

ELECTROCHEMICAL AND METALLURGICAL ASPECTS OF STRESS CORROSION CRACKING OF SENSITIZED ALLOY 600 IN SIMULATED PRIMARY WATER CONTAINING SULFUR CONTAMINATION

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ABSTRACT

The stress corrosion cracking (SCC) of sensitized Alloy 600 was investigated in aerated solutions of sodium thiosulfate containing 1.3% boric acid. The aim of the investigation was to determine the existence, if any, of a threshold level of sulfur, and lithium to sulfur ratio governing the SCC. Reverse U-bends were tested at room temperature, whereas slow strain rate and constant load tests were performed at 80 C. All tests were performed in solutions open to the atmosphere. Our results indicate that in the borated thiosulfate solution containing 7 ppm sulfur, 5 ppm lithium as lithium hydroxide is sufficient to inhibit SCC in U-bends. The occurrence of inhibition seems to correlate to the rapid increase of pH and conductivity of the solution as a result of the lithium hydroxide addition. In the slow strain rate tests in the borated solution containing 0.7 ppm lithium as lithium hydroxide, significant SCC is observed at a sulfur level of 30 ppb, i.e., a lithium to sulfur ratio of 23. In a parallel test in 30 ppb sulfur level but without any lithium hydroxide, the SCC is more severe than that in the lithiated environment, thus implying that lithium hydroxide plays some role in the SCC inhibition. In the constant load test on a specimen held initially at a nominal stress near the yield strength of the material, cracks continue to grow until fracture during controlled, progressive dilution of the bulk solution, leading to final lithium concentration of 1.5 ppm and sulfur concentration (as thiosulfate) of 9.6 ppb i.e., a lithium to sulfur ratio of about 156, although lithium hydroxide retards the rate of crack propagation to some extent. The crack growth rate is strongly influenced by the electrochemical potential which is primarily governed by the local crack tip chemistry. Therefore, it may not be possible to stop a propagating crack in the aerated solution by manipulating simply the bulk environment.

INTRODUCTION

In November 1981, primary to secondary side leaks were detected in both of the once-through steam generators (OTSG) at the Three Mile Island Unit 1 nuclear power plant¹. The phenomenon was identified as low temperature intergranular SCC initiating from the inner surfaces of the Alloy 600 tubes exposed to the primary coolant. The tubing was sensitized by its stress relief treatment following fabrication of the steam generators. A testing program was initiated to examine the material and environmental factors relevant to these failures, which were found to be associated with the sensitization of the material and the accidental contamination of the borated primary coolant by sodium thiosulfate and air.

These investigations showed that sensitized Alloy 600 suffers rapid SCC in simulated pressurized water reactor primary water in the presence of oxygen and contaminated with sulfur compounds such as sodium thiosulfate (Na₂S₂O₃) and sodium tetrathionate (Na₂S₄O₆)¹⁻³. They also indicated that the crack propagation rate (CPR) decreased with decreasing concentration of sulfur, implying the existence of a threshold sulfur concentration for SCC. In the absence of lithium hydroxide additions, the threshold sulfur concentration for SCC (as Na₂S₂O₃ added to aerated 1.3% boric acid at 40 C) was found to be around 70 ppb. The studies showed that crack propagation rate increased with increasing temperature, with a maximum around 80-90 C. Lithium hydroxide was found to be an effective inhibitor for SCC and at a certain critical lithium to sulfur ratio, initiation of cracks could be prevented, and crack growth could be hindered or completely stopped. As a general guide, in 1.3% boric acid solution at 40 C with ppm levels of Na₂S₂O₃, the critical ratio for lithium to sulfur to prevent SCC was established to be around 10.

Several important aspects of SCC, however, were not addressed in the earlier investigations. Notably among them is the question

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regarding the existence of a threshold level of sulfur, especially around 80 to 90 C where the crack propagation rate was found to be very rapid. The other issue is the threshold level of lithium to sulfur ratio for crack inhibition around 80 to 90 C. Finally, information regarding the critical amount of chromium depletion for SCC initiation in thiosulfate is also lacking. The aim of this investigation was to determine the above SCC factors. The results were to be used in the safety evaluation of the TMI-1 steam generators following their return to service.

EXPERIMENTAL

Tests were conducted on commercially produced nuclear grade Alloy 600 materials following procedures described elsewhere¹⁻². Briefly, slow strain rate tests were performed at a strain rate of 2×10^{-6} /s using smooth flat tensile specimens of 25 mm gage length and a cross section of 5 x 2.5 mm. These tests were conducted at 80 C in borated thiosulfate solution with or without lithium hydroxide. Constant load tests were performed on smooth flat tensile specimens on an MTS servo-hydraulic machine. For constant deflection tests, reverse U-bends were used¹. Highly sensitized specimens (SAS) were first solution annealed at 1135 C for 45 min., water quenched and then sensitized at 621 C for 18 h. An intermediate level of sensitization (MAS) was obtained by heating mill annealed (MA) specimens directly to 621 C for 18 h. All tests were conducted in 1.3% boric acid solutions open to the atmosphere. Potential control, when desired, was obtained with a PAR Model 173 potentiostat. All potentials were measured and are reported versus a saturated calomel electrode (S.C.E.). Solution conductivity and pH were measured, when necessary, with a Radiometer Copenhagen CDM 3 conductivity meter and an Orion Research Model 901 pH meter, respectively. Grain boundary Cr-depletion was investigated by analytical electron microscopy using electropolished thin foils, and a JEOL100 C transmission electron microscope (with scanning and energy dispersive attachments).

RESULTS AND DISCUSSION

The various test results and their significance are described in the following:

1. Slow Strain Rate Tests

Figure 1 shows the average CPR of SAS samples based on the deepest crack and the total testing time, in slow strain rate tests at 80 C in borated thiosulfate solution with varying amounts of sulfur as $\text{Na}_2\text{S}_2\text{O}_3$. No lithium hydroxide was present in these environments. The propagation rate is nearly independent of the sulfur concentration at 30 and 60 ppb level of

sulfur and at 90 ppb, the rate is somewhat higher. In all these tests, the specimens exhibited considerable elongation — 40%, 39% and 34% at the 30, 60 and 90 ppb sulfur levels and the maximum stress was 543, 543 and 513 MPa, respectively at these three concentrations. The open circuit potentials of the specimens varied between -290 to -350 mV vs. S.C.E. during the tests.

