data up to 1000 hours are summarized in Figure 4.11 for specimens aged at 1200° to 2000°C. As noted previously, the increase in hardness of W – 30Re – 30Mo alloy at 1400°C and 1600°C at the longer aging times is attributed to the sigma phase that develops in amounts up to about 7.5 percent at these temperatures.

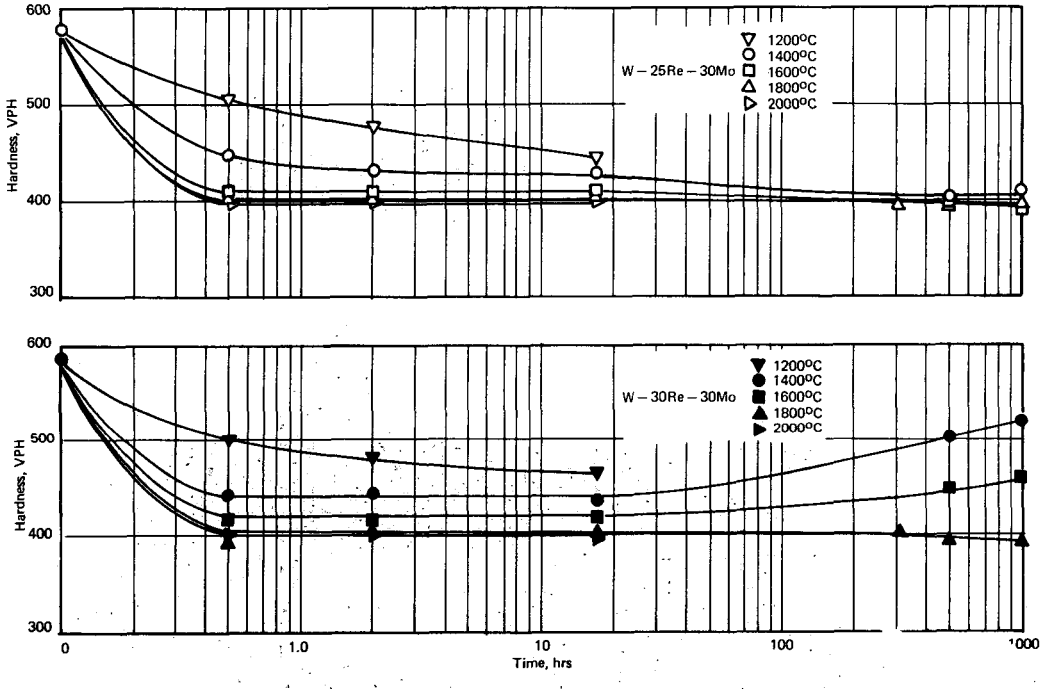

Fig. 4.11 – Change in room-temperature hardness of cold-rolled W-Re-Mo alloys after aging at elevated temperatures

DUCTILITY

Bend ductility measurements under a variety of heat treatment and microstructural conditions established that good room-temperature ductility could be achieved in W–25Re–30Mo with stress relieving at 1150°C following about 80 percent cold reduction or following a combination of hot and cold reduction of recrystallized material. This behavior was a factor in the selection of modified production procedures outlined in Figure 4.1. Similar treatment

provided only moderate ductility (40- to 50-degree bends at room temperature) in the W – 30Re – 30Mo alloy. This material is ductile in the recrystallized condition, however, provided recrystallization is carried out at temperatures above that at which the sigma phase is in solution, approximately 1700°C.

Bend ductilities were determined by means of the 4T bend test. Because of the sample quantities required, the earlier rather than the later definition of this bend test recommended by the Materials Advisory Board was followed.[7] Bends were made both parallel and normal to the rolling direction on 0.05-cm-thick sheet specimens.

