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Aluminum Alloy Corrosion

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Sept. 1962

The trend in high flux research reactors has resulted in higher proposed fuel cladding temperatures and longer core lifetimes. Sufficient "in-reactor" corrosion experience (i.e. EBWR, SL-1) has been accumulated for a nickel bearing aluminum alloy (X8001) to engender confidence in its corrosion safety in high temperature, low flow velocity reactors with modest heat fluxes. The high temperature (above about 315°C) corrosion resistances of the newer nickel bearing alloys have been significantly improved over X8001 by careful control of the impurities, particularly silicon and these alloys should prove superior to X8001 in reactor applications of this type.

Unfortunately from the designers' viewpoint, the dynamic corrosion of all of the aluminum alloys tried has proven to be particularly sensitive to testing parameters in the 200-325°C temperature range. Frequently it is difficult to reproduce corrosion data in a given dynamic test loop, while variations from laboratory to laboratory have shown rate factors of 25 or more for the same nominal conditions of temperature and velocity.

Several hypotheses have now been proposed to account for these variations. Dillon(1) and his associates first suggested that the protective aluminum oxide was dissolved in a dynamic stream. Calculating the corrosion rate becomes a matter of knowing the equilibrium concentration of oxide in the water and the effective rate of oxide removal by such means as refreshment streams and temperature induced precipitation.

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Recently(2) we have proposed a modified hypothesis in which it is assumed that the corrosion rate is strongly influenced by the availability of a precipitating colloid at the outer surface of the corroding aluminum. The colloids in question are not necessarily restricted to forms of aluminum oxide and the hypothesis can be used to explain other observed peculiarities of dynamic aluminum corrosion.

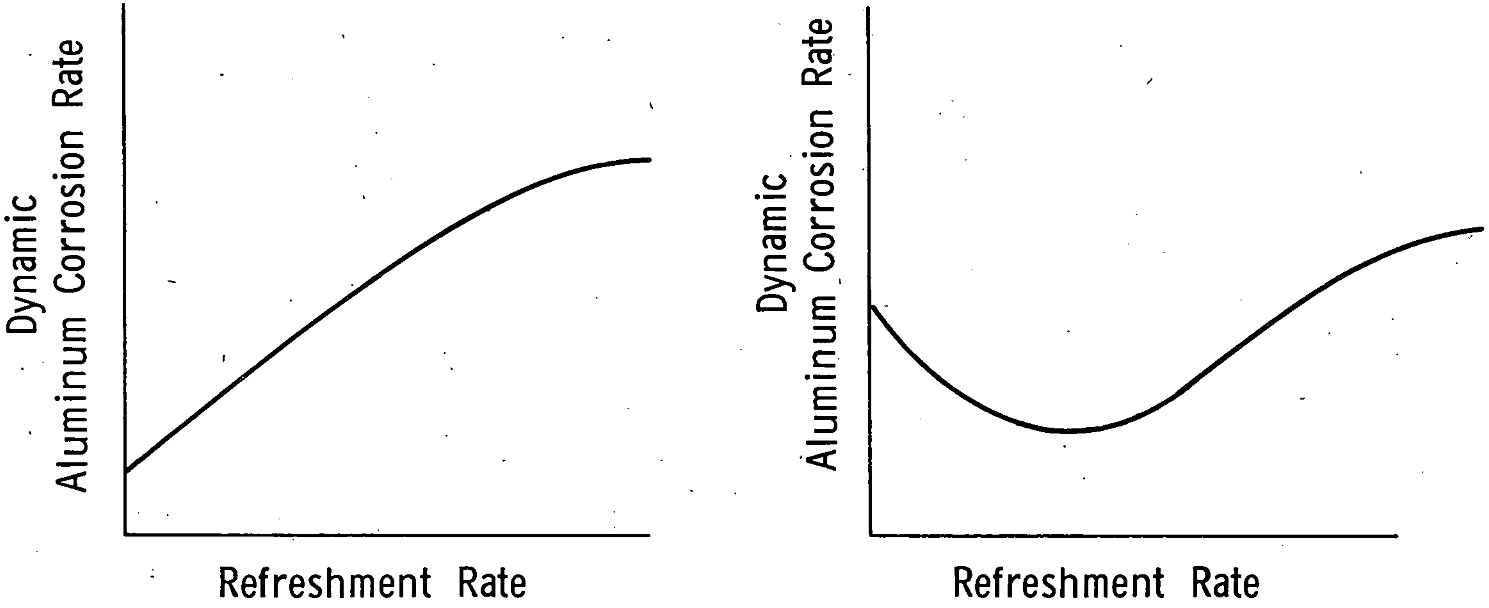
In this paper an attempt will be made to examine some potential research reactor corrosion problems in terms of hypotheses' predictions. The effect of the high level of radiation encountered in such reactors is an unknown factor and only a full scale "in-reactor" test can provide final answers.