Another slow strain rate test was performed at 80 C in borated solution containing 30 ppb sulfur and 0.7 ppm lithium as hydroxide. The CPR, elongation to failure and maximum stress were 0.5 nm/s, 37% and 537 MPa, respectively. Thus, the CPR in this case was somewhat slower than that shown in Figure 1 where no lithium was added.

Figures 2(a) and (b) show scanning electron micrographs of the fracture surfaces of specimens after the tests in 30 ppb sulfur without and with 0.7 ppm lithium respectively. The cracking was a little less extensive in the lithiated environment. Note that, in spite of a lithium to sulfur ratio of about 23, i.e., a lithium of 0.7 ppm and sulfur of 30 ppb, the specimens in these tests at 80 C still suffered SCC, whereas previous tests³ at 40 C with 0.7 ppm sulfur, showed inhibition of SCC at a lithium to sulfur ratio of around 10. Also, the threshold sulfur for SCC at 40 C was about 70 ppb³. Thus, the new results show that the threshold sulfur level decreases and the threshold Li:S increases with increasing temperature. It is likely that increasing temperature decreases the oxygen uptake rate and enhances the sulfur mobility and thus increases the nucleation probability of sulfide formation on the surface of the metal. The sulfide pockets, as we will discuss later, are the primary sites of SCC initiation.

2. Constant Load Test

A smooth tensile SAS specimen was immersed in a borated solution containing 6.4 ppm sulfur, (10^{-4} M $\text{Na}_2\text{S}_2\text{O}_3$) without any lithium hydroxide. The temperature was raised to 80 C and then load was slowly increased at a stressing rate of 0.027 MPa/s, until a nominal load of 210 MPa (yield strength) was reached. The load was held constant at this level throughout the test. The specimen potential was -16 mV at this point. The displacement signal for the MTS machine soon began to move steadily indicating crack growth. In about 30 minutes, several cracks could be detected visually. The solution was then progressively diluted with a boric acid - lithium hydroxide mixture heated to 80 C. At each lithium to sulfur ratio value thus established, the displacement signal was recorded for a sufficient length of time until

it was confirmed that the crack was still growing. The strength of boric acid was maintained at 1.3% throughout the test.

Figure 3 shows the rate of change of the displacement signal with time against lithium to sulfur ratio. Since the specimen had several cracks, all of which were contributing, perhaps at different rates, to the increase of the displacement signal, quantitative crack growth measurement was not possible from the rate of change of displacement, although a reasonable qualitative correlation can be made. Thus, it appears that the crack growth was in two stages, with a transition from the high to the low growth rate occurring around a lithium to sulfur ratio between 2 to 5. The open circuit potential of the specimen moved in the noble direction with each dilution of the solution, i.e., increase of the lithium to sulfur ratio, and was about +55 mV after the final dilution. The final dilution corresponded to a lithium to sulfur ratio of 156. The crack continued to grow at this level and the specimen failed in a few hours, with an average propagation rate of 74 nm/s based on the total time to failure. Using the percentage of testing time spent in the high and low crack growth regions, the average crack growth rates in these two regions are approximately 147 and 21 nm/s respectively.

Note that in the slow strain rate tests described in Figure 1, the average CPR in borated thiosulfate solution with 30 ppb sulfur, where the specimen potential is between -290 and -350 mV, is only about 1 nm/s, whereas in similar concentration of sulfur and even with lithium present, the growth rate is much higher in Figure 3, where the potential is much more anodic. Thus, it is evident that the CPR in this environment is primarily under electrochemical control which to a large extent is determined by the crack tip chemistry. It is possible that the growing crack in this case is very tight and with progressive addition of lithium and dilution of sulfur, the local crack tip chemistry does not change sufficiently to inhibit the crack. Some change within the crack probably occurs, which accounts for the slowing down of the growth rate. However, even the slow growth rate is sufficient to allow the crack to outrun any further chemical repair processes.

In an earlier test at 40 C with a specimen held under displacement control, a lithium to sulfur ratio of about 10 was established as the inhibition criterion³. The present test was at a higher temperature of 80 C and under load control where the stress intensity actually increases as the crack grows in contrast to the earlier displacement control test³ where the stress intensity may decrease with crack growth. These two factors are primarily responsible for the more severe crack growth results in the present case.

At the end of the final dilution, the sulfur and lithium concentrations were only 9.6 ppb and 1.5 ppm respectively. From the relatively high and rather steady crack growth rate even in this environment, one may anticipate that there is probably no threshold sulfur level for stopping a propagating crack. In fact, the sulfur concentration in the bulk solution may be irrelevant in this context.

3. Relationship Between Chromium Depletion and U-Bend Cracking

MAS reverse U-bends of two different heats were tested in 1.3% boric acid solution with varying amounts of thiosulfate. One heat (heat #2) suffered rapid SCC even in dilute thiosulfate solution (Figure 4). The other heat (heat #1), tested earlier, did not suffer SCC even in 0.1 M thiosulfate solution¹. This led us to believe that instead of thiosulfate, some other reduced sulfur species such as tetrathionate or polythionic acid was perhaps the causative agent for SCC of the TMI-1 tubes¹. The new results (Figure 4) provide evidence that thiosulfate can initiate SCC in MAS U-bends, and therefore, failure mechanisms involving other species need not be invoked.

4. Electron Microscopy

Figures 5(a) and (b) show typical grain boundary structures of MAS heat #1 and #2, respectively, with the former showing generally discontinuous carbide precipitates and the latter showing a high coverage of lamellar carbides.

Figure 6 gives a comparison of typical chromium levels as a function of distance from the grain boundary in MAS heat #1 and #2, respectively. The chromium concentration is normalized to the concentration of the center of the grain of the as received MA material. Due to the limitation of the spatial resolution (approximately 35-50 nm, which is about 100 times better than in a conventional microprobe), the actual amount of Cr-depletion could be larger and a little less broad than that shown in Figure 6 due to the summing effect (addition of X-ray signals from both the depleted and nondepleted areas).

Clearly, the amount of Cr-depletion in MAS #2 is more pronounced than in MAS #1. The MA structures of the two heats were also examined and they exhibited very little variation in the chromium distribution near the grain boundaries.

