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SUMMARY

The effect of prior cold reduction (up to 40 percent by rolling) on the room-temperature tensile ductility of L-605 (HS-25) after aging at 1600° F for times up to 1000 hours was determined. Prior cold work was found to lessen the embrittling effect of 1600° F exposure and cause increased room-temperature tensile strength and hardness, which were largely maintained even after long (1000 hr) aging times. The nature of the precipitation was changed from that of a preferential intergranular type, as observed in unworked L-605 after aging, to a much more homogeneous type within the grains. This effect was believed to be the primary reason for improved postaging ductility. X-ray diffraction studies confirmed the previously reported precipitation of Co_2W and an M_6C type carbide, but showed that prior cold work tended to alter the carbide reaction.

INTRODUCTION

Because of its fabricability, weldability, elevated-temperature strength, and oxidation resistance, the cobalt-base alloy L-605 (HS-25; composition given in table I) has many high-temperature applications. The mechanical and physical properties of L-605 are summarized in references 1 and 2. This alloy, however, tends to become brittle, at room temperature, after longtime exposure to high temperatures (ref. 3). Even though substantial high-temperature ductility is retained, the loss of low-temperature ductility is undesirable in most engineering applications, particularly those subject to mechanical and thermal cycling (e.g., aircraft gas turbines).

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TABLE I. - COMPOSITION OF L-605 (HS-25)

Element	Aerospace Materials Specification,[a] weight percent	Composition of heat investigated, weight percent[c]
Chromium	19 to 21	20.07
Tungsten	14 to 16	14.62
Nickel	9 to 11	10.06
Iron	[b]3	1.67
Manganese	1 to 2	1.52
Silicon	[b]1	.63
Carbon	0.05 to 0.15	.08
Phosphorous	[b]0.04	.012
Sulfur	[b]0.03	.011
Cobalt	Balance	Balance

[a]AMS 5537B (ref. 14).
[b]Maximum.
[c]As determined by supplier.

Wlodek (ref. 4) attributed the embrittlement of L-605 mainly to the precipitation of the Laves phase Co_2W during high-temperature exposure (with possible contributions due to the precipitation of carbides) and to the formation of hexagonal-close-packed (hcp) cobalt from the face-centered-cubic (fcc) matrix during the fracture process. It was suggested (ref. 4) that lowering the amount of silicon in the alloy would lessen the amount of Laves phase (Co_2W) precipitation and that increasing the iron content would prevent the embrittling fcc → hcp transformation. Sandrock, Ashbrook, and Freche (ref. 5 and discussion of ref. 4) have shown that L-605 can be substantially improved, with respect to its embrittling characteristics, by a reduction in silicon content (to 0.23 percent, or less), which tends to reduce the amount of Laves phase precipitation during high-temperature exposure. Variations in iron content (up to 3.24 percent), on the other hand, seemed to have no overall effect on embrittlement due to longtime high-temperature exposure.

Although this compositional change afforded substantial improvements in the postaging ductility of L-605, it was desirable to consider other methods as well. Since the nature of the precipitation in L-605 has been shown to be strongly intergranular (refs. 4 and 5) and to lead to an almost completely intergranular brittle fracture, any procedure that prevents the tendency for intergranular precipitation would be expected to lessen the embrittling effect of high-temperature exposure in this alloy. The method considered in this investigation was the introduction of precipitate nucleation sites within the grains by cold deformation prior to high-temperature exposure. It was believed that this would lead to increased precipitation within the grains and would restrict the amount of solute available for precipitation at grain boundaries. The fact that plastic deformation can substantially affect the nature of precipitation by the introduction of nucleation sites has been known for some time (ref. 6). Keh and Porr (ref. 7) have studied the effect of cold work on the temper brittleness of 5140 steel. They found that cold work greatly reduced the susceptibility to embrittlement and attributed this improvement to a redistribution of embrittling solute atoms (such as phosphorous) from the prior austenite grain boundaries to the sites of imperfections created by plastic deformation. This cold work also resulted in less tendency for brittle intergranular fracture.

The present investigation was conducted to study the effect of prior cold deformation on the ductility (as measured by room-temperature tensile elongation) of L-605 aged for long periods of time at 1600° F. Deformations up to 40 percent by cold rolling and aging times up to 1000 hours were used. The effects of cold deformation and longtime aging on the room-temperature tensile strength, hardness, and microstructure were also investigated. X-ray diffraction analyses were made to study structural changes due to cold rolling and/or aging.

INVESTIGATIVE PROCEDURE

Material Investigated

The material used in this investigation was a single commercial heat of L-605 (HS-25). The composition, as reported by the supplier, is shown in table I. The material was received in the form of 0.048-inch-thick sheet in the mill-annealed (2250° F solution treated - rapid air cooled) condition.

Specimen Preparation

The mill-annealed sheet was first cut into rectangular blanks 1.5 by 6 inches, with the long dimension parallel to the original hot rolling direction. Rolling was done at room temperature on a four-high rolling mill utilizing 2.5-inch work rolls of 52100 steel. The blanks were rolled at a speed of approximately 7 feet per minute and in passes, each of which gave approximately 5 percent reduction of the original thickness, until the desired total reductions ranging from 5 to 40 percent were achieved. After cold rolling and prior to aging, the blanks were ground to obtain the specimen configuration shown in figure 1.

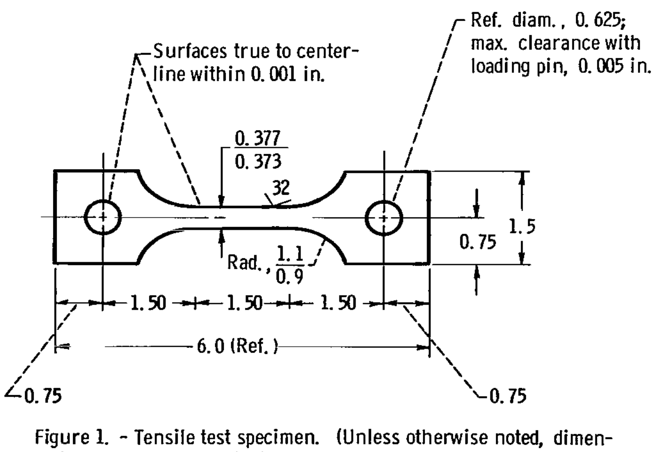


Figure 1. - Tensile test specimen. (Unless otherwise noted, dimensions may vary ±0.01 in.)

The machined tensile specimens were aged in air at 1600° F, the temperature at which the greatest rate of embrittlement (as shown by room-temperature bend tests) had been observed (ref. 4). Furnace temperature was continuously recorded. Specimen temperature was monitored periodically by means of a separate thermocouple located immediately adjacent to the specimens. At no time was the specimen temperature found to have varied more than 10° F from 1600° F.

All cold-reduced specimens were aged simultaneously for uninterrupted times of 50, 200, and 1000 hours. The data for the unrolled specimens are those reported for heat 4 of reference 5, which was the same heat used in this investigation. After aging, specimens were air-cooled to room temperature. Surface oxidation during aging was slight (less than 0.001 in. film), even after 1000-hour exposure at 1600° F. As will be discussed in the Intergranular oxidation section, some intergranular oxidation was observed after longtime aging.

Tensile Testing

Room-temperature tensile tests were made with a 60 000-pound capacity hydraulic tensile machine. Universal joints were used on both pull rods to minimize loading eccentricities. A standard 1-inch "snap on" extensometer was used to obtain the load-strain curve to a strain of about 0.5 percent. The extensometer was then removed, and the test was continued to fracture. Ultimate tensile strength, 0.2-percent-offset yield strength, and elongation at fracture (1-in. gage length) were determined for each specimen. At least two specimens were tested for each rolling and aging condition investigated. Any fractures that occurred at or outside the gage marks were not included in the reported results.

Although strain rate was not directly controllable with the tensile machine used, a constant valve setting was used in conducting all tests. A rough measure of average plastic strain rate was determined for each specimen by dividing the percent elongation at fracture by the time of the test. By this measure, strain rates were found to vary between 0.7 and 4.3 percent per minute. Variations of this order would not be expected to significantly affect the tensile properties of L-605 at room temperature (ref. 2).

Hardness Testing

Rockwell A hardness testing was done on the shoulders of untested tensile specimens. Surface oxide was first removed with a small, low-pressure dental sandblasting unit using 50-micron alumina powder. Five readings were taken on each sample and averaged.

Metallographic Studies

Longitudinal sections were taken through material that had been subjected to various rolling and aging conditions, as well as through selected tensile fractures, and were metallographically prepared. Unaged specimens were electrolytically etched in an HCl-H_2O_2 (hydrochloric acid - hydrogen peroxide) solution (100 cc of 30-percent HCl plus a few drops H_2O_2). Aged specimens were electrolytically etched either in Water's etch (30 cc of saturated boric acid + 70 cc of 5-percent sulfuric acid) or the HCl-H_2O_2 solution. Any stains produced during etching were removed by swabbing with ammonium hydroxide. Photomicrographs were taken at X70, X500, and X750.

