THE EFFECT OF COOLING RATE ON THE DUCTILE-BRITTLE BEND-TRANSITION TEMPERATURE OF CHROMIUM WIRE

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Although it is known that, in general, the ductile-brittle transition temperature of the Group VI-A refractory metals increases as the interstitial content increases(1), it is difficult to distinguish effects due to interstitials in solution from those due to the presence of second-phase interstitial compounds. The problem of making this distinction has proved to be particularly difficult for chromium, which has very low equilibrium solubilities for the ~~common~~ interstitials(1) and, in the case of nitrogen, very rapid precipitation kinetics due to high interstitial diffusivities(2). In view of these difficulties, it is not safe to assume that a "quenched" specimen of chromium contains a significantly greater fraction of its total impurities in solution than does a "slow-cooled" specimen.

In order to make a meaningful comparison of the mechanical properties of quenched and slow-cooled material, some sensitive measure is needed of the amount of interstitial retained in solution compared to that present as second phase. The purpose of these experiments was to make such a comparison on chromium which had been quenched at a very high rate, using internal friction as an indicator of the amount of nitrogen in solution. Nitrogen has been considered to be the interstitial primarily responsible for the brittleness of chromium.

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Crystals of iodide chromium were compacted, hot-extruded, swaged, and then centerless ground to produce a rod of 1/10-inch diameter. The rod was then warm-drawn to wire .017 inch in diameter, the material on which the experiments were conducted. A 10-inch length was annealed in a quartz capsule containing argon for 1 hour at 1150 C, and was directly quenched into water (breaking the capsule) from 1000 C. Previously, a chromium wire .037 inch in diameter had been used in experiments to determine the actual cooling rate under these conditions.(3) From the output of a thermocouple spot-welded to the specimen surface (recorded using a cathode-ray oscilloscope), the surface-cooling rate was found to be ~9000 C/second. It is, therefore, reasonable to expect that the cooling rate for the present thinner wire was at least this high, and probably higher. The heat treatment produced a recrystallized structure containing approximately 40 grains in a cross-section area, and chemical analysis showed the wire to contain 50 ppm oxygen, 2 ppm hydrogen, 15 ppm carbon, and nitrogen in the range 10-15 ppm.

A 152 C aging curve was obtained on one-half of the quenched wire, taking intermittent internal-friction readings (0.7 cycles per second). After 3000 minutes, the internal-friction peak was found to have decreased to the background level, indicating that the nitrogen retained in supersaturated solid solution by the high quenching rate(3) had fully aged out. Specimens were cut from the half of the wire still in the quenched state, and also from the fully aged material, for comparative bend tests. Because of the relatively small length of wire available, a 3-point bend jig was constructed, which was capable of testing specimens greater in length than 5/16 inch. The specimens were electropolished and tested at 0.1 inch/minute crosshead speed on a table-model Instron, elevated temperatures being obtained in an electrically heated silicone oil bath.

The aging curve for the chromium wire, represented by the decreasing height of the internal-friction peak with increased aging time, is presented in Figure 1. The conversion to ppm nitrogen is obtained using Reference 3.

Bend-test results for quenched and for quenched and aged chromium wire, corresponding to the beginning and end, respectively, of the curve of Figure 1 are listed in Table 1. As has been seen previously for chromium(4), it was found that the transition from ductile to brittle behavior was extremely sharp, in that a specimen either failed in a completely brittle manner (described as brittle in Table 1) or bent to the maximum extent permitted by the jig (ductile in Table 1). The lowest temperature at which a quenched specimen was ductile was 74 C below the lowest temperature at which an aged specimen was ductile, and the highest temperature at which a quenched specimen was brittle was 97C below the equivalent temperature for aged material. Thus, regardless of how the ductile-to-brittle transition is defined, the quenched material has a transition temperature between 74 and 98 C below that for aged material. Ductile specimens exhibited yield drops on the load-time curve which were more pronounced for quenched than for aged specimens to the extent shown in Table 1.

Previous investigations(5-7) into the effect of cooling rate on the ductile-brittle transition temperature of chromium have shown "quenched" material to be more brittle than "furnace-cooled" material, in contrast to the present results. Recent experimental results, however, suggest that the quenching rates used in previous work have been insufficient to maintain <u>all</u> the nitrogen in solution. This conclusion is based on the data quoted in Table 2(8) which shows that quenching rates of the order of several thousand degrees centigrade per second are necessary to

TABLE 1. BEND-TRANSITION BEHAVIOR OF .017-INCH-DIAMETER CHROMIUM WIRE

Specimen Number	Test Temp., °C	Bend Behavior	Upper Yield Point Load, lb	Lower Yield-Point Load, lb	Yield Drop, %	Brittle Fracture Load, lb
			Quenched Wire			
1	30	Brittle	Preliminary test; no load recorded.			--
2	53	"	--	--	--	1.56
3	71	Ductile	1.08	0.84	29	--
4	85	Brittle	--	--	--	1.12
5	94	Ductile	1.07	0.86	24	--
6	98	Brittle	--	--	--	1.07
7	105	Ductile	0.96	0.72	33	--
8	113	"	1.30	1.14	12	--
9	129	"	1.52	1.32	15	--
10	142	"	1.03	0.75	37	--
11	164	"	1.12	0.98	14	--
			Quenched and Aged Wire			
12	30	Brittle	Preliminary test; no load recorded.			--
13	105	"	--	--	--	1.10
14	128	"	--	--	--	1.30
15	145	Ductile	0.87	0.84	3	--
16	166	Brittle	--	--	--	1.36
17	192	Ductile	0.72	0.64	12	--
18	195	Brittle	--	--	--	0.71
19	225	Ductile	1.09	0.91	20	--
20	260	"	0.89	0.78	15	--