The bend ductility of the two alloys was measured as a function of amount of cold reduction. Prior to reduction, the materials were annealed 2 hours at 2000°C, a recrystallization anneal for both alloys. They were then cold rolled to reductions in thickness ranging from 10 to 60 percent. Bend tests (4T) were made on the as-reduced sheet parallel to the rolling direction. Results showed decreases in ductility of the W – 30Re – 30Mo with increasing amounts of reduction up to about 35 percent. The ductile-to-brittle transition temperatures (DBTT) were still below room temperature after 10 percent reduction, but with 35 percent reduction, room-temperature bends (parallel) of only 10 to 20 degrees were obtained. No further reduction of ductility occurred with additional cold reductions in thickness up to 60 percent. The ductile-to-brittle behavior of W – 25Re – 30Mo alloy differed from that of the W – 30Re – 30Mo in that it did not change after the 2000°C recrystallization anneal; the DBTT remained at 250° to 300°C. There was no apparent reduction in ductility in this alloy as a function of increased cold working.

Ductility changes as a function of the annealing temperature following various amounts of cold reduction of the recrystallized structure indicated that approximately 80 percent reduction was necessary to attain good room-temperature ductility (with 90-degree bends) with non-recrystallization anneals of 0.5 hour at 1150°C. Recrystallized specimens 0.5 mm thick were subjected to room-temperature bend tests parallel to the rolling direction after 50 percent reduction. Results following 0.5-hour anneals at temperatures from 800° to 2000°C in 200°C steps (Figure 4.12) show an increase in bend ductility of the W–30Re–30Mo alloy with increasing annealing temperature; 90-degree bends or greater were obtained at or above 1800°C. For the 0.5-hour time period involved, 1800°C was the lowest temperature of those examined that recrystallized the material and did not result in precipitation of sigma phase. The W – 25Re – 30Mo alloy increased in ductility to a maximum 30-degree bend after 0.5 hour at 1600°C and did not increase beyond this value at higher temperatures.

Ductility changes on aging the alloys are essentially predictable on the basis of recrystallization and sigma formation. The W – 30Re – 30Mo alloy is ductile in the recrystallized condition; hence aging at 1600°C or higher temperatures at which sigma does not precipitate does not induce brittleness, although secondary recrystallization in some cases reduced the bend angles at room temperature to 50 to 70 degrees. At 1400°C and lower, sigma formation in this alloy apparently contributed to embrittlement even when recrystallization occurred and parallel room-temperature bends of only 10 to 20 degrees were obtained after aging times greater than about 70 hours. The W – 25Re – 30Mo alloy is brittle in the recrystallized condition; hence aging for sufficient time at temperatures greater than about 1200°C resulted in parallel bends of only 10 to 20 degrees. Somewhat surprisingly, aging periods of 7 to 25 hours at 1800°C resulted in 70-degree parallel bends in this material; this relatively good ductility region was not observed at 1600°C or 2000°C.

The DBTT for different production procedures are summarized in Table 4.2. Other than material produced by the improved production procedure, which had a DBTT of less than

[7]The earlier bend definition was given in MAB-176-M, "Evaluation Test Methods for Refractory Metal Sheet Materials," November 1961. The later definition is given in MAB-192-M (same title) April 1963. Both reports by National Academy of Sciences, National Research Council, Washington, D.C.

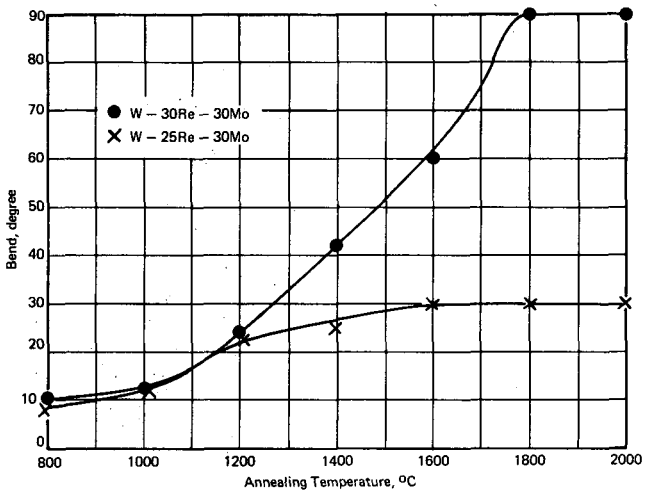

Fig. 4.12 – Influence of isochronal (0.5 hour) anneals in H_2 on the bend ductility of two W-Re-Mo alloys cold-rolled 50 per cent to 0.51-mm thickness before annealing