X-ray Diffraction Studies

Samples of material in various rolled and aged conditions were prepared for X-ray diffraction analysis. Small segments of sheet were ground into rods 0.020 to 0.030 inch in diameter and approximately 0.5 inch in length. These were then electropolished in a 10-percent H_2SO_4 (sulfuric acid) solution to wires 0.014 to 0.016 inch in diameter. In all cases, the axis of the wire was essentially parallel to the rolling direction of the original sheet. Debye patterns were taken with a 114.6-millimeter-diameter Debye-Scherrer X-ray diffraction camera and chromium radiation. The wire specimen was continuously rotated during the exposure. Interplanar spacings were determined and indexed using as reference the results of Beattie and VerSnyder (ref. 8) for the carbides, of Wlodek (ref. 4) for the Laves phase Co_2W, and of Hofer and Peebles (ref. 9) for the hcp-cobalt.

Specimens of sheet that had been aged 50 hours were also examined by the back-reflection Laue method to determine if recrystallization had occurred. Before exposure to X-rays, at least 0.005 inch of surface was removed by electropolishing in 10-percent H_2SO_4. The X-ray beam was normal to the flat surface during exposure.

RESULTS AND DISCUSSION

The effects of prior cold reduction on the room-temperature mechanical properties and microstructure of L-605 (HS-25) after various aging times at 1600° F are discussed in the following sections.

Mechanical Properties

Ductility. - Figure 2 shows the ductility (tensile elongation) as a function of aging time at 1600° F for various degrees of prior cold reduction. In general, scatter of the

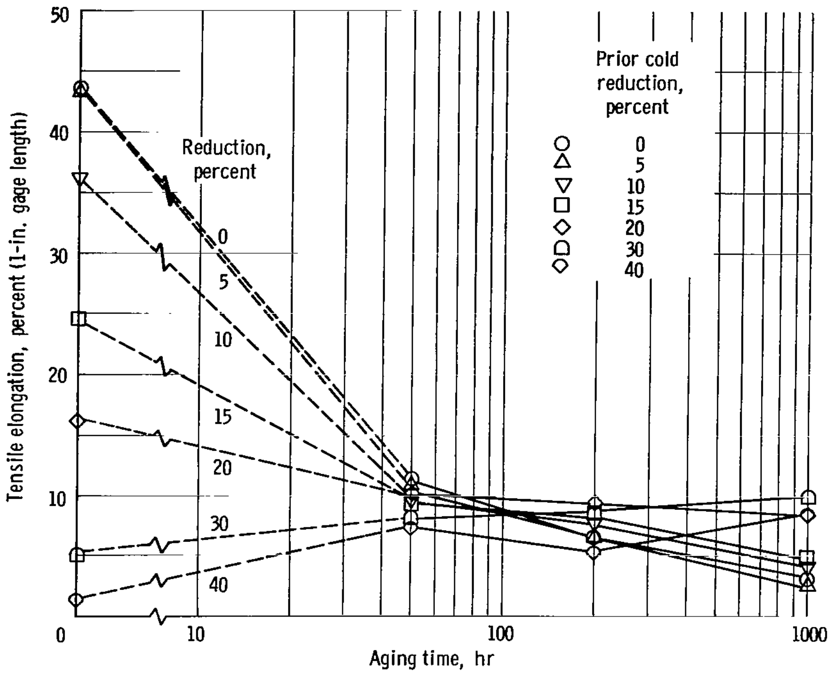


Figure 2. - Effect of prior cold reduction and aging time at 1600° F on room-temperature ductility of L-605.

data was small (table II), and only average values are plotted. For the material that had been cold rolled 20 percent or less there was a fairly rapid drop in ductility after the first 50 hours of aging, followed by a continued but slower loss of ductility after longer aging times. It is also important to note that, for the material that was cold reduced up to 20 percent, the rate of embrittlement generally decreased with increasing prior cold reduction. Because of the high amount of cold work, the 30- and 40-percent as-rolled specimens showed relatively low elongations (about 5 and 1.5 percent, respectively); however, with aging, the ductilities of the 30- and 40-percent rolled material increased rather than decreased. These trends generally resulted in improved ductility after aging 200 and 1000 hours for material with prior cold reduction, as compared with material that had not been rolled.

This is more specifically illustrated in figure 3, which shows ductility after aging 200 and 1000 hours as a function of prior cold-reduction. Both curves show that tensile ductility first increased with prior cold reduction to a maximum value and then decreased. All degrees of prior cold reduction below the crossover of the two curves in figure 3 (approximately 24 percent) resulted in decreasing ductility with increased aging time from 200 to 1000 hours, while the two reductions (30 and 40 percent) above the crossover showed increasing ductility during the same aging period. After aging 200 hours, the maximum ductility was obtained with the 20-percent reduced material, while the maximum after 1000-hour aging was obtained with the 30-percent reduced material. The trend of

TABLE II. - SUMMARY OF TENSILE TEST DATA

Cold reduction, percent	Aging time at 1600° F, hr	Yield strength (0.2 percent offset), psi	Ultimate tensile strength, psi	Ductility, percent elongation in 1 inch
0	0	70 600	138 500	45.0
		71 000	142 500	42.2
	50	67 300	114 300	11.0
		66 500	119 400	11.5
	200	70 700	128 000	7.0
		71 200	125 800	5.5
		70 900	128 300	7.5
	1000	73 400	119 100	3.0
		71 600	120 200	3.5
		70 600	119 400	3.0
		[a]76 200	[a]135 700	[a]3.0
5	0	89 000	153 700	42.5
		85 700	153 800	44.5
	50	81 500	130 400	10.5
		83 400	138 200	10.0
	200	81 300	147 700	6.5
		85 200	149 300	7.0
	1000	78 800	137 500	2.5
		86 700	139 600	3.0
10	0	103 100	162 000	37.0
		103 900	161 000	35.5
	50	93 800	156 900	11.0
		89 600	146 900	8.5
	200	90 400	160 100	8.0
		93 100	159 600	7.0
	1000	89 900	149 800	4.5
		88 900	149 200	4.0
15	0	114 100	172 800	23.5
		107 700	171 500	25.5
	50	98 600	167 500	9.5
		105 300	169 900	9.5
	200	102 600	171 900	7.5
		99 100	168 200	8.5
	1000	97 300	157 400	4.5
		99 800	160 900	5.5

Cold reduction, percent	Aging time at 1600° F, hr	Yield strength (0.2 percent offset), psi	Ultimate tensile strength, psi	Ductility, percent elongation in 1 inch
20	0	138 700	179 300	15.0
		130 100	182 900	17.5
	50	117 900	184 800	10.0
		120 600	183 600	10.0
	200	109 900	179 200	10.0
		114 100	181 700	9.0
	1000	99 300	168 700	10.0
		104 400	169 000	6.5
30	0	133 900	216 900	6.0
		139 700	216 700	4.5
	50	121 300	187 800	8.5
		123 400	192 300	8.0
	200	119 100	188 600	8.5
		118 400	189 100	9.5
	1000	105 400	176 500	11.0
		104 900	174 000	9.0
40	0	140 600	238 400	1.0
		164 800	249 500	2.0
	50	124 300	189 600	7.0
		121 500	184 300	8.0
	200	115 200	179 900	5.0
		115 900	181 500	6.0
	1000	100 600	170 900	10.5
		97 400	165 100	7.0

[a]Specimen machined and polished after aging.

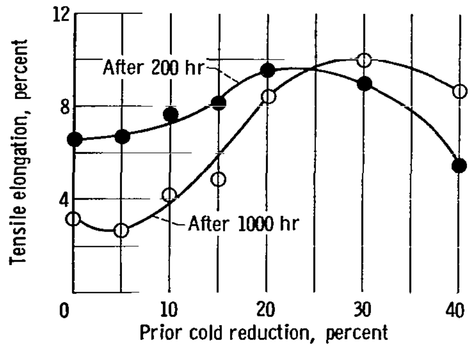
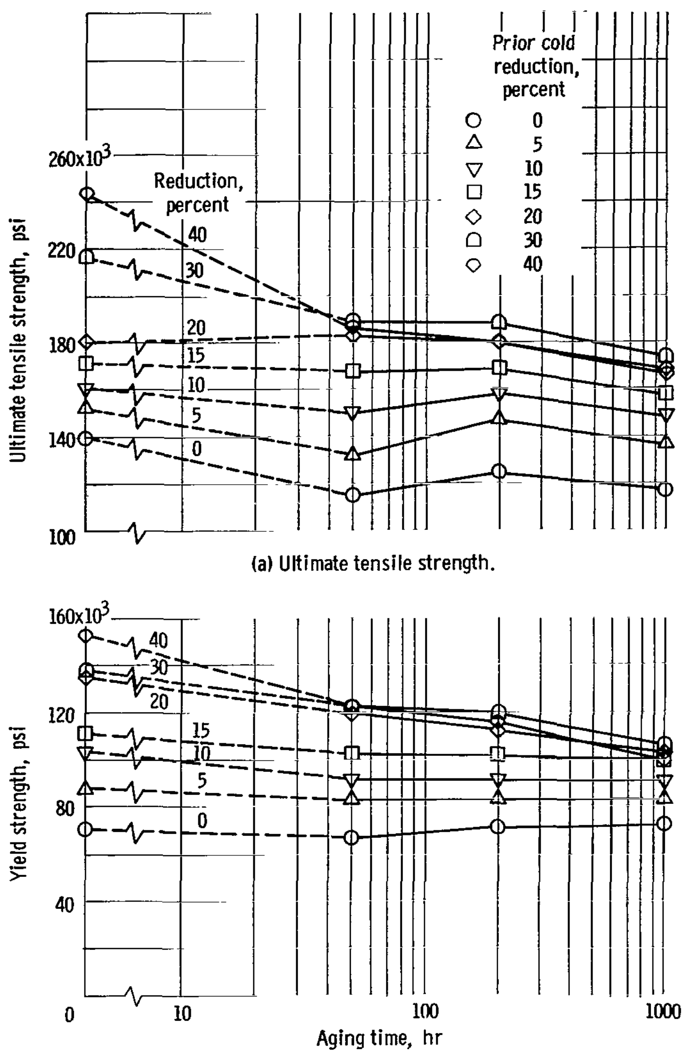