5. Ferric Sulfate - Sulfuric Acid Test

For detecting susceptibility to intergranular attack as a result of Cr-depletion, MAS specimens of each tubing were tested separately

for 24 h in a boiling solution of ferric sulfate and sulfuric acid following the appropriate ASTM standard⁴. The weight loss of the heat #1 specimen was 41.6 mm/y compared to a much higher weight loss of 116.2 mm/y for the heat #2 specimen. The weight loss for the MA materials were 4.5 and 6.9 mm/y for #1 and #2 specimens, respectively. The above results provide additional evidence that the MAS heat #2 is much more severely sensitized compared to the MAS heat #1. This apparent difference may arise from different processing histories of the tubes. For example, if a tubing receives the final annealing at a relatively high temperature allowing a large percentage of the carbon to go into solution and is then rapidly cooled, a significant amount of carbon will remain in solid solution, thereby rendering the material amenable to severe sensitization and Cr-depletion along the grain boundaries. Our results reveal that although initiation of SCC in MAS U-bends can be caused by sodium thiosulfate, it perhaps occurs only after a critical or threshold level of Cr-depletion is achieved.

6. Role of LiOH in Inhibition of SCC Initiation

The relationship between time to failure of SAS U-bends and lithium concentration in borated thiosulfate solution containing 7 ppm sulfur (1.1×10^{-4} M $\text{Na}_2\text{S}_2\text{O}_3$) at 20 C is shown in Figure 7. The time to failure reported is the time when a through-wall crack was first noticed under a low power stereo microscope. It is evident that SCC occurred rapidly in the presence of up to 4 ppm of lithium and the time to failure was rather independent of lithium concentration up to this level. However, no SCC was observed in six months at a lithium level of 5 ppm, i.e., a lithium to sulfur ratio of about 0.7, thus indicating that a threshold concentration of lithium hydroxide is required for inhibition of SCC in U-bends at 20 C. Recent tests in our laboratory indicate that increasing temperature accelerates the initiation process and causes the LiOH requirement for inhibition to go up. For example, in the borated solution containing 0.7 ppm lithium and 1.5 ppm sulfur, SCC occurred in 2 days at 80 C, whereas no failure occurred in 7 days at 20 C. However, when the lithium and sulfur concentrations were 0.7 ppm each, no SCC was observed in 2 weeks even at 80 C. This suggests that a Li:S of unity is perhaps sufficient for inhibition of initiation at all temperatures.

Figures 8(a) and (b) show the variation of room temperature conductance and pH respectively, of a borated thiosulfate solution containing 7 ppm sulfur, with progressive addition of LiOH. The conductance rises rapidly, especially starting at a lithium concentration of 5 ppm where inhibition seems to be very effective. The increase in pH due to LiOH addition is also significant.

Lumsden et al.⁵ have recently investigated the effect of lithium hydroxide on the composition of surface films of sensitized Alloy 600 in boric acid solution with and without sodium thiosulfate. In boric acid, the film consists of a nickel-chromium mixed hydroxide (passive film), which in the presence of thiosulfate contains large amounts of sulfur as pockets of sulfide. Apparently, SCC initiates at these sulfide pockets.⁵ Lithium hydroxide as well as sodium hydroxide prevent the incorporation of sulfur and breakdown of the passive film, and in 1.3% boric acid solution with 7 ppm sodium thiosulfate, a few ppm of lithium hydroxide is sufficient to achieve this⁵. Our results in Figure 7 are consistent with the observation of Lumsden et al. SCC in U-bends is generally initiation controlled, and therefore lithium hydroxide can modify the film composition to prevent initiation. The existence of a critical amount of hydroxide implies that the boric acid needs to dissociate to generate enough HB_3O_7^- ions before they can either displace or possibly prevent ingress of $\text{S}_2\text{O}_3^{2-}$ ions into the surface film.

It is clear that the Li:S for inhibition of crack initiation is much lower than that for crack propagation. However, from a practical point of view, the higher value of Li:S required for inhibition of propagation is a more realistic criterion for the safe operation of the steam generators during shutdown with air present in the system.

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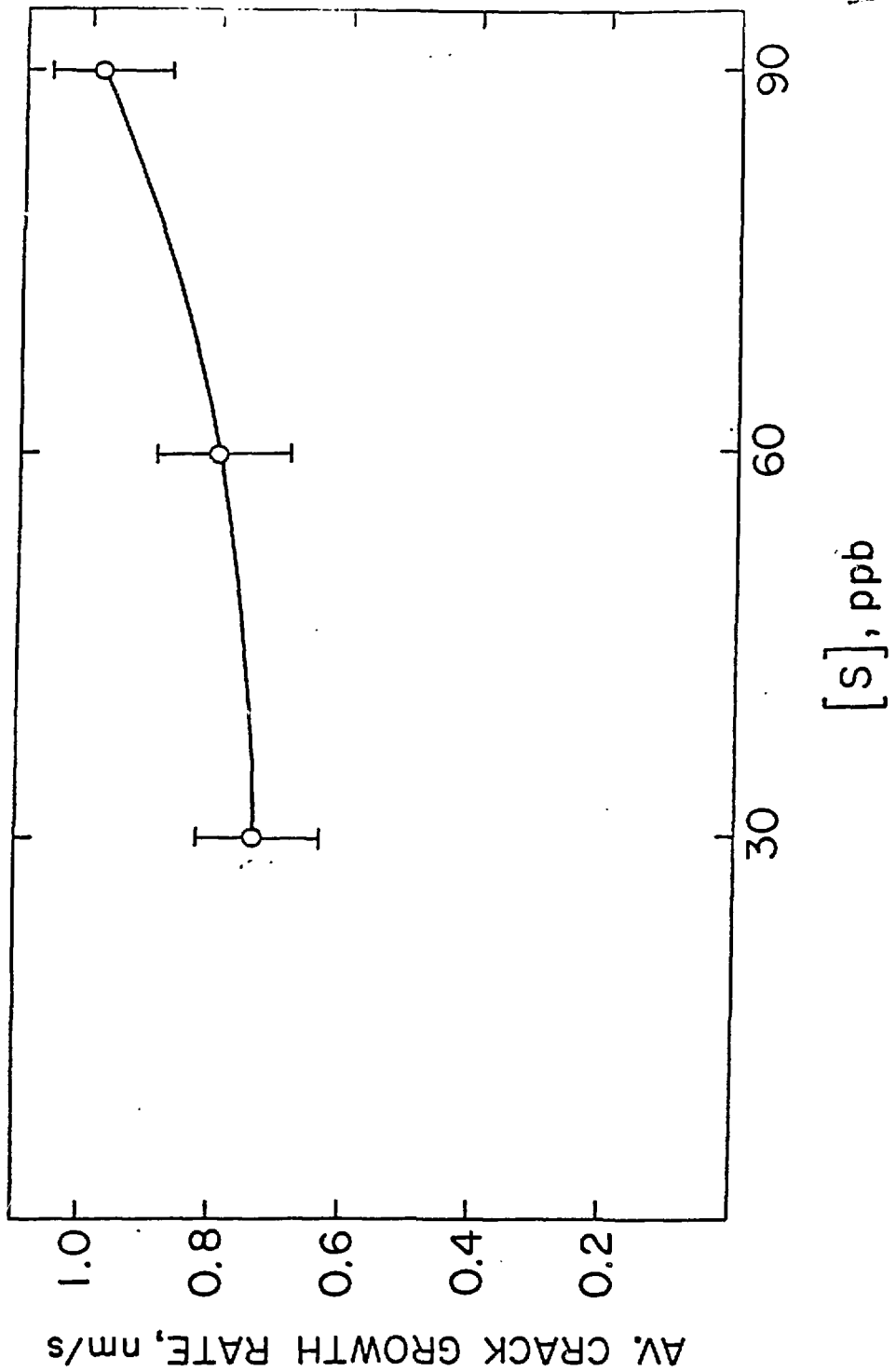