Refreshment or Clean-up Rate

A very practical problem is how much and what kind of clean-up of the primary stream is required for minimum cladding corrosion? The two hypotheses predict quite differently as shown in Figure 1.

The reasoning in Figure 1A is straightforward: the more soluble aluminum oxide removed, the greater the driving force for the dissolution of the protective oxide and hence corrosion. The colloid prediction is slightly more devious. At very low refreshment rates, stable oxide particles can grow in the stream and these particles act as a large area sink for the freshly formed colloid in competition with the aluminum surface.(3) The possibility of the fine suspension of stable particles acting as a "liquid hone" should not be overlooked.

At very high refreshment rates significant quantities of the freshly formed colloids are physically removed before they have an opportunity to beneficially deposit on the aluminum surface. A limiting value of corrosion rate, corresponding to colloid free water, would be approached on the high side. The minimum corrosion rate would be a function of the physical characteristics of the particular equipment.



OXIDE DISSOLUTION HYPOTHESIS

COLLOID PRECIPITATION HYPOTHESIS

Figure 1. PREDICTIONS OF THE RELATIONSHIP BETWEEN CORROSION RATE AND REFRESHMENT RATE

The type of refreshment is also important. The typical ion exchange system encourages very fine particulate growth while a "bleed and feed" or high temperature distilling system effectively removes the solid material as well as ionic constituents.

Experimental verification of the prediction of either hypothesis on a single test loop has not been completed so it is necessary to piece together data from several sources. Corrosion penetration has been observed to remain essentially constant or (more typically) increase when ion exchange streams have been reduced or valved off (4,5,6,7) as predicted by the colloid hypothesis.

The corrosion rate has also been observed to increase by a factor of only two(2) as the refreshment rate was increased by a factor of about 35 in an isothermal loop refreshed by a "bleed and feed" method. (Time for one water change decreased from 7 hours to 0.2 hour). The relatively small increase in corrosion with a large increase in refreshment also tends to favor the colloid hypothesis.

Exposed Aluminum Area - Temperature Differentials

Some designers have been comforted by the low dynamic aluminum corrosion rates typically obtained in an isothermal loop charged with sufficient extra aluminum area. The extra area is usually calculated to bring the ratio of aluminum surface to water volume to that equivalent to an operating reactor. Both hypotheses suggest caution in applying results of this type testing to reactor design, but for fundamentally different reasons.