Figure 3. - Effect of prior cold reduction on room-temperature ductility after aging 200 and 1000 hours at 1600° F.



(a) Ultimate tensile strength.

(b) 0.2 Percent yield strength.

Figure 4. - Effect of prior cold reduction and aging time at 1600° F on room-temperature tensile strength of L-605.

the data indicates that the maximum ductility value might be shifted to even higher cold deformations with aging times longer than 1000 hours. Even though the ductility of the material rolled 40 percent generally increased with aging time, it was still lower after 1000 hours than that of the material rolled 30 percent.

Figure 3 shows that cold rolling prior to aging at 1600° F can result in significant improvements in post-aging ductility. This effect was most pronounced in the specimens aged 1000 hours. Here the unrolled material showed an average elongation of only about 3 percent, while the 30-percent cold-rolled specimens showed an average elongation of 10 percent. The latter value may be compared to a maximum elongation of about 16 percent obtained with a very low (0.12 percent) silicon heat (similarly aged but without prior cold reduction) investigated earlier at NASA Lewis Research Center (ref. 5).

It has been reported (ref. 2) that decreasing specimen thickness results in decreased elongation for mill-annealed L-605; however, in the present investigation, material with higher reductions (thinner specimens) showed improved ductility after aging. If specimen size effects influenced the present results, ductility might be further enhanced in thicker specimens subjected to similar rolling and aging treatments.

Tensile strength. - Figure 4

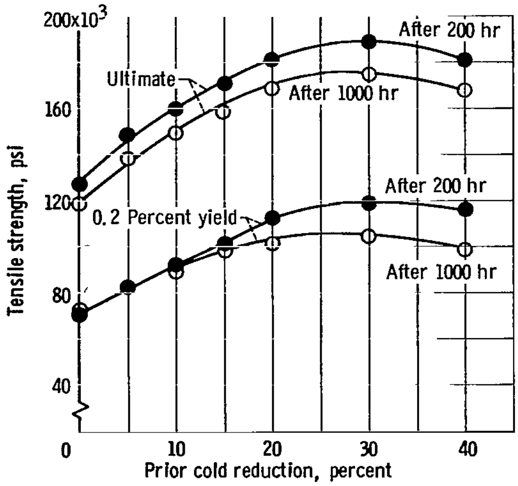


Figure 5. - Effect of prior cold reduction on room-temperature tensile strength after aging 200 and 1000 hours at 1600° F.

shows the effect of aging time at 1600° F on the average room-temperature tensile strength for various degrees of cold reduction prior to aging. There is an overall trend toward decreasing ultimate tensile strength with longer aging times for all reductions. In general, the higher the prior cold reduction, the higher were both the ultimate tensile strength and the 0.2 percent yield strength for all aging times. The one exception to this was the 40-percent cold reduced material, which had tensile strengths less than the 30-percent cold reduced material for all aging times and less than that of the 20-percent cold reduced material after aging 1000 hours.

The effect of prior cold reduction on the ultimate and yield strength of L-605 after aging 200 and 1000 hours is shown in figure 5. The curves show maximums at 30-percent prior cold reduction. As pointed out previously, the greatest ductility also was observed in specimens that had been cold reduced 30 percent prior to aging for long times (1000 hr). For the 1000-hour aging time, the zero-percent prior cold reduced material had an average ultimate tensile strength of about 120 000 psi, compared with 175 000 psi for the 30-percent cold reduction. Similarly, the average yield strength of material aged 1000 hours was increased from 72 000 to about 105 000 psi by 30 percent prior cold reduction.

Hardness. - The effect of aging time and prior cold reduction on hardness is shown in figure 6. The hardness of the material reduced 10 percent or less increased with aging time up to 1000 hours at 1600° F. The hardness of the 15- and 20-percent material increased to maximum values followed by slight decreases. The 30- and 40-percent reduced material showed general decreases in hardness with aging time. The hardness of the 40-percent cold rolled material dropped below that of the 30-percent cold rolled material after aging for 50 hours. It will be noted that the same crossover was observed in the tensile strength comparisons in figure 4. The hardness and tensile strength will be discussed in relation to microstructure in a later section of the report.

After aging 1000 hours, the average Rockwell A hardnesses of all the cold-rolled specimens fell in the relatively narrow range of 70.8 to 72.2, compared with the average Rockwell A hardness of 68.4 for the unrolled specimen (table III).

Microstructure

Cold reduction. - Figure 7 shows the effect of cold reduction on the microstructure

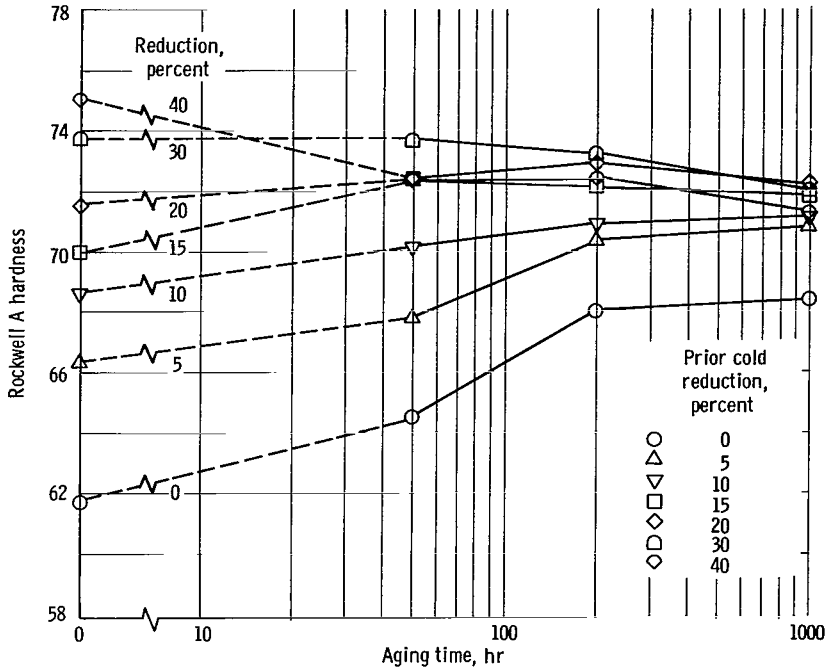
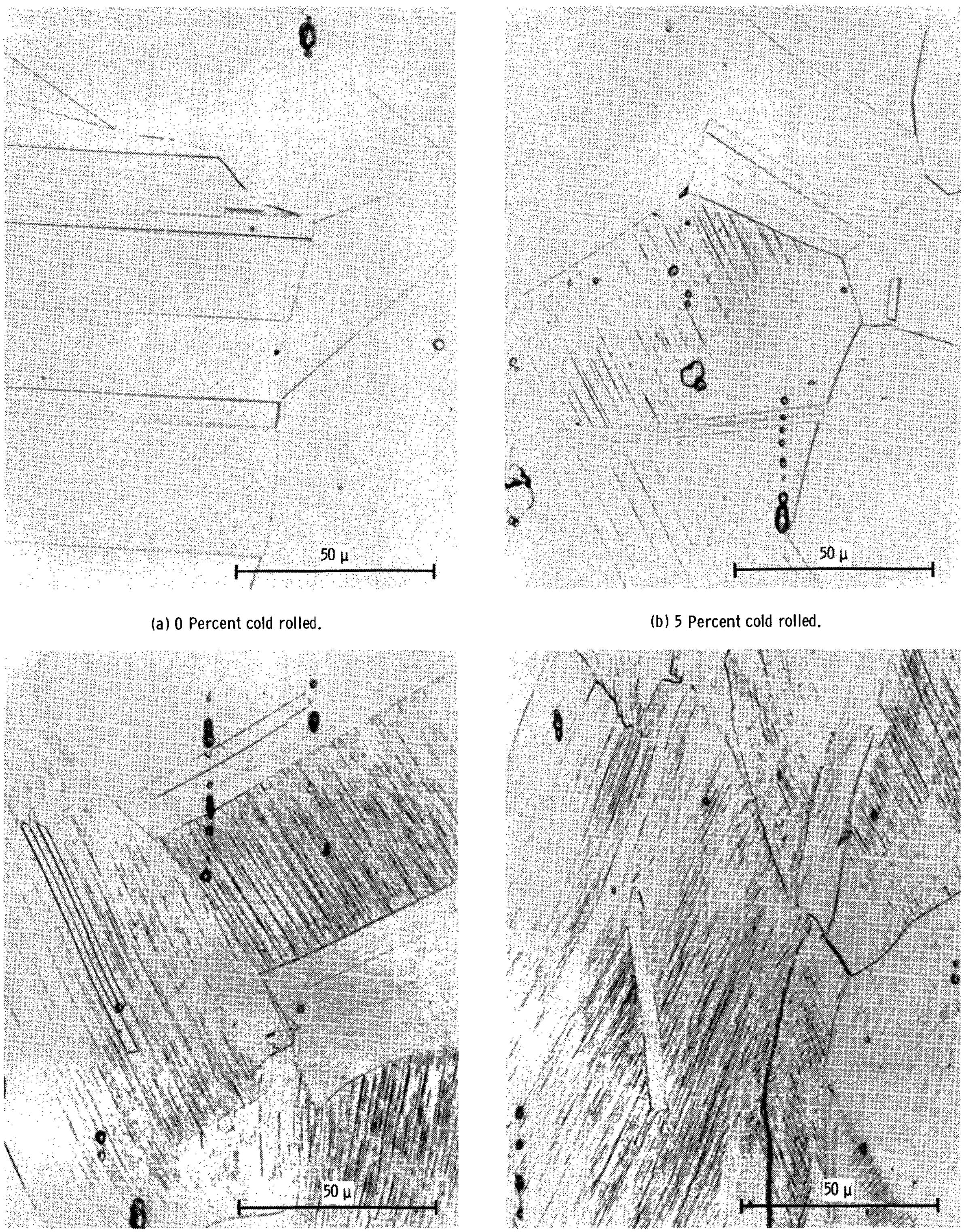