Figure 1 Average crack propagation rate of sensitized (SAS) Alloy 600 in slow strain rate tests in borated thiosulfate solutions at 80 C containing very small sulfur contaminations.

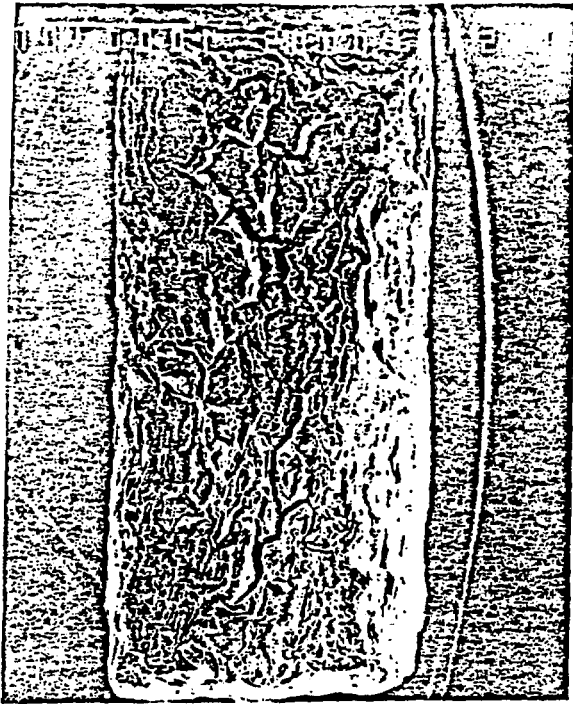


Figure 2 a) Scanning electron fractograph of a sensitized (SAS) Alloy 600 specimen after a slow strain test in borated thiosulfate solution at 80 C with 30 ppb sulfur and without any lithium hydroxide.

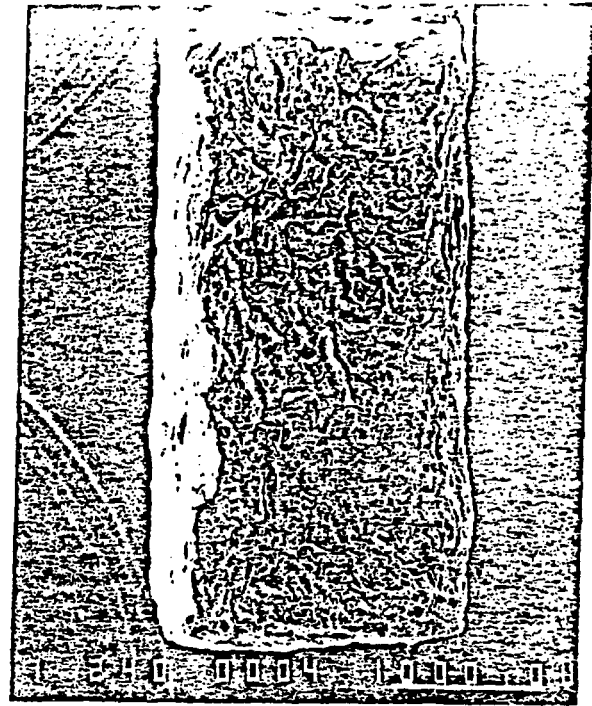


Figure 2 b) Scanning electron fractograph of a sensitized (SAS) Alloy 600 specimen after a slow strain test in borated thiosulfate solution at 80 C containing 30 ppb sulfur and 0.7 ppm lithium as LiOH