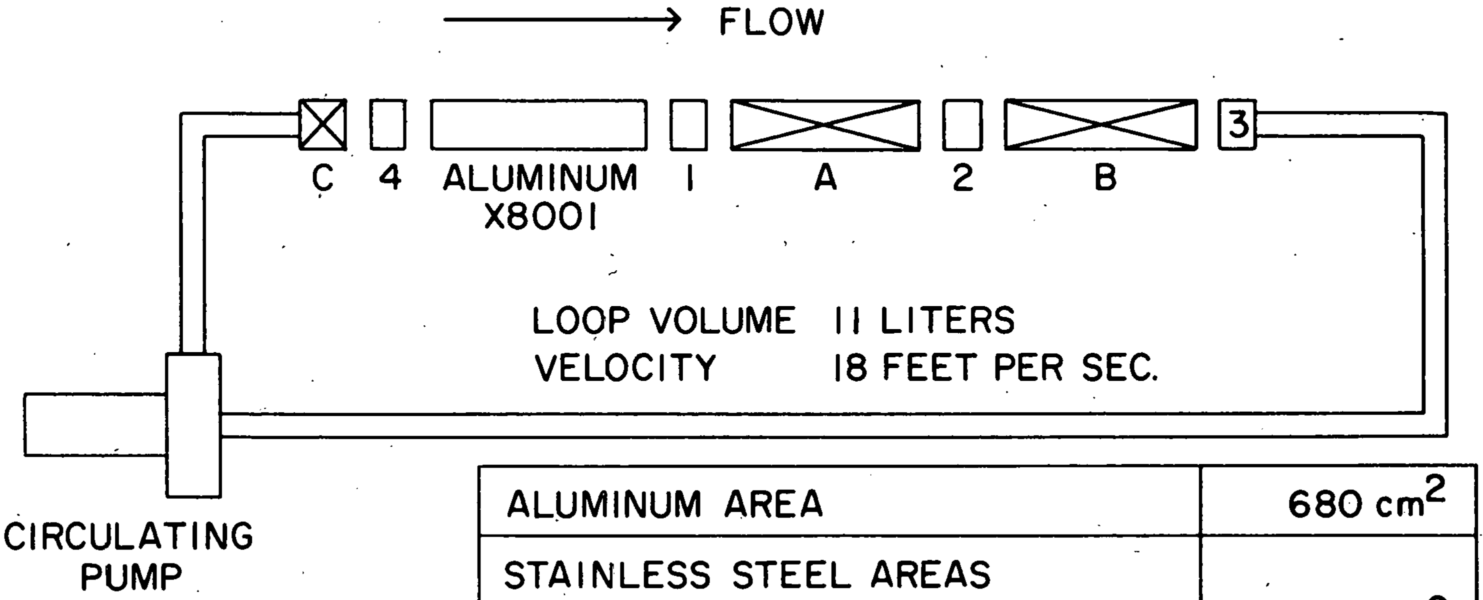
The oxide dissolution hypothesis emphasizes the difference in equilibrium oxide solubility (higher at higher temperatures) between the hot fuel metal cladding-oxide interface and the relatively cool heat exchanger. This is considered(1) to be equivalent to a large refreshment rate as far as removal of soluble oxide is concerned and is predicted to increase the aluminum corrosion.

The colloid hypothesis is more concerned with all of the factors contributing to the loss of colloid which otherwise could precipitate on the aluminum cladding. Increased path time (length), more changes in velocity and direction, and as a secondary matter, temperature differentials, would be expected to deplete the colloid concentration in a reactor compared with a typical test loop.

One possible practical difference in predictions that might be considered is the role of a sacrificial large area aluminum structure just upstream of a reactor core. Oxide dissolution does not predict a significant beneficial effect because the main corrosion driving force (oxide solubility difference between fuel plate temperature at the metal-oxide interface and incoming stream temperature) would still exist. The colloid hypothesis does suggest a beneficial effect. The authors are not aware of any reactor test of these predictions.

If such a sacrificial structure were contemplated, it would be advantageous to know the distance downstream (or time) through which the precipitation would be heavy enough to be effective. Some estimate of the distance can be derived from a recent loop experiment in which coiled bundles of corroded stainless steel were used as collectors of the precipitated corrosion product released by corroding aluminum samples. The schematic of the test is shown in Figure 2.

The increase in weight is given as a function of time in Table 1. During the initial corrosion, the deposition falls off very rapidly with distance downstream. Subsequent to one week the continuing deposition is nearly uniform over the entire small circuit. This suggests that in order to be effective during the start-up period in a reactor a sacrificial structure would necessarily be immediately upstream from the reactor core.