Figure 6. - Effect of prior cold reduction and aging time at 1600° F on hardness of L-605.

TABLE III. - SUMMARY OF HARDNESS DATA

Cold reduction, percent	Aging time at 1600° F, hr			
	0	50	200	1000
	Average Rockwell A hardness[a]			
0	61.7±0.6	64.5±0.2	68.0±0.5	68.4±0.5
5	66.3±0.3	67.7±1.2	70.3±0.5	70.8±0.5
10	68.6±0.4	70.1±0.4	70.9±0.5	71.1±0.2
15	70.0±0.5	72.3±0.3	72.1±0.5	71.8±0.5
20	71.6±0.3	72.4±0.4	72.9±0.2	72.2±0.1
30	73.8±0.5	73.7±0.9	73.2±0.2	72.0±0.1
40	75.1±0.3	72.3±0.5	72.4±0.4	71.3±0.2

[a](Average of five readings) ± (standard deviation).



(a) 0 Percent cold rolled.

(b) 5 Percent cold rolled.

(c) 15 Percent cold rolled.

(d) 30 Percent cold rolled.

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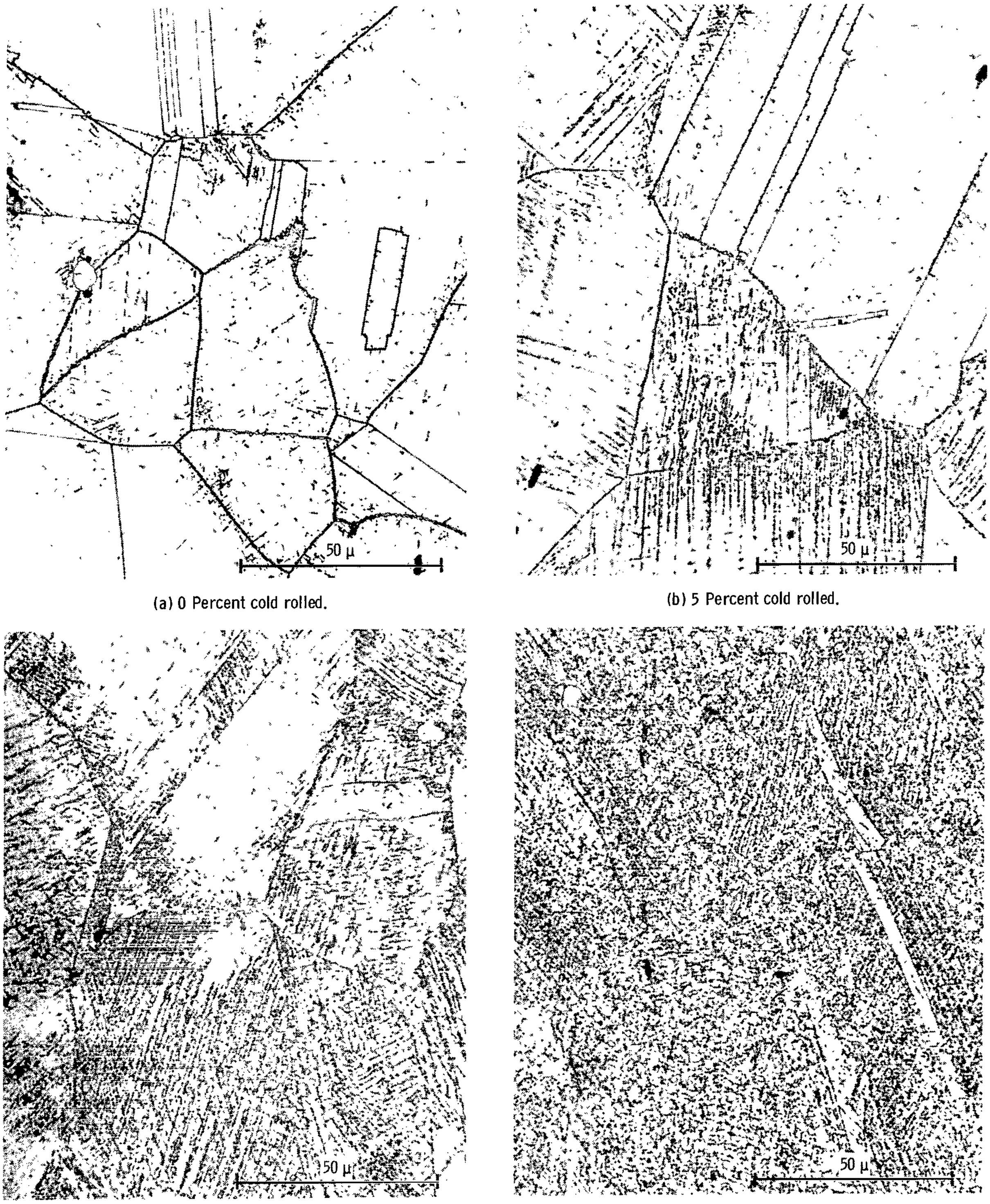
Figure 7. - Effect of cold reduction on microstructure of mill-annealed L-605. Etchant, HCl + H_2O_2.



(a) 0 Percent cold rolled.

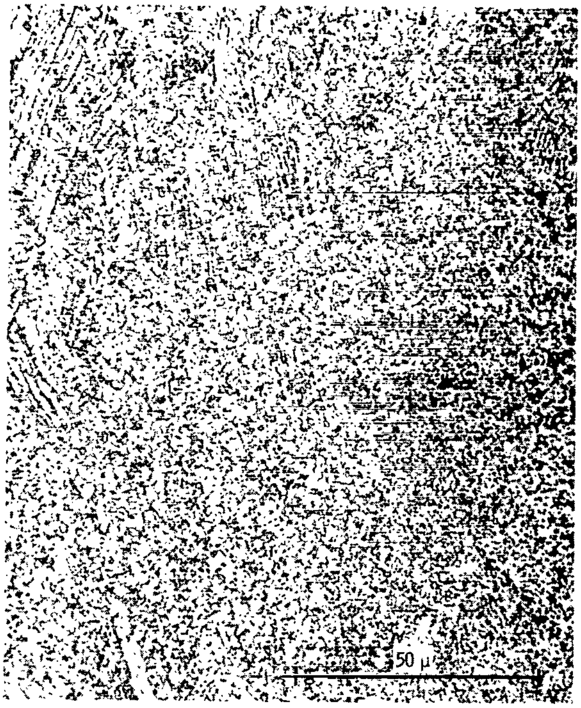
(b) 5 Percent cold rolled.

(c) 15 Percent cold rolled.

(d) 30 Percent cold rolled.