-70°C, the W – 25Re – 30Mo yielded 10- to 20-degree bends at room temperature under all conditions investigated. The normal sharp transition from ductile-to-brittle bending was evident usually from 50 to 90 degrees rather than from 0 to 90 degrees. In all cases other than the improved process material, bends parallel to the rolling direction had a higher transition temperature than those normal to the rolling direction. Parallel bends of approximately 90 degrees were obtained in the original process material at approximately 300°C for the as-processed; for the 2000°C anneal, and for the aged conditions, although some change in the shape of the curve occurred with these different treatments. Ninety-degree bends normal to the rolling direction occurred at approximately 150° to 200°C and were approximately independent of the condition of the material.

As with the W–25Re–30Mo alloy, the improved production procedure yielded W–30Re–30Mo material with a DBTT of less than -70°C. The ductile-to-brittle behavior of normally processed W – 30Re – 30Mo alloy, however, differed from that of the W – 25Re - 30Mo alloy, particularly with respect to the effects of 2000°C anneals and aging treatments at 1400°C or anneals at 2000°C. As indicated in Table 4.2, the original process material had a DBTT of 100° to 150°C (normal to the rolling direction) in the as-produced condition, somewhat lower than that of the W – 25Re – 30Mo alloy. In the specially purified material, the DBTT for bends normal to the rolling direction was about 400° to 500°C; that for bends parallel to the rolling direction was greater than 500°C. This difference in behavior of the purified material is attributed, at least partly, to the sigma developed as a result of the final purification treatment. This conjecture is supported by the results for materials annealed 2 hours at 2000°C to place the sigma in solution; in this condition both the original process and purified materials had a DBTT of less than -70°C, appreciably lower than that of the original process material. Aging of the original process and purified materials at 1400°C raised the DBTT higher than 500°C in both the as-produced and solution-treated conditions; again, presumably because of the growth of the sgima phase at this temperature.

4.2 MOLYBDENUM

Studies of NMPO-processed molybdenum under this task are directed toward improving fabrication and properties of powder metallurgy material. Since molybdenum is brittle in the recrystallized condition, its fabrication in high-purity form presents the same problem

TABLE 4.2

BEND TEST DUCTILE-TO-BRITTLE TRANSITION TEMPERATURES OF W-Re-Mo ALLOYS

Alloy	Production Process[a]	Treatment	Bend Direction[b]	DBTT, °C[c,d]
W – 25Re – 30Mo	Original Process	15 min final anneal at 1400°C	P	250 – 300
			N	150 – 175
W – 25Re – 30Mo	Original Process	520 hr at 1400°C	P	200 – 250
			N	100 – 125
W – 25Re – 30Mo	Original Process	2 hr at 2000°C	P	30° at 150 90° at 300
			N	150 – 190
W – 25Re – 30Mo	Original Process	2 hr at 2000°C, 520 hr at 1400°C	P	20° at 200 90° at 300
			N	20° at 100 90° at 190
W – 25Re – 30Mo	Improved Process Modification No. 2	0.5 hr at 1150°C, stress relief	P	<–70
			N	<–70
W – 30Re – 30Mo	Original Process	As-produced, 15 min final anneal at 1400°C	P	50° at 25 90° at 150
			N	100 – 150
W – 30Re – 30Mo	Original Process	2 hr at 2000°C	P	50° at 25 90° at 100
			N	–50
W – 30Re – 30Mo	Original Process	As-produced, 520 hr at 1400°C	P	~410
			N	10° at 200 50° at 500
W – 30Re – 30Mo	Original Process	2 hr at 2000°C then 520 hr at 1400°C	P	10° at 200 30° at 350–500
			N	10° at 200 40° at 500
W – 30Re – 30Mo	Special Purified	As-produced, 15 min final anneal at 1400°C	P	10° at 200 25° at 500
			N	10° at 100 45° at 400 90° at 500
W – 30Re – 30Mo	Special Purified	2 hr at 2000°C	P	<–70
			N	<–70
W – 30Re – 30Mo	Special Purified Modification No. 2	1 hr at 1700°C or higher	P	<–70
			N	<–70
W – 30Re – 30Mo	Special Purified	As-produced, 520 hr at 1400°C	P	10° at 200 30°–40° at 500
			N	15° at 200 30°–40° at 500
W – 30Re – 30Mo	Special Purified	2 hr at 2000°C, then 520 hr at 1400°C	P	10° at 200 40°–50° at 500
			N	25° at 200 45° at 500