ALUMINUM AREA	680 cm^2
STAINLESS STEEL AREAS	
NUMBERED COLLECTORS, EACH	1,450 cm^2
A AND B, EACH	10,900 cm^2
C	2,170 cm^2

Figure 2. SCHEMATIC OF DYNAMIC TEST FOR MEASURING ALUMINUM CORROSION PRODUCT DEPOSITION

Table 1

Deposition of Corrosion Product from Aluminum Samples

Collector	Time, Days 7.0	 14.0	 28.0
1 - Immediately downstream	35.9	44.4	55.2 mg
2 - Downstream	23.0	33.0	44.7
3 - Downstream	16.6	28.0	40.7
4 - Immediately upstream	6.6	16.0	26.2

Collector areas 1450 cm^2

Colloid Additions

Another possible mode of protection if the colloid hypothesis is correct would consist of injecting a colloid of the correct precipitation characteristic directly into the water. To date we have unsuccessfully tried this approach with graphite (purified Aquadag) and purified ferric hydroxide and aluminum oxide colloids at the 1 and 4 ppm levels. One difficulty appears to be associated with securing the desired precipitation characteristics. A more reliable source of the colloid appears to be corroding materials such as aluminum scrap or fresh stainless steel(8) in the loop. At present other possible sources are being investigated.

Powder Products

High flux research reactors typically require narrow, dimensionally stable coolent channels. Unfortunately the creep resistance of wrought aluminum products is poor, particularly above 250°C, causing serious design limitations. Products fabricated from some treated aluminum powders have excellent high temperature creep resistance but securing adequate corrosion resistance to high temperature aqueous environments has been difficult.

Although there are numerous variations, the flow diagram shown in Figure 3 represents a typical practice. Each step, while simple in concept, turns out to be a function of interrelated variables. Consistant good results are difficult to achieve, since only a few of the variables are controlled in the usual commercial operation.

Our group has corrosion tested numerous aluminum powder products based on corrosion resistant alloy compositions. Samples have been supplied by Alcoa, Argonne, Armour Research Foundation, AIAG (Swiss) and Torrance Brass Company. The corrosion results have been characterized by a lack of reproducibility, not only from one extrusion to the next, but sometimes within the length of a given extrusion. Some samples have equalled or bettered the corrosion resistance of wrought products while others have failed in short tests.

Catastrophic failures of powder products in short (several days) tests have occurred only for samples produced from powders treated to greatly decrease the interoxide spacing as compared with atomized powder. In American practice this occurs in the ball milling step (Figure 3). It is believed that a kneading action in the mill entraps milling lubricant (typically a stearic acid solution)so that it cannot be effectively removed by the subsequent washing operation. The remnants of this lubricant are then incorporated into the extruded product, possibly as an aluminum-carbon compound and hydrogen gas. The aluminum-carbon compound is suspected in catastrophic corrosion. A new type milling lubricant or a fresh approach