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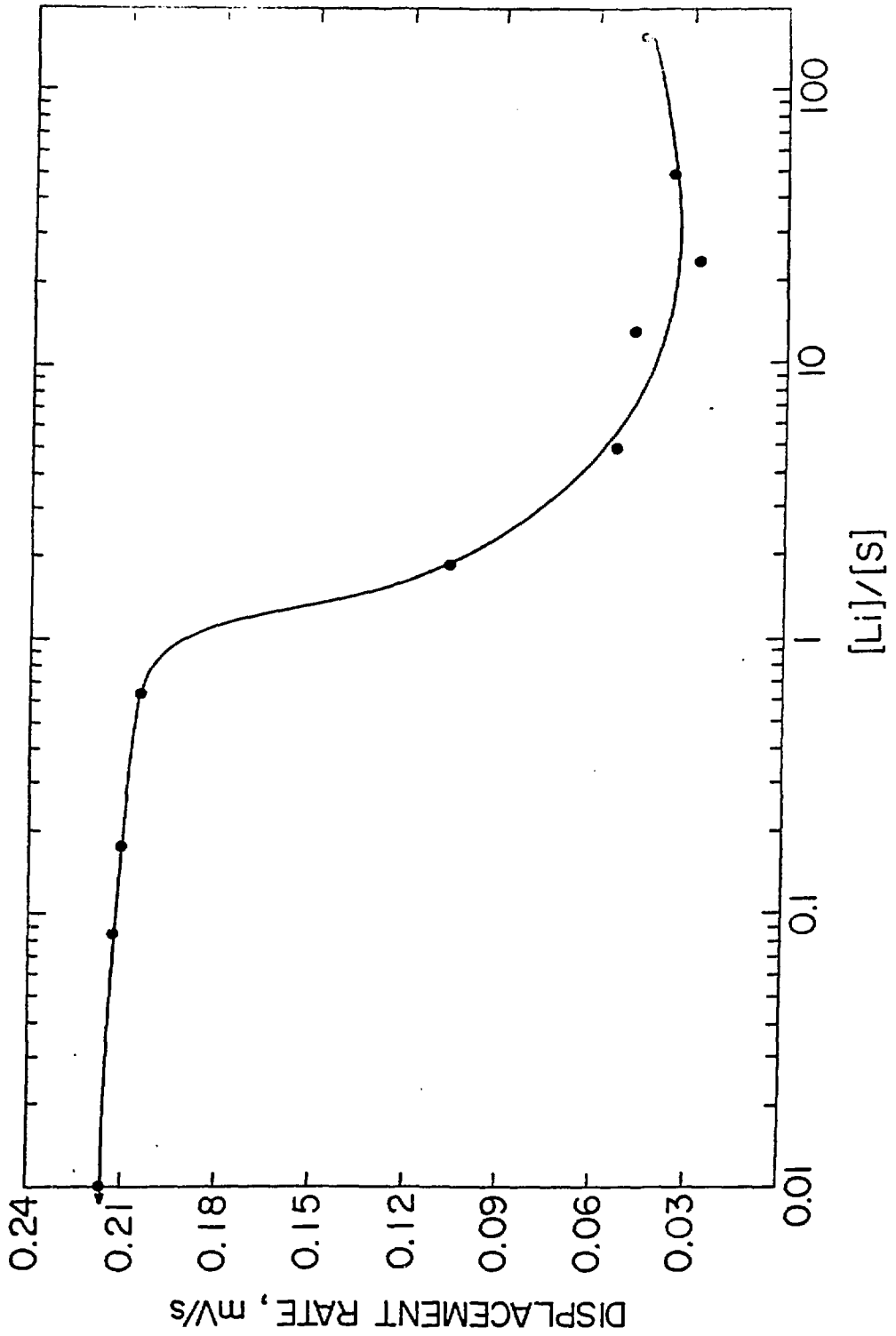


Figure 3 Rate of change of displacement signal of an MTS servo-hydraulic machine with lithium to sulfur ratio in a constant load test on a sensitized (SAS) Alloy 600 specimen at 80 C in borated thio-sulfate solution and held initially at a nominal stress equal to the yield strength of the material.

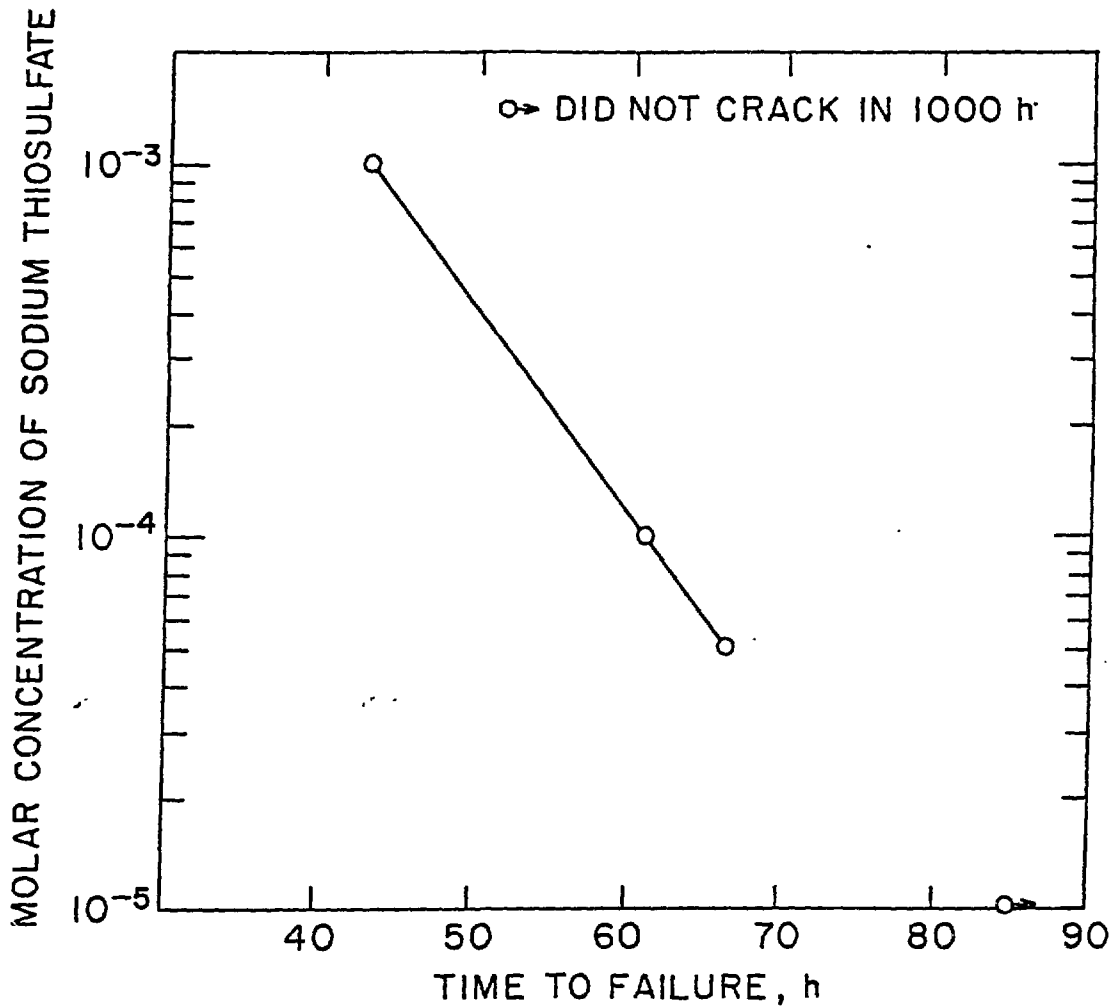


Figure 4 Relationship between molar concentration of thiosulfate and time to failure of U-bends of MAS No. 2 tested at room temperature in 1.3% boric acid solutions in deionized water.