C-66-1612

Figure 8. - Effect of prior cold reduction on microstructure of L-605 after aging 50 hours at 1600° F. Etchant, boric acid + H_2SO_4.



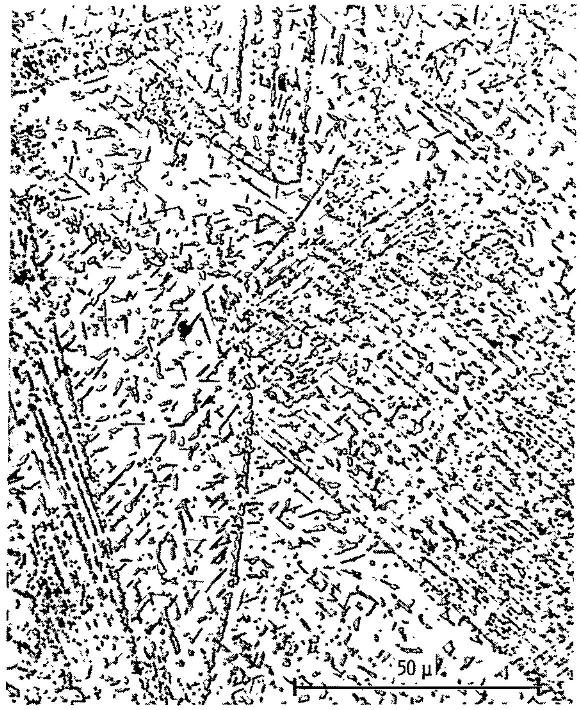
(e) 40 Percent cold rolled. C-66-1613

Figure 8. - Concluded.

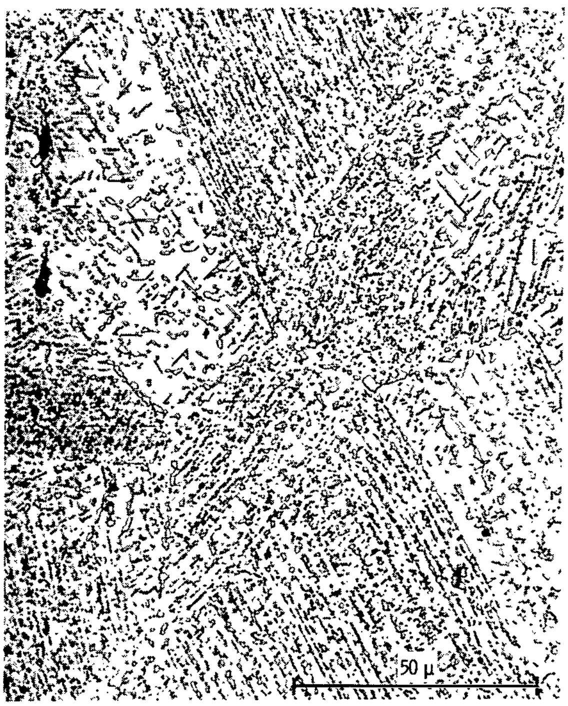
of mill-annealed L-605. In the unrolled (as-received) condition (fig. 7(a)) the microstructure consisted largely of a solid solution of fcc-cobalt. Numerous annealing twins were present. A few carbides, which were not taken into solution during the annealing treatment, were scattered throughout the matrix. After cold rolling 5 percent (fig. 7(b)) numerous parallel striations (slip bands) were evident in some, but not all, of the grains. This is consistent with the fact that not all grains would have been equally oriented with respect to their slip systems. With increasing degrees of cold deformation (15 percent in fig. 7(c)) the number of deformation bands increased greatly. After 30-percent cold deformation (fig. 7(d)), essentially all of the matrix showed deformation bands.

Nature of precipitation. - After aging 50 hours at 1600° F, a substantial amount of precipitation had occurred (fig. 8). In the unrolled specimen (fig. 8(a)) the precipitate was particularly concentrated along grain boundaries and annealing twins, although some randomly located precipitate particles within the grains were also present. Many of these randomly located precipitate particles appeared to be platelike or rodlike in shape and were seen to have a preferred crystallographic relation to the matrix. Several of the grain boundaries shown in figure 8(a) have an almost continuous layer of precipitate. This type of structure led to complete intergranular fracture in the work of Wlodek (ref. 4). In the specimen that had been cold reduced 5 percent prior to aging (fig. 8(b)) preferential precipitation at the grain boundaries was again observed, but a substantial amount of precipitation also occurred on deformation bands such as were seen in figure 7(b). The amount of precipitate at the grain boundaries, however, appeared to be less than that in the zero-percent prior cold reduced specimen (fig. 8(a)), especially in those regions where substantial slip-band precipitation had occurred. With greater amounts of prior cold deformation (15 percent in fig. 8(c) and 30 percent in fig. 8(d)) precipitation appeared to occur more on slip bands and less on grain boundaries. The amount of matrix area that was relatively free of precipitate particles after aging 50 hours at 1600° F decreased with increasing prior cold reduction. In the 30-percent prior cold rolled specimen aged 50 hours (fig. 8(d)) an essentially uniform dispersion of fine precipitate particles was present. Most of these particles were apparently lined up along parallel

(a) 0 Percent cold rolled.



(b) 5 Percent cold rolled.

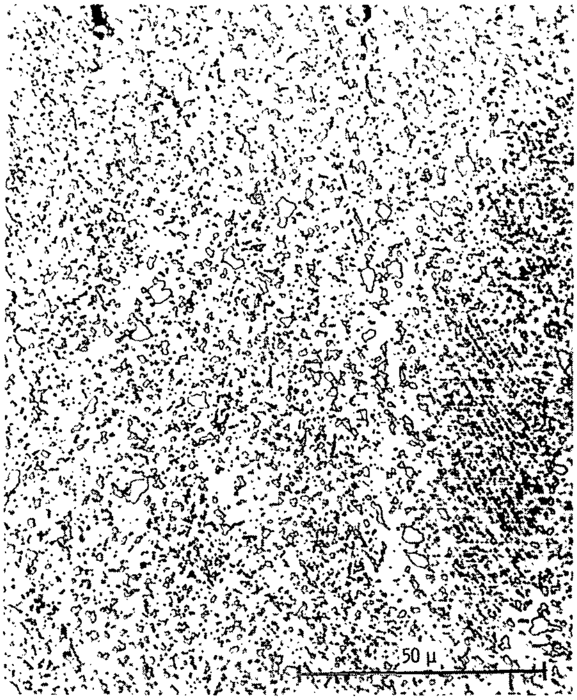


(c) 15 Percent cold rolled.

(d) 30 Percent cold rolled.

C-66-1614

Figure 9. - Effect of prior cold reduction on microstructure of L-605 after aging 1000 hours at 1600° F. Etchant, boric acid + H_2SO_4.



(e) 40 Percent cold rolled. C-66-1615

Figure 9. - Concluded.

slip bands such as were shown in figure 7(d); however, some areas of random precipitate dispersion could be seen. In the 40-percent cold reduced specimen (fig. 8(e)) a more random dispersion of precipitate particles was apparent compared with the 30-percent reduced specimen (fig. 8(d)). A greater degree of cold deformation would be expected to nucleate more precipitate particles within the grains and enhance diffusion, leading to more rapid spheroidization. The net effect would be to modify the slip-band dispersion to a more random one.

Figure 9 shows the microstructure after aging 1000 hours at 1600° F for various degrees of prior cold reduction. In material that was not given any prior cold reduction (fig. 9(a)) evidence existed of substantial growth and agglomeration of the particles in comparison with the microstructure of a similar specimen aged only 50 hours (see fig. 8(a)). The heavy concentration of precipitate particles along grain boundaries and twins was still apparent. The microstructures of the specimens that were cold rolled prior to aging 1000 hours (figs. 9(b), (c), (d), and (e)) are quite similar to those of correspondingly rolled specimens that were aged only 50 hours, except for the particle growth and agglomeration. Many of the particles remained lined up along slip bands as was observed in the specimens aged 50 hours. The precipitate particles in the 40-percent cold rolled specimen (fig. 9(e)) appear to be somewhat more coarse and, again, more randomly located than those in the 30-percent cold rolled specimen (fig. 9(d)).