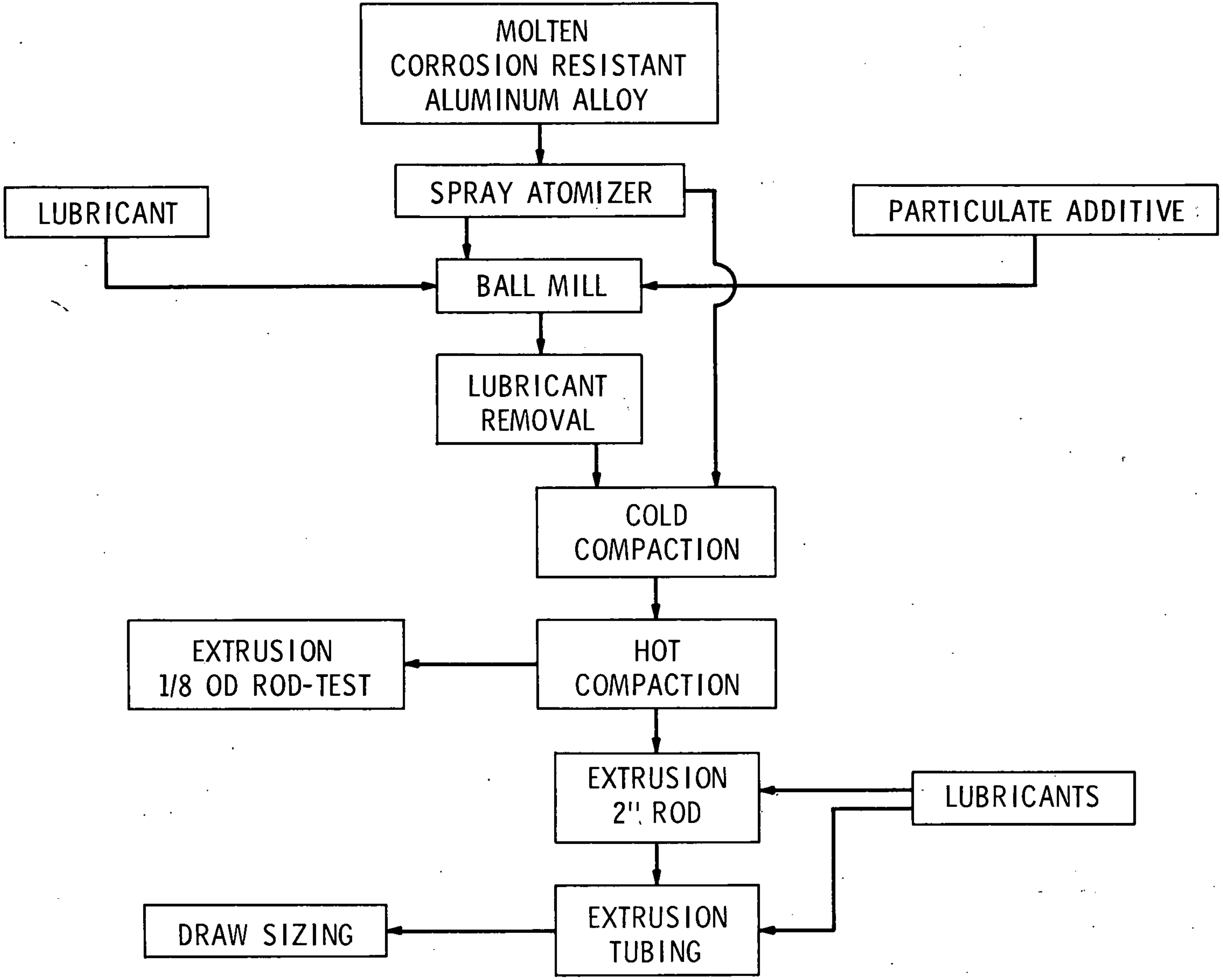


FIGURE 3. PRODUCTION STEPS IN ONE METHOD OF FABRICATING ALUMINUM POWDER PRODUCTS

to the problem of reducing the interoxide spacing may be required to secure corrosion resistant powder products with mechanical properties approaching those of the better SAP products.

Examination of the microstructure of two products produced by ARF illustrates that porosity is one of the common reasons for mediocre to poor corrosion resistance (Figure 4). Samples of the rod were corroded in water for 270 days at 290°C and were in excellent condition at that time. The tube samples were badly blistered at about 90 days and showed corrosion swelling of cut edges, a common mode of corrosion failure for powder products. The problem of porosity, as illustrated by this example, is usually traced to moisture contamination of the powder, although decomposition of trapped milling lubricant may sometimes be partially responsible. During exposure to hot water a portion of the corrosion produced hydrogen enters the metal, auguments the hydrogen in the voids, and raises blisters. The process is accelerating since the blister locally breaks the exterior protective oxide, causing more corrosion. Encouraging results on the prevention of porosity have been obtained recently by the Montecatini Company in Italy through vacuum degassing of the extrusion billet and extreme precautions in powder handling.

Figure 5 illustrates the current state of the art for the creep resistance of adequately corrosion resistant tubing. These tubes, about 0.4" OD with a 1/32" wall, were extruded by ARF through a bridge die. To put the values in perspective, one of the best high temperature wrought alloys, X2219, crept about 5% in one week under these conditions.