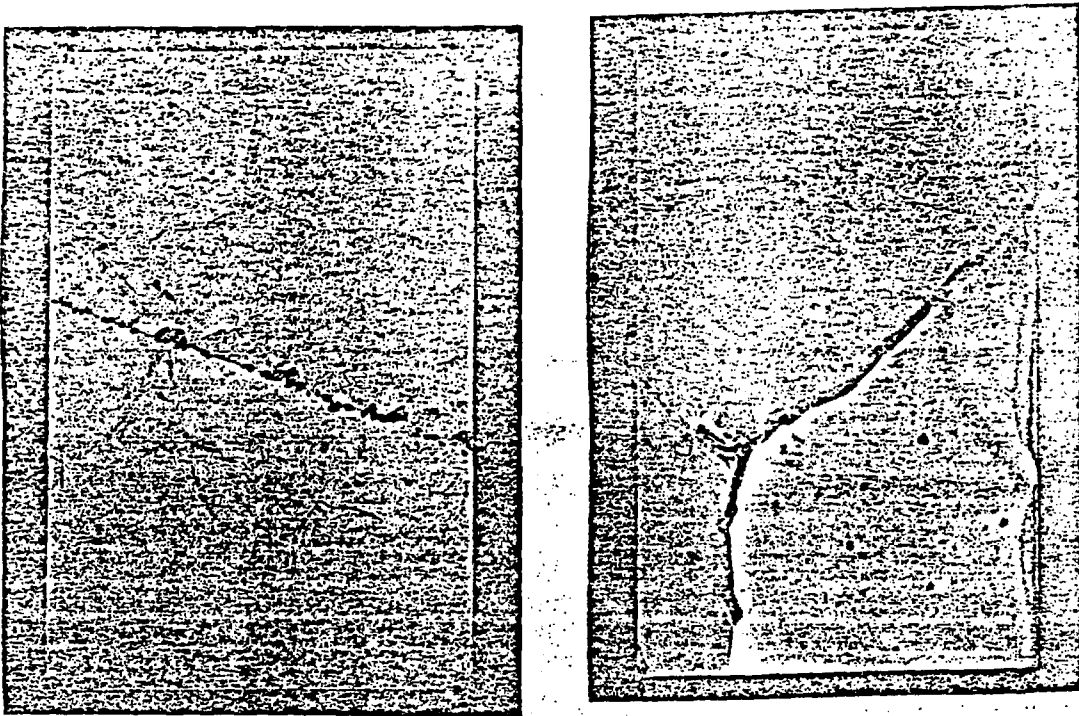
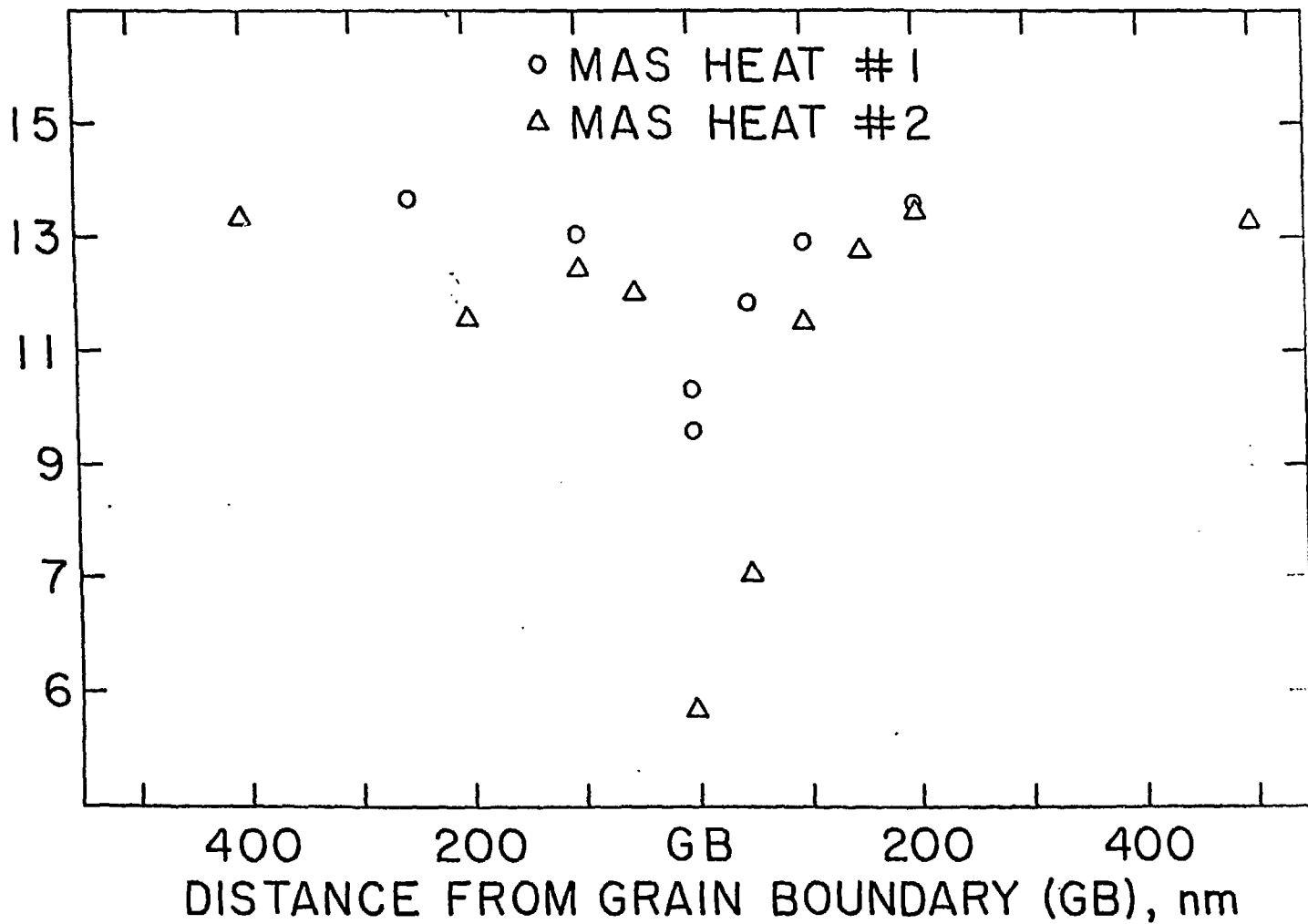


Figure 5 Transmission electron micrographs of the grain boundary regions of (a) MAS No. 1 specimen and (b) MAS No. 2 specimen.