Recrystallization. - Because of the profusion of precipitate particles in cold-rolled and aged specimens, etching and observation of the matrix grain structure was difficult; however, by somewhat overetching (with respect to the precipitate particles) with HCl-H_2O_2 some observation of the grain microstructure was possible in specimens aged 1000 hours. A few recrystallized grains were observed in specimens that were cold reduced 15 percent prior to aging, but a substantially larger number were observed in the 20-, 30-, and 40-percent cold rolled specimens. None was observed in the 5- or 10-percent reduced specimens. The typical appearance of some recrystallized grains is shown in figure 10, which shows the microstructure of material cold rolled 30 percent and aged for 1000 hours. An equiaxed, recrystallized grain showing several twins can be seen at

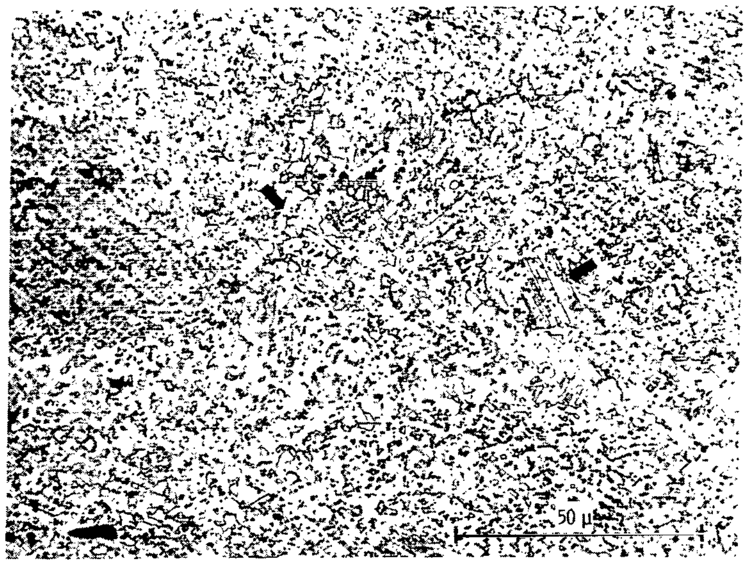


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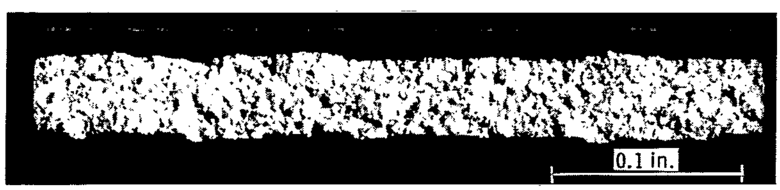
Figure 10. - Photomicrograph of specimen cold rolled 30 percent and aged 1000 hours at 1600° F showing partial recrystallization of matrix. Etchant, HCl + H_2O_2.



0 Percent cold rolled

30 Percent cold rolled C-66-1617

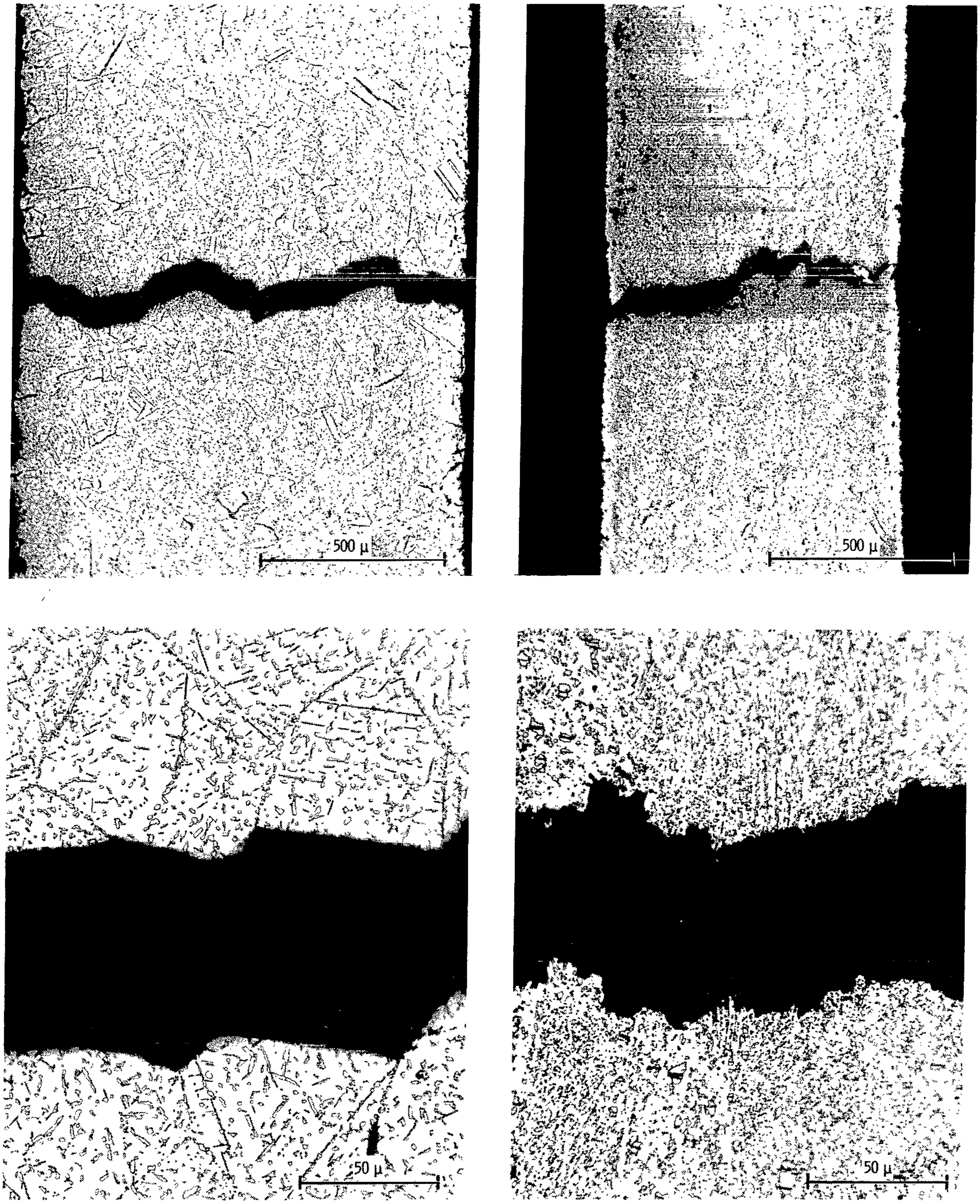
Figure 11. - Effect of prior cold reduction on texture of fracture surface of L-605 aged 1000 hours at 1600° F.

the point of the arrow on the right. Several smaller recrystallized grains can be seen around the point of the arrow on the left as well as in other locations. The limitations of the etching technique precluded accurate quantitative determinations of the amounts of matrix recrystallization; however, in no case did the metallographic study suggest that recrystallization was 100 percent complete after 1000-hour aging at 1600° F.

Because the matrix grain structure could not be observed metallographically on specimens aged only 50 hours, back-reflection X-ray diffraction patterns were made for these specimens. These X-ray patterns indicated recrystallization after 50-hour aging for essentially the same degrees of cold reduction for which the metallographic investigation showed recrystallization after 1000-hour aging.

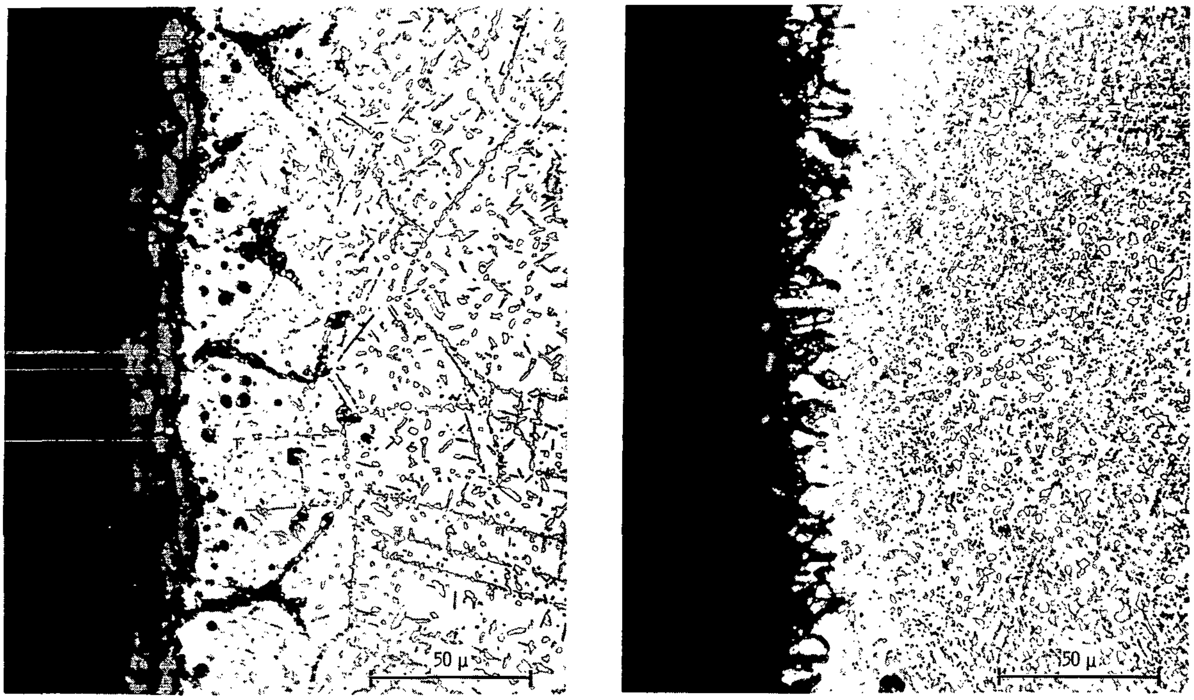
Nature of fracture. - The fracture textures of aged and tested tensile specimens depended on the degree of prior cold reduction. This dependence is illustrated in figure 11, which shows the fracture surfaces of two 1000-hour aged specimens, one with no prior cold reduction and another with 30-percent cold reduction. The fracture texture of the unrolled specimen was much coarser than that of the 30-percent rolled specimen. Examinations of the profiles of these fractures at higher magnifications (fig. 12) showed that fracture in the unworked and aged specimen (fig. 12(a)) took place mainly on grain boundaries or straight twin boundaries where the preferential precipitation had occurred; however, in the specimen that was cold rolled 30 percent prior to aging (fig. 12(b)) the fracture surface was much rougher or serrated on a fine scale, which suggests a more tortuous and difficult fracture path. This may be explained by the more random distribution of the precipitate particles in the cold rolled and aged specimen and possibly also by the finer partially recrystallized structure.