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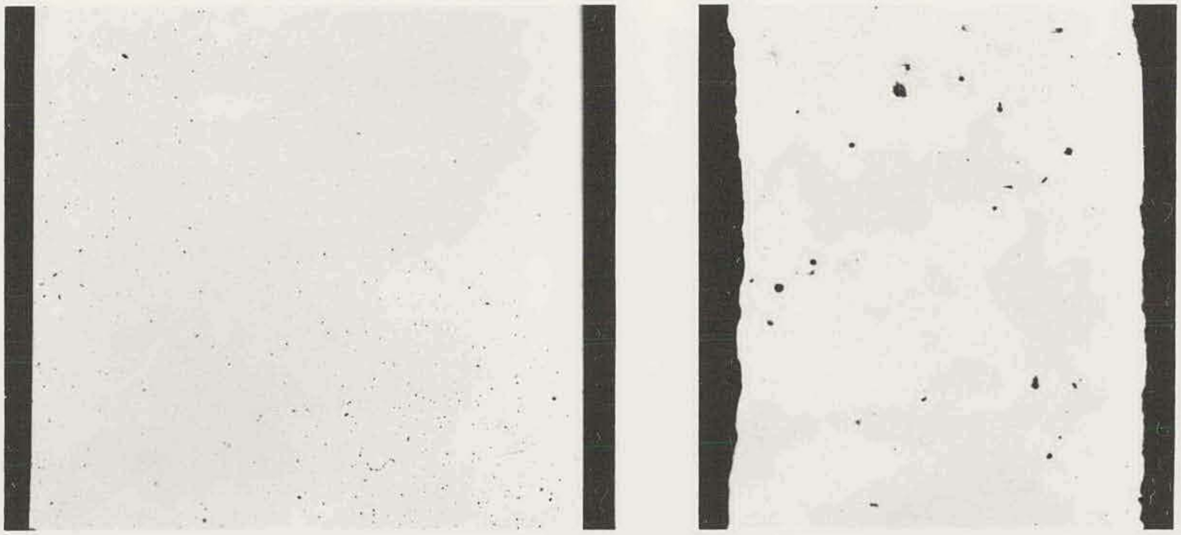

11065 64X

Rod 2Q-1 - As Received 3 w/o SiO_2 in A288 Aluminum (Excellent Corrosion Resistance to 290°C Water)

110606 64X

Tubing G - As Received "As Atomized" A288 Aluminum (Poor Long Term Corrosion Resistance to 290°C Water)