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Figure 6 Distribution of wt% chromium along the grain boundaries of MAS No. 1 and MAS No. 2 specimens.



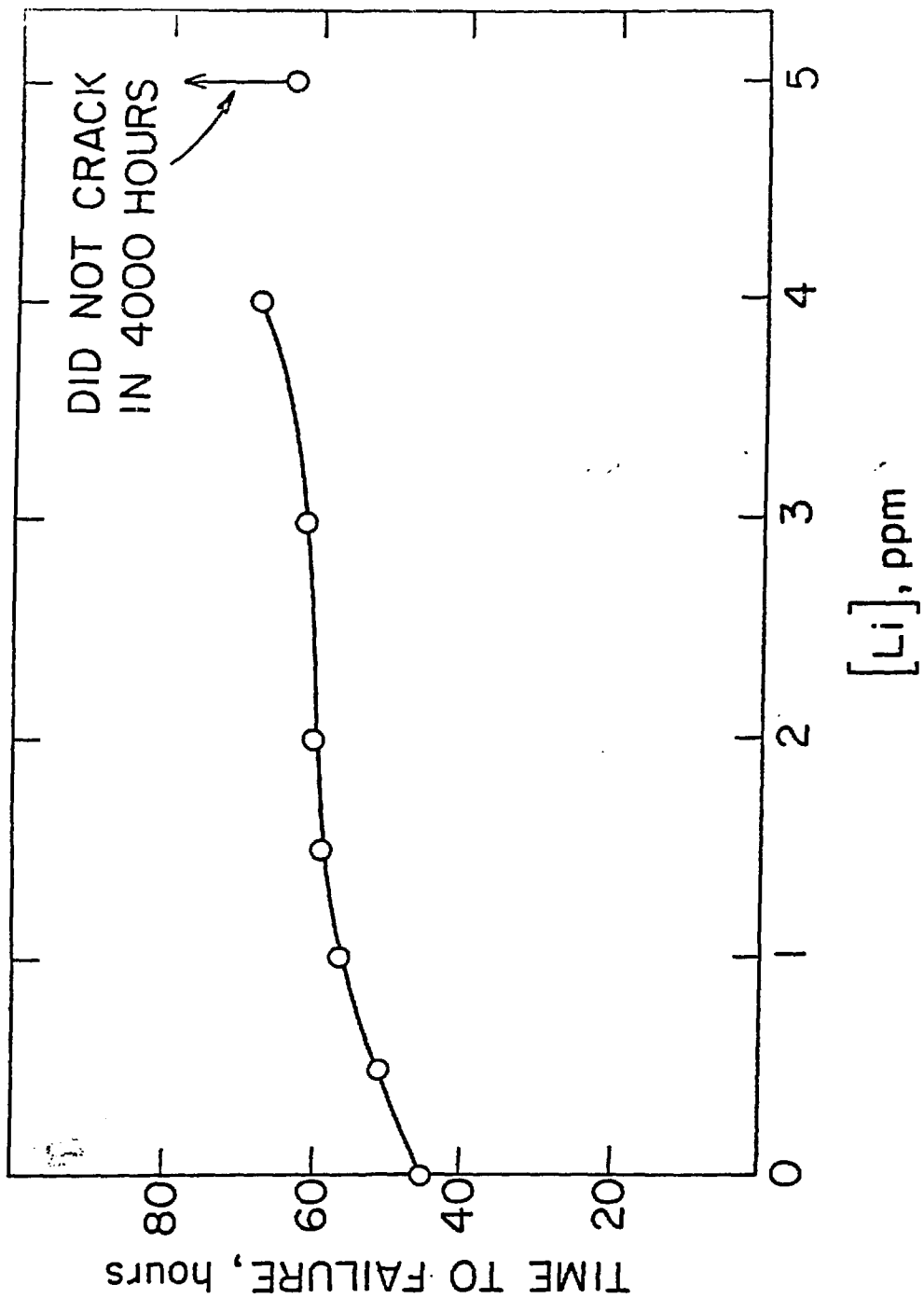


Figure 7 Relationship between time to failure of sensitized U-bends (SAS) of Alloy 600 in borated thiosulfate solution containing 7 ppm sulfur (1.1×10^{-4} M $\text{Na}_2\text{S}_2\text{O}_3$) at room temperature and concentration of lithium added as LiOH.