[a]Refer to Figure 4.1 for outline of the different production processes.

[b]P = bend made parallel with the rolling direction; N = bend made normal to rolling direction.

[c]The DBTT was based on a 90-degree bend in 4T bend tests on 0.05-cm-thick sheet. The 4T bend test was as defined in MAB-176-M.

[d]Entries with degree symbol indicate bend angle at temperature cited.

described previously for W – 25Re – 30Mo; specifically, avoiding recrystallization conditions in final purification treatments. The principal options are the three modified production procedures outlined in Figure 4.1, as applied to molybdenum.[8] Pending better definition of the important impurity concentrations, efforts have been concerned mainly with modification No. 2, i.e., omission of the final purification treatment. For this procedure the reduction, recrystallization, grain growth, and ductility measurements described in the following paragraphs indicated that stress-relieving treatments of 0.5 hour at 1000°C after 40 percent reduction at room temperature yielded sheet material with a DBTT below -70°C and good grain size stability on aging.

FABRICATION

The powder metallurgy molybdenum is readily cold rolled in the wrought condition induced by hot rolling sintered compacts from 1.1-cm to 0.1-cm thickness; reductions of up to 25 percent per pass are achieved at room temperature. As illustrated in Figure 4.13, material in the as-hot-rolled condition[8] could be satisfactorily cold reduced up to 60 percent with and without stress relief treatments of 0.5 hour at 1000°C including cross rolling, but fracturing occurred if the material was recrystallized. Cold reductions up to 80 percent without stress relieving were achieved but the sheet contained laminations. Some lamination occurred at 60 percent reduction, but 40 percent reductions appeared sound. The sheet was successfully cross rolled provided a stress-relief treatment preceded changes in rolling direction.

RECRYSTALLIZATION

A few recrystallization anneals of cold-reduced sheet material were made to verify that the powder-metallurgy molybdenum conformed to existing data on recrystallization.[9] Specimens of "N"- and "C"-processed molybdenum sheets were annealed at 1000° to 1200°C in the as-hot-rolled condition and after room-temperature reductions of 20, 40, 60, and 80 percent without intermediate stress-relief treatments. ("N" and "C" materials refer to nitric or hydrochloric acid leaching of powders prior to compaction.)[10] In 1-hour anneals of the as-hot-rolled condition, recrystallization of the "N" material was approximately 50 percent complete at 1100°C and complete at 1200°C; the "C" material was about 50 percent recrystallized at 1050°C and complete at 1100°C. These recrystallization temperatures were lowered only about 50°C by the additional room-temperature reductions, evidently adding little to the wrought structure developed in the hot rolling.

DUCTILITY

Bend ductility measurements indicated reasonable ductility in the as-reduced condition and very good ductility after stress-relieving treatments. All bends were made parallel to the rolling direction on strip 6.4 mm wide. Tests were made at room temperature on a die with 6.4-mm span and a 2T radius punch operated at 1.27 mm per minute until the first indication of failure or until a 90-degree bend was attained. In the as-reduced condition, the hot-rolled material bent 55 degrees and the materials cold rolled 40 and 60 percent bent approximately 40 and 20 degrees, respectively. After stress relieving 0.5 hour at 1000°C, the hot-rolled material bent 80 to 90 degrees and the cold-rolled materials bent 90 degrees or more. Recrystallized material yielded bends of about 5 degrees regardless of reduction history.

[8]GEMP-475A, p. 114.