TABLE 2. NITROGEN RETAINED IN SOLUTION IN CHROMIUM AS A FUNCTION OF COOLING RATE

Cooling Times and Approximate Cooling Rates From 1000 to 100°C		Nitrogen, ppm
Time, sec.	Rate, °C/sec.	
0.1	~9000	26
25	40	6
200	5	2
1,800	0.5	<1
10,800	0.09	-

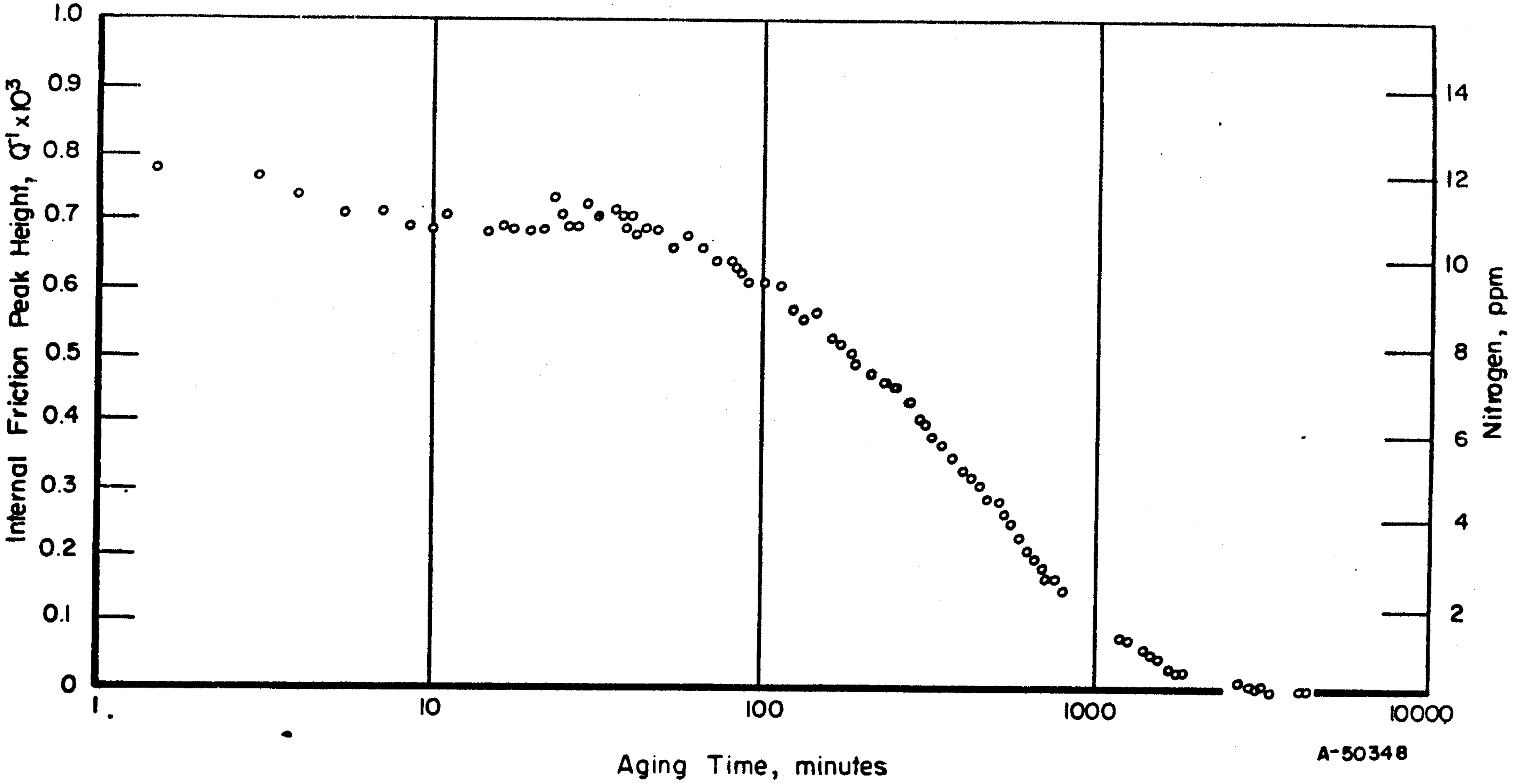

FIGURE 1. CHANGE IN HEIGHT OF THE NITROGEN INTERNAL FRICTION PEAK AND SOLUBLE NITROGEN CONCENTRATION FOR CHROMIUM AGED AT 152°C

retain even 20-30 ppm in solution. The larger specimens used in previous investigations (5-7) together with use of oil as a quenching medium(5,7) could not have permitted such a high cooling rate. Furthermore, previous work has been performed on chromium containing higher nitrogen concentrations which, aging studies have shown(3), increases the kinetics of nitride precipitation, and correspondingly increases the critical cooling rate necessary to maintain the nitrogen in solution. In the light of these considerations, it seems likely that the quenching rates used previously served primarily to modify the morphology and distribution of the nitride phase rather than to maintain all the nitrogen in solution. This certainly seemed to be the case in earlier work by one of the present authors(10) in which quenched tensile specimens gave every indication of being dispersion hardened by a much finer precipitate than did slow-cooled specimens, a conclusion supported by the transmission electron microscopy results of Yoshida, et. al.(11), who showed oil quenched chromium to contain many precipitates of varying size.

In the present work, however, the data in Figure 1, together with the nitrogen analysis, show that all the nitrogen present in the material is in solid solution as a result of the quench, and that after aging for times greater than 3000 minutes, it is largely present as a precipitated phase in accordance with the predictions of equilibrium-solubility data(1). It thus appears that nitrogen completely in solution is less detrimental to ductility than nitrogen combined in a second phase.

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