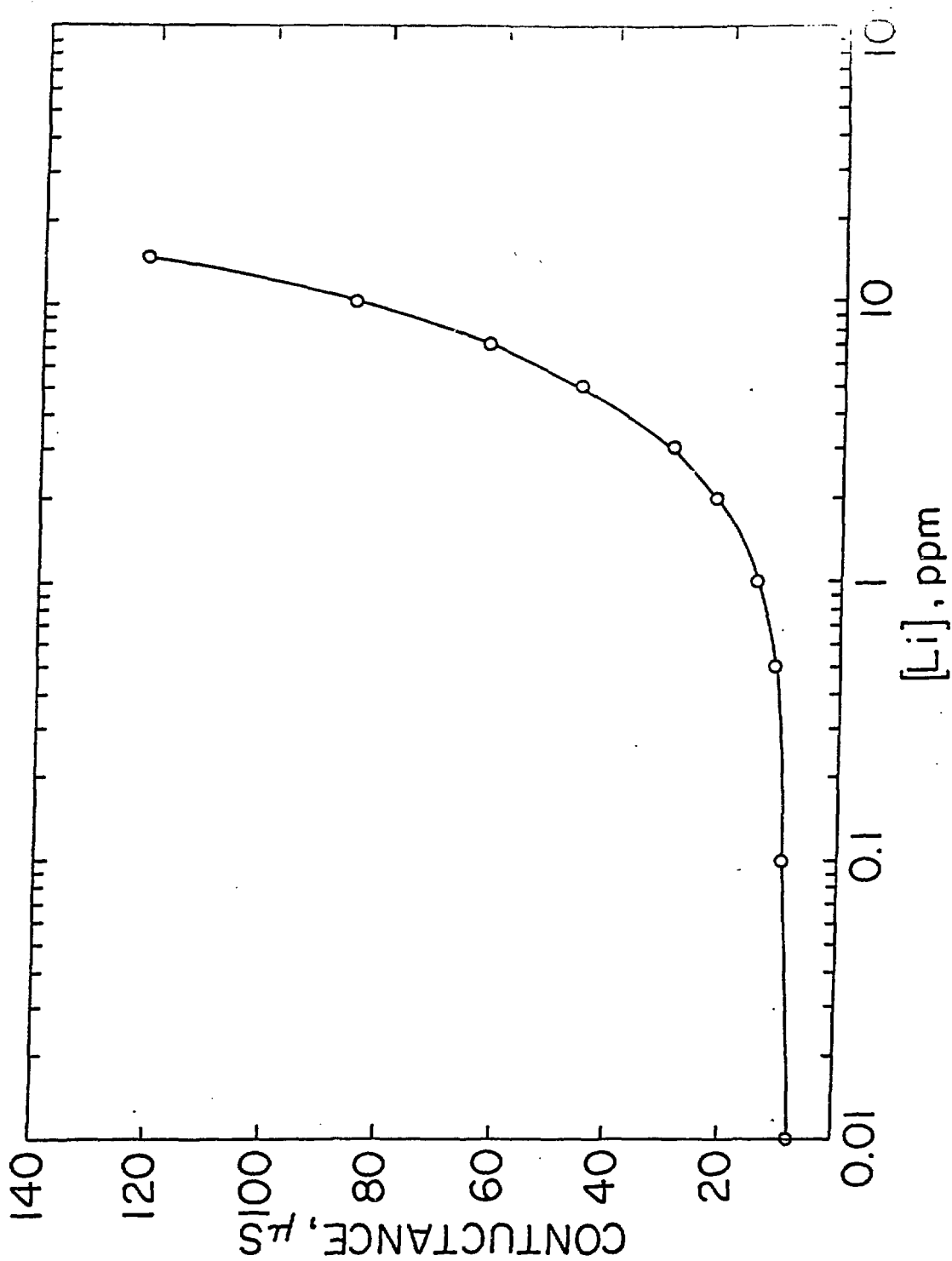


Figure 8 a) Variation of conductance of a borated thiosulfate solution containing 7 ppm sulfur (1.1×10^{-4} M $\text{Na}_2\text{S}_2\text{O}_3$) with lithium hydroxide at room temperature.

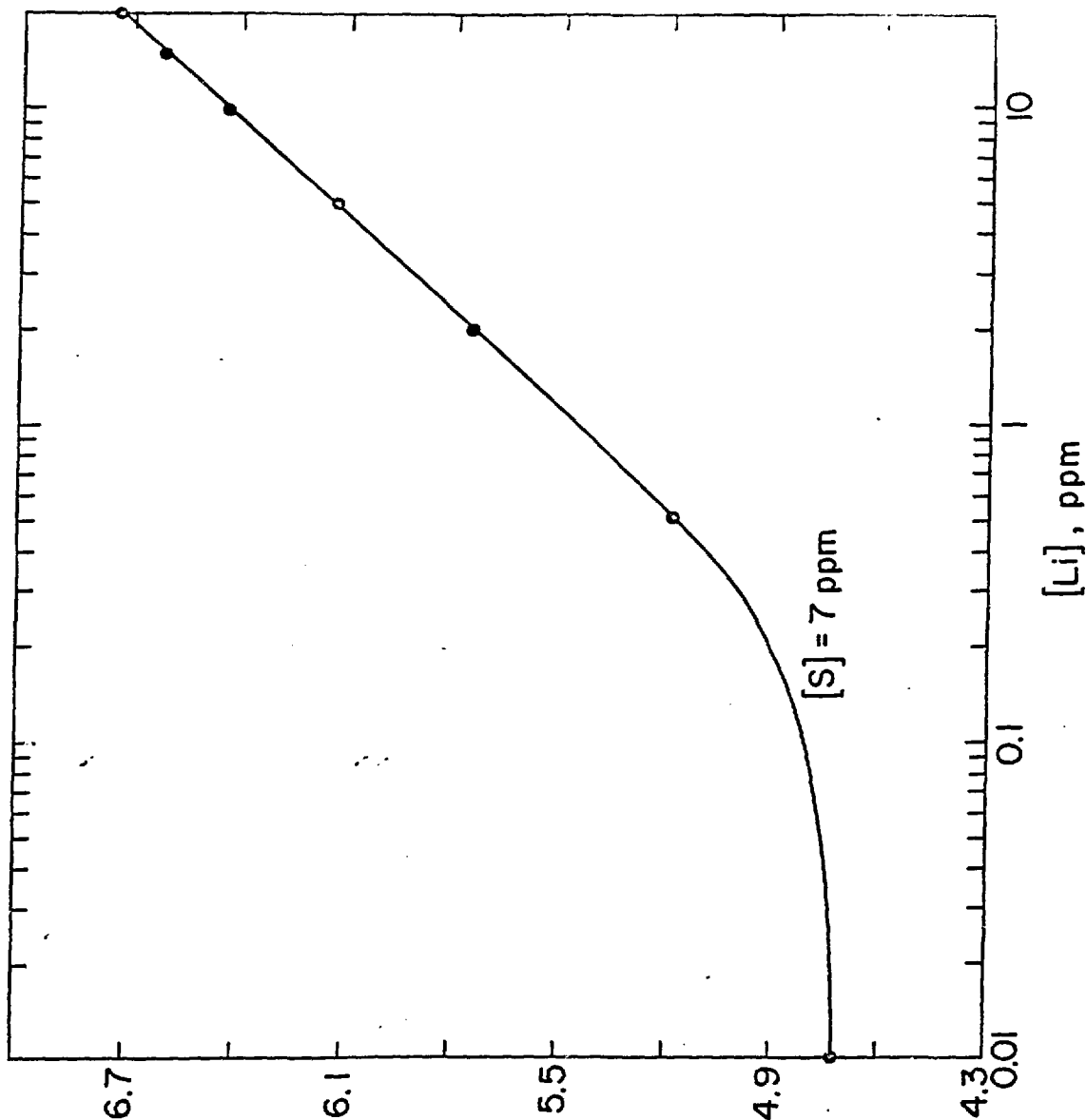


Figure 8 b) Variation of room temperature pH of a borated thiosulfate solution containing 7 ppm sulfur (1.1×10^{-4} M $\text{Na}_2\text{S}_2\text{O}_3$) with lithium hydroxide.

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