[9]"Refractory Metals and Alloys," M. Semchyshen and J. J. Harwood, editors, Interscience Publishers, New York, N.Y., 1960, pp. 290–293.

[10]"AEC Fuels and Materials Development Program Progress Report No. 71," GE-NMPO, GEMP-1002, December 29, 1967, pp. 65–66.

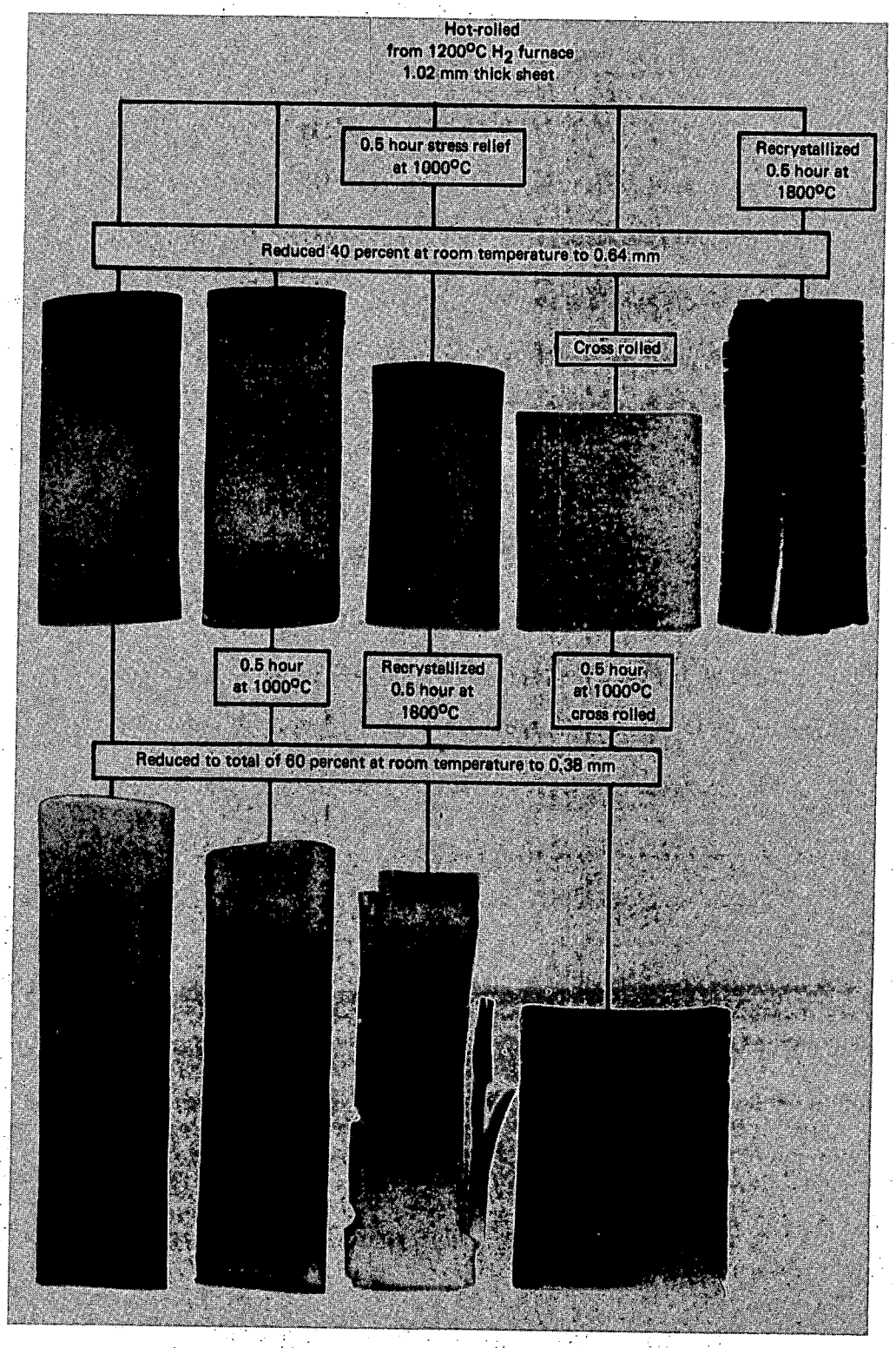

Fig. 4.13 – Unalloyed powder-metallurgy molybdenum reduced at room temperature. Preferred procedure involves 0.5 hour at 1000°C stress-relief treatment.