Intergranular oxidation. - In figure 13(a), which shows an unrolled, 1000-hour aged specimen, a small amount (up to 0.002 in. depth) of intergranular oxidation can be seen near the surface. Intergranular oxidation was reported by Wlodek (ref. 4) as a possible factor in the embrittlement of L-605 which had been aged in air. Figure 13(b), which shows a 30-percent cold rolled and aged specimen, shows a much lesser penetration of oxide. It was thought that this reduction in the depth of intergranular oxidation might have contributed to the improvement in the postaging ductility; however, an unrolled specimen that was machined after aging 1000 hours to remove all intergranular oxidation showed essentially the same low ductility as that shown by specimens which had not been machined after aging (table II, p. 7). From this limited result it appears that intergranular oxidation did not affect the ductility of aged L-605 in this investigation. A 6-percent higher yield strength and an approximately 13-percent higher ultimate strength were obtained with the machined specimen, however, which indicates that the intergranular oxidation may have reduced the load bearing ability of L-605 slightly by reducing the effective cross-sectional area.



(a) 0 Percent cold rolled. (b) 30 Percent cold rolled. C-66-1618

Figure 12. - Effect of prior cold reduction on tensile fracture of L-605 aged 1000 hours at 1600° F. Etchant, boric acid + H_2SO_4.



(a) 0 Percent cold rolled. (b) 30 Percent cold rolled. C-66-1784

Figure 13. - Effect of prior cold reduction on intergranular oxidation of L-605 during 1000-hour aging in air at 1600° F. Etchant, boric acid + H_2SO_4.

Figure 13 also shows a thin layer at the surface which was relatively free of precipitate particles. This layer was seen regardless of the degree of prior cold reduction and is probably the result of depletion of the alloying elements, such as tungsten, chromium, silicon, and carbon, which are involved in the formation of the Laves phase and/or the M_6C carbide.

Relation of mechanical properties to microstructure. - The preceding sections have shown that prior cold reduction can profoundly affect the nature of the precipitation in L-605 during aging at 1600° F by the introduction of numerous nucleation sites within the grains. The reduction of preferential grain boundary precipitation appears to be the major reason for improved postaging ductility with prior cold reduction.

The increased strength and hardness obtained in cold-reduced and aged L-605 is the result of retaining some of the effect of the initial deformation and also of precipitation hardening resulting from the profuse dispersion of fine precipitate particles. Of course, an opposing softening effect due to recrystallization of the matrix exists. The hardness curves (fig. 6) show that for the 5- to 20-percent cold reduced specimens the hardness generally increased with aging, whereas the 30- and 40-percent reduced specimens (especially the 40 percent) showed general softening with aging. It appears that for high deformations the amount of softening due to recrystallization is in excess of the amount of hardening due to precipitation. This effect probably also accounts for the fact that after aging at 1600° F the tensile strength of the 40-percent cold reduced material falls below that of the 30-percent cold reduced material (see figs. 4 and 5). The general slow decrease in tensile strength (with all cold reductions) after long aging times may be attributed partly to the growth and agglomeration of the precipitate particles and possibly also to intergranular oxidation. This overall loss in strength, however, is not reflected in the hardness curves, even though hardness might be expected to behave in a manner similar to tensile strength. After aging 1000 hours, agglomeration had occurred somewhat more in the 40-percent cold reduced material than in material that was cold reduced 30 percent prior to aging (figs. 9(d) and (e)). This agglomeration, along with the recrystallization of the matrix, helps explain why the 40-percent cold reduced material had lower strength and hardness than the 30-percent reduced material after aging 1000 hours.

X-ray Diffraction Patterns

X-ray diffraction data are summarized in table IV. Table IV(a) shows the effect of cold rolling on the X-ray diffraction pattern from mill-annealed (unaged) L-605. Because of inadequate filtering of the X-ray beam, $K\beta$ lines were recorded on the films along with the desired $K\alpha$ lines. All the lines for the unworked (as-received) specimen were easily indexed as fcc-cobalt. These fcc-cobalt lines became more diffuse after rolling 30 percent. Also, another faint line (line 11, table IV(a)) could also be seen falling between the $K\alpha$ and $K\beta$ reflections of the (111) plane of the fcc-cobalt phase. The d-value for this reflection was calculated as 2.192 angstroms, which compares fairly well with a value of 2.165 angstroms for unalloyed hcp-cobalt as determined by Hofer and Peebles (ref. 9). Line 16, which coincides closely with a $K\beta$ reflection of fcc-cobalt, could also be indexed as hcp-cobalt. Thus, cold reduction evidently caused a small amount of fcc → hcp transformation in the mill-annealed L-605. The fact that cold work can directly cause such a transformation in unalloyed cobalt has been shown before by Troiano and Tokich (ref. 10).

The fcc lattice parameter a_0 for as-received (unrolled and unaged) L-605 was calculated to be 3.59 angstroms. This value is slightly larger than the 3.544-angstrom value determined by Taylor and Floyd (ref. 11) for unalloyed fcc-cobalt and, of course, is an expected effect of alloying.

The patterns of the aged specimens are tabulated in table IV(b). Numerous additional lines (compared with patterns from unaged material) could be seen resulting from the precipitation of Co_2W and M_6C. One possible $M_{23}C_6$ line was seen. The pattern from the unrolled and 1000-hour aged specimen showed the most lines. The d-values are tabulated and indexed for this specimen in table IV(b). All the lines from all samples were present

TABLE IV. - SUMMARY OF X-RAY DIFFRACTION DATA

[Chromium radiation, 114.6-mm Debye camera.]

(a) Unaged specimens

Line number[a]	Interplanar spacing (Å) and intensity[c]: Zero-percent cold rolled	Interplanar spacing (Å) and intensity[c]: 30-Percent cold rolled	Phase[d]	hkl[d]
[b]9	2.062 MW	2.063 W	βCo	111
11	---------	2.192 W	αCo	10·0
13	2.065 S	2.065 S	βCo	111
16	---------	1.933 W	αCo	10·1
[b]16	1.789 MW	1.759 W	βCo	200
18	1.789 S	1.792 MS	βCo	200
[b]23	1.265 MW	1.265 W	βCo	220
30	1.267 VS	1.266 VS	βCo	220
[b]33	1.080 M	1.081 VW	βCo	311

(b) 1600° F Aged specimens

Line number[a]	Interplanar spacing (Å) and intensity[c]						Phase[d]	hkl[d]
	Percent of cold rolling							
	0	20	30	30	30	40		
	Aging time, hr							
	1000	1000	50	200	1000	1000		
1	4.085 W	W	VW	W	W	W	Co_2W	10·0
2	3.822 VW	W	VW	W	W	W	$M_{23}C_6$	200
3	3.613 W	W	VW	W	W	W	Co_2W	10·1
4	2.799 W	W	---	VW	W	W	Co_2W	10·2
5	2.740 W	---	---	---	---	---	M_6C	400
[b]6	2.361 VW	VW	---	---	VW	VW	Co_2W	11·0
7	2.516 W	---	VW	---	---	---	M_6C	331
8	2.364 M	M	MW	M	M	M	Co_2W	11·0
[b]9	2.061 M	MW	MW	MW	MW	MW	βCo	111
10	2.241 W	---	---	---	---	---	M_6C	422
11	2.173 M	M	M	M	M	M	αCo, Co_2W	10·0, 10·3
12	2.113 MW	VW	W	W	VW	VW	M_6C	333
13	2.063 VS	VS	VS	VS	VS	VS	βCo	111
14	2.016 M	M	M	M	M	M	Co_2W	11·2
15	1.981 MW	M	MW	M	M	M	Co_2W	20·1
[b]16	1.787 VW	VW	---	VW	VW	VW	βCo	200
17	1.942 W	VW	---	---	VW	VW	M_6C	440
18	1.787 S	S	S	S	S	S	βCo	200
19	1.603 W	W	W	W	W	W	Co_2W	20·3
20	1.539 VW	---	---	---	---	---	M_6C	711
21	1.521 VW	VW	W	VW	W	VW	?	?
22	1.434 MW	MW	W	MW	MW	MW	M_6C	731
[b]23	1.258 MW	MW	MW	MW	MW	MW	βCo	220
24	1.362 MW	MW	W	MW	MW	MW	Co_2W	30·0
25	1.339 VW	---	---	---	---	---	M_6C	733
26	1.322 M	M	M	M	M	M	Co_2W	21·3
27	1.293 MW	---	MW	W	---	---	M_6C	822
28	1.285 MW	MW	MW	MW	MW	MW	αCo	11·0
29	1.267 VW	VW	---	---	VW	VW	M_6C	751
30	1.260 VS	VS	VS	VS	VS	VS	βCo	220
31	1.228 MW	M	M	M	M	M	Co_2W	20·5
32	1.205 VW	VW	VW	VW	VW	VW	M_6C	842
[b]33	1.076 MS	MS	M	M	MS	MS	βCo	311

[a]Standard for line number is zero percent cold rolled plus 1000-hr aged specimen.