Figure 4. POROSITY IN ALUMINUM POWDER PRODUCTS

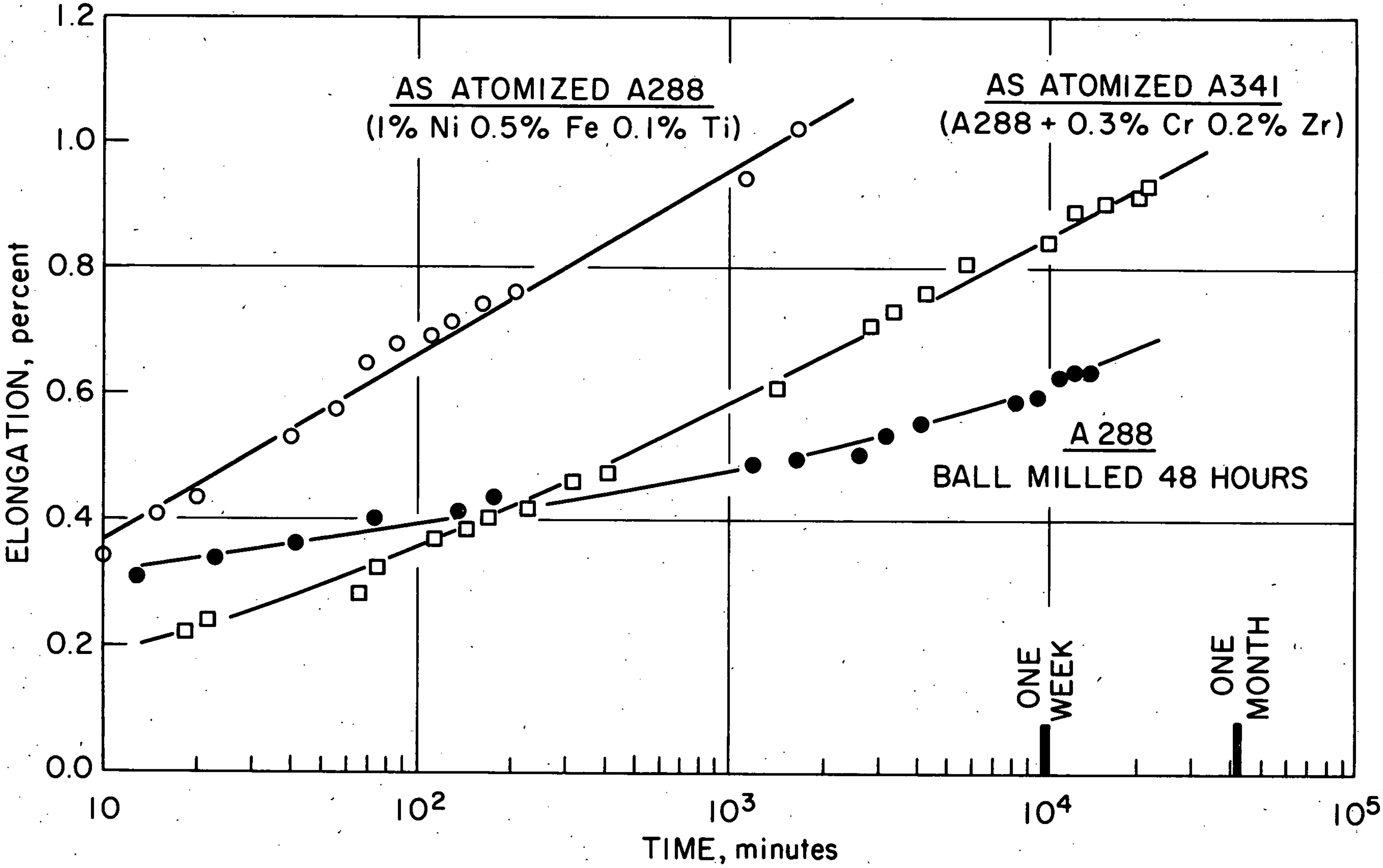

Figure 5. CREEP OF ALUMINUM POWDER PRODUCT TUBING AT 4000 PSI, 290°C

BIBLIOGRAPHY

1. Dillon, R. L., Dissolution of Aluminum Oxide as a Regulating Factor in Aqueous Aluminum Corrosion, HW 61089, August 1959.

2. Draley, J. E., and W. E. Ruther, The Corrosion of Aluminum Alloys in High Temperature Water, I.A.E.A. Conference, Salzburg, June 1962.

3. Hatcher, S. R., and H. K. Rae, Turbidity in Aluminum Water Reactor Systems, Nuclear Science and Engineering 10 316-330 (1961).

4. Biefer, G. J., and P. G. Anderson, Corrosion Behavior of Al-Ni-Fe Alloys in High Temperature Water Under Dynamic Conditions, AECL 763 (CRMet - 799) December 1958.

5. Biefer, G. J., and J. R. Keenan, Corrosion Behavior of 10197 Al-Ni-Fe Alloy in High Temperature Water Under Dynamic Conditions, AECL 1006 (CRMet 882) April 1960.

6. Wilkins, N. J. M., J. T. Dalton and J. N. Wanklyn, Corrosion of Al Alloys in High Temperature Flowing Water, AERE-R3649, 1961.

7. Riskevics, Karlis, Investigation of the Corrosion Aspects of Selected Aluminum Alloys, ACNP 6009, January 1961.

8. Reactor Chemistry Division Annual Progress Report - January 1962, ORNL 3262 - p. 93-96.