Additional measurements established that the DBTT of the hot-rolled material given a subsequent 40 to 60 percent reduction at room temperature and stress relieved 0.5 hour at 1000°C was below -70°C. For material with this same reduction, a stress relief of 0.5 hour at 1100°C raised the DBTT to 0°C.

AGING STUDIES

The "C" and "N" materials were aged in hydrogen for 1000 hours at temperatures of 1200° to 2000°C to assess the stability of the structures developed in processing. As in the other studies, the specimens were obtained from as-reduced hot-rolled material that was subsequently cold reduced up to 80 percent.

All materials exhibited very good microstructural stability at temperatures to 1400°C, and those reduced 20 percent prior to aging were stable at 1600°C. In this stable temperature region grain growth appeared normal; e.g., the specimen reduced 60 percent recrystallized at 1200°C to a grain size of 27 microns which, on aging 1000 hours at this temperature, increased to 39 microns. Secondary recrystallization occurred at 1600°C in materials reduced 40 percent or more and in all materials aged at higher temperatures.

4.3 FAST REACTOR FUEL CLADDING ALLOYS

The program on fast reactor fuel cladding alloys is concerned with varying heat treatment of the alloys to obtain better ductility in creep-rupture tests and, ultimately, under irradiation. Principal areas to be pursued initially are fine grain size materials, various carbon distributions obtained in work – heat-treatment combinations and in single and double aging treatments, and some work on cavitation fracture. Evaluation of the heat treatments will be based primarily on creep and rupture tests of pressurized tube specimens and of sheet specimens. All tests will be conducted in argon. Tensile tests as a function of strain rates extending to very low strain rates will be utilized as a supplementary means of evaluating heat treatments. Tests will be conducted mainly at 650°C; selected materials will also be investigated at 538°C and 760°C.

Materials included in the program are the following:

316 stainless steel
316 + Nb stainless steel
Incoloy 800
12R72HV *
19-9DL
Vanadium alloys[11]
- HSV 207
- HSV 208
- HSV 209
- V – 15Cr – 5Ti

Haynes 56

Initial efforts are concerned with 316 stainless steel and 19-9DL.

4.4 SUMMARY AND CONCLUSIONS

Studies on W – 30Re – 30Mo and W – 25Re – 30Mo (at. %) alloys led to simpler, lower-cost production procedures and greatly improved room-temperature ductility properties for powder metallurgy materials. Data were obtained on recrystallization, grain size,

*Product of Sandvik Steel, Inc., Fairlawn, N.J. Nominal composition is Fe–15Cr–15Ni–1.2Mo–0.45Ti–1.8Mn–0.5Si–0.1C.

[11] "Vanadium Cladding Alloy Development, Quarterly Progress Report December 31, 1967," Westinghouse Electric Corp., Adv. Reactors Division, Madison, Pennsylvania, WARD-3791-13.

hardness, and ductility changes on aging of these alloys at temperatures to 2000°C for periods up to 1000 hours.

Similar studies have resulted in procedures for producing molybdenum sheet; parts of this procedure are still under study.

4.5 PLANS AND RECOMMENDATIONS

Work on fast reactor fuel cladding alloys will include investigation of heat treatment and work combinations on 316 stainless steel, and 19-9DL in terms of ductility changes as a function of strain rates; creep-rupture tests will be initiated on selected materials. Other materials will be included in the studies as they become available.

Effort on the refractory metals will concentrate in two areas: (1) definition of impurity concentrations obtained in molybdenum processed by modifications No. 1 and 2 through internal friction and improved chromatographic analysis, and (2) completion of weld integrity and porosity studies currently in progress to define material purity requirements and welding conditions.