[b]Kβ reflections.

[c]Very strong VS, strong S, medium to strong MS, medium M, medium to weak MW, weak W, very weak VW.

[d]αCo, hexagonal-close-packed (hcp); βCo, face-centered-cubic (fcc); carbides indexed from data in ref. 8, Co_2W from data in ref. 4, and αCo from data in ref. 9.

in the diffraction pattern of the unrolled plus 1000-hour aged specimen. Therefore, this specimen was used as a standard and all lines are numbered according to this standard. By superposition of the film patterns the d-values for all the aged specimens investigated were found to be virtually the same. Therefore, only the d-values of the unrolled plus 1000-hour aged specimen were determined and are tabulated in table IV(b). The relative intensities, determined by visual inspection of film darkening, for all the patterns taken are included, however.

Patterns from all the aged specimens investigated indicated two possible hcp-cobalt lines (lines 11 and 28); however, it should be noted that line 11 could also be indexed as Co_2W. It is interesting that these lines were observed even in patterns from the aged specimen that had not been given prior cold reduction. The equilibrium temperature for the fcc → hcp transformation is about 783° F in pure cobalt (ref. 12). As was shown earlier, however, the diffraction pattern of the mill-annealed (unrolled and unaged) L-605 specimen showed only fcc lines. Possibly, then, the large amount of precipitation that occurred in L-605 during aging depleted enough solute from the matrix to increase the transformation temperature or transformation rate, thus allowing some formation of hcp-cobalt on cooling from the 1600° F aging temperature to room temperature. Wlodek reported some X-ray evidence of hcp-cobalt on the fracture surface of aged L-605, but not on untested, aged material (ref. 4). The hcp form of cobalt has been reported to be substantially less ductile than the fcc form (ref. 13). In this investigation it was impossible to determine if the formation of hcp-cobalt had an embrittling effect on L-605. The amounts of hcp-cobalt, as determined by observation of the film patterns (see intensities of lines 11 and 28 in table IV(b)), appeared to be about the same for all the aged specimens investigated. It is, therefore, believed that the hcp-cobalt probably did not play a major role in the relative ductility results.

The lattice parameter a_o of the fcc cobalt matrix after aging 1000 hours was calculated to be 3.57 angstroms, a slight decrease from the value of 3.59 angstroms for the mill-annealed material mentioned earlier. This decrease is a direct consequence of the precipitation of solute atoms from the matrix solid solution.

A significant effect of prior cold reduction on the diffraction patterns of 1000-hour aged L-605 is that several M_6C lines were eliminated or decreased greatly in intensity by cold work prior to aging (see table IV(b)). All the cold reduced and 1000-hour aged specimens investigated by X-ray diffraction showed the absence of the same M_6C lines (lines 5, 7, 10, 20, 25, and 27) as compared with the unrolled and aged specimen. Carbon analyses were made on both unrolled and rolled specimens aged 1000 hours to determine if enhanced diffusion of carbon resulting from prior cold working, as well as the thinner specimen cross sections, may have accelerated the rate of decarburization during the high-temperature exposure. These analyses gave identical results, indicating that this was not the case. It appears that prior cold work altered the carbide reaction so as either to reduce the amount of carbide precipitation or to change the carbide chemistry. Reduction in the amount of M_6C precipitation, especially if it tended to precipitate at the grain boundaries, could have been a significant contributing factor to the reduction of embrittlement in L-605 with prior cold reduction. It should be noted, however, that previous investigators considered Co_2W, not M_6C, as the major grain boundary phase in aged L-605 (refs. 3 and 4).

Insofar as the effect of prior cold rolling on the amount of Co_2W precipitation is concerned, little or no change in the intensity of the Co_2W lines with prior cold reduction was seen from the patterns of specimens aged 1000 hours.

CONCLUDING REMARKS

The results of this investigation have shown that the embrittlement of L-605 with longtime, high-temperature exposure can be reduced by prior cold reduction. Alteration in the distribution of precipitates appears to be a major reason for this enhancement of ductility. The deformation treatment also increases the room-temperature tensile strength and hardness, which is largely maintained even after long aging times. A drawback of this method, of course, is that the low as-rolled ductility and corresponding high as-rolled hardness and strength associated with the optimum prior cold reduction (30 percent) may make fabrication of usable components more difficult; however, a heat treatment prior to the final fabrication operations might help alleviate this problem.

In order to evaluate this technique for longtime application more completely, the effect of prior cold reduction on the elevated-temperature creep-rupture properties of L-605 should be determined.

Earlier work at the Lewis Research Center (ref. 5 and discussion of ref. 4) has shown that reductions in silicon content (0.23 percent or less) substantially lower the embrittling tendency of L-605 during high-temperature exposure. The precipitation that occurred in low-silicon L-605 was still intergranular (even though less in amount than in high-silicon heats). Therefore, application of the prior cold reduction technique to low-silicon content L-605 might further lessen its tendency for embrittlement.

SUMMARY OF RESULTS

The following results were obtained from an investigation of the effects of prior cold reduction on the embrittlement of L-605 (HS-25) after aging for times up to 1000 hours at 1600° F:

1. Prior cold reduction improved the tensile ductility of aged L-605. This effect was

most pronounced after longtime (1000 hr) aging, when the unrolled material showed a room-temperature tensile ductility of only about 3 percent elongation, and the 30-percent prior reduced material showed an elongation of 10 percent. This elongation compares to a maximum of about 16 percent obtained with a very low (0.12 percent) silicon heat (similarly aged but without prior reduction) investigated earlier at NASA Lewis Research Center (ref. 5).

2. The distribution of the precipitate formed during aging was greatly changed by prior cold reduction. The greater the degree of prior cold reduction, the greater was the tendency for fine precipitation to occur within the grains rather than preferentially at grain boundaries. The overall improvement in the room-temperature ductility of longtime (200 and 1000 hr) aged L-605 was attributed mainly to this reduced tendency for preferential intergranular precipitation.

3. Both room-temperature ultimate tensile strength and yield strength after aging increased with prior cold reduction. In L-605 aged 1000 hours, average ultimate tensile strength increased from 120 000 (no prior deformation) to 175 000 psi (cold rolled 30 percent prior to aging). The corresponding increase in average yield strength was from 72 000 to 105 000 psi.

4. The increased tensile strength of aged L-605 with prior cold reduction was believed to be due both to the retained effect of cold work and also to a more uniform distribution of precipitate particles. The degree of tensile strength that could be retained after aging was limited by the softening effect due to partial recrystallization of the matrix.

5. The optimum amount of prior cold reduction with respect to both ductility and tensile strength after aging 1000 hours was found to be about 30 percent.

6. Hardness was increased by prior cold rolling. For low prior cold reductions (zero to 10 percent) hardness continually increased with aging time up to 1000 hours. For intermediate reductions (15 and 20 percent) it increased to a maximum followed by a slight decrease, and for high reductions hardness generally decreased with aging time.

7. X-ray diffraction studies indicated that the mill-annealed (as-received) material was a fcc- (face-centered-cubic) cobalt solid solution. Traces of hcp- (hexagonal-close-packed) cobalt were found in a cold-rolled, unaged specimen. All aged specimens, regardless of the amount of prior cold reduction, indicated about equal traces of hcp-cobalt. Thus, the fcc $\rightarrow$ hcp transformation of the matrix was not believed to play a significant part in the relative ductilities of the aged specimens.

8. X-ray diffraction analyses also confirmed the precipitation of the Laves phase Co_2W and M_6C carbide during aging; however, prior cold reduction seemed to substantially alter the M_6C reaction by reducing the apparent amount of M_6C precipitation. The amount of Co_2W precipitation seemed relatively insensitive to prior cold reduction.

9. Prior cold work reduced the depth of intergranular oxide penetration near the surface during aging in air, which may have contributed to higher effective tensile strengths.

Lewis Research Center,
National Aeronautics and Space Administration,
Cleveland, Ohio, April 13, 1966.

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