ANL-5927
Metallurgy and Ceramics
(TID-4500, 14th Ed.)
AEC Research and
Development Report

ARGONNE NATIONAL LABORATORY
P. O. Box 299
Lemont, Illinois

CORROSION RESISTANCE AND MECHANICAL PROPERTIES
OF ALUMINUM POWDER PRODUCTS

by
J. E. Draley and W. E. Ruther

Metallurgy Division

Program 10.1.9

Portions of the material given in this report
appeared in the following Metallurgy Division
Quarterly Report:

ANL-5797, pp. 28-29 July, Aug., Sept., 1957

March, 1959

Operated by The University of Chicago
under
Contract W-31-109-eng-38

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency Thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

DISCLAIMER

Portions of this document may be illegible in electronic image products. Images are produced from the best available original document.

TABLE OF CONTENTS

	<u>Page</u>
ABSTRACT	3
INTRODUCTION	3
EXPERIMENTAL	4
DATA AND RESULTS	5
Corrosion Resistance	5
Mechanical Properties	8
DISCUSSION	9

LIST OF TABLES

<u>No.</u>	<u>Title</u>	
I	Corrosion of Mixed Powder Extrusions	5
II	Mechanical Properties of X8001 and M457	8
III	Mechanical Properties of ANL Powder Extrusions	9

LIST OF FIGURES

<u>No.</u>	<u>Title</u>	
1	Corrosion of Aluminum Wrought Alloy vs. Powder Products in 290°C Refreshed Distilled Water	6
2	Corrosion of Aluminum Powder Products at 290°C in Refreshed Distilled Water	7
3	Corrosion of Aluminum Powder Extrusions in Refreshed Distilled Water at 290°C	7
4	Ultimate Tensile Strength of Aluminum Products at Various Temperatures	9

CORROSION RESISTANCE AND MECHANICAL PROPERTIES OF ALUMINUM POWDER PRODUCTS

J. E. Draley and W. E. Ruther

ABSTRACT

Experimental extrusions were prepared from mixtures of atomized aluminum alloy and several powdered additives, including SiO_2 , AlPO_4 and Al_2O_3 . Some of the extrusions failed during corrosion testing in water at 290° and 350°C . Others corroded in approximately the same fashion as wrought X8001 alloy.

The ultimate tensile strengths of these extrusions at 316°C were approximately two and one-half times greater than that of wrought X8001 alloy.

INTRODUCTION

An aluminum alloy X8001 (1 w/o Ni in 1100 alloy), which combines high-temperature aqueous corrosion resistance with low neutron-capture cross section, is now available. Unfortunately alloys of this type are relatively poor in mechanical properties at temperatures of the order of 300°C , thereby being unsuitable for certain reactor applications. Since this alloy system does not possess age-hardening properties, an enhanced high-temperature strength can be achieved most easily by dispersion hardening. Since the type of additives which can be supplied by conventional alloying are frequently limited by disparity of melting points, a powder metallurgical technique has been adopted for effecting these additions.

The commercial process usually involves: (1) reduction of the alloy to powder, (2) compacting the powder, with or without sintering, and (3) extrusion of the compacted powder. The Research Laboratory of ALCOA first demonstrated that a corrosion-resistant powder product, M457, could be made from X8001 powder.

Experience with wrought alloys had shown that the coating formed on most aluminum specimens during corrosion at high temperatures were at least duplex in nature: a relatively porous outer coating covered a more compact inner layer. It is possible that the corrosion rate of the alloy is determined by the rate of transformation of the compact layer into a porous coating.

The corrosion rate of the X8001-type alloys in a dilute phosphoric acid solution is only a tiny fraction of that in water. Presumably the acid permeates the porous coating and acts on the compact layer. It was hoped that supplying an inhibitor powder from the metal side of the corrosion film would place it in a favorable spot for corrosion inhibition.

A coextrusion of solid inhibitor and powdered metal alloy provided a method of testing this type of inhibitor addition for improved corrosion resistance, and simultaneously improving the high-temperature mechanical properties of the product. The experimental work described in this report was initiated with this dual objective in mind.

EXPERIMENTAL

The atomized X8001 and 1100 alloy powders were purchased from the Aluminum Company of America. Various potential inhibitor powders were mixed with the atomized aluminum, using a mechanical "V"-type blender. The powder mixtures were loaded into an aluminum can, using a Syntron vibrator to achieve maximum densities. The containers were made of 1100 alloy and were $3\frac{1}{2}$ in. OD by 9 in. long. Caps containing a gas-vent tube were welded in place. The cartridges were heated in a 455°C oven for a period of at least 3 hours to bring the entire cartridge to the extrusion temperature.

The extrusions were performed by the Precision Extrusion Company of Bensenville, Illinois. A rectangular die, $2\frac{1}{2}$ in. x $1/8$ in. was used, providing an area reduction of about 31 to 1.

Sheared pieces of the extrusion were prepared for corrosion testing by wet grinding (240 grit) on metallographic polishing wheels to remove the 1100 alloy cladding (~ 0.005 in.) derived from the extrusion can. In most cases the powder product produced a different surface texture upon grinding so removal of the clad was easy to determine.

The corrosion tests were in two parts. First, a small sample of the extrusion was given a 48-hour test in 350°C water. If the extrusion did not disintegrate or show signs of early failure in this exposure, a careful test using sixteen samples was performed at 290°C in refreshed autoclave systems.

One other type of test was performed in small volume, static autoclaves at 290°C . Six small samples, each $2 \times 2.5 \times 0.1$ cm in dimension, of one extrusion were suspended by artificial sapphire rods in about 100 cc of water. The water was replaced only at the times the autoclave was opened: after 10, 17 and 24 days.

In all tests at 290°C, the adherent corrosion product was removed by a one-minute electrolytic treatment (20 g/l boric acid; 880 v AC vs platinum; temperature 20-25°C). Defilming was easier than with the usual wrought alloy.

The potential inhibitors for coextrusion were chosen to meet certain requirements. All were only slightly soluble at high temperatures to prevent rapid leaching. The oxides and compounds of elements in the phosphorus group and SiO_2 were chosen to provide acidic conditions and possible inhibiting ions. The Nicrobraz-10 (a commercial hard brazing alloy containing nickel and phosphorus) offered the possibility of a product with an 1100 aluminum base.

The $\alpha\text{-Al}_2\text{O}_3$ was tried in the hope that crystallites of this substance would initiate the formation of a corrosion-product barrier of this crystal structure rather than one of the more soluble hydrated aluminas (gamma or eta) normally formed.

DATA AND RESULTS

Corrosion Resistance

The compositions of all extrusions prepared and the initial corrosion data are given in Table I. Two of the eight extrusions failed the short

Table I

CORROSION OF MIXED POWDER EXTRUSIONS

Extrusion No.	Composition, w/o	350°C H ₂ O, 2 days
1	X8001 Powder 96 AlPO ₄ 4	Passed
2	1100 Powder 96 Nicrobraz-10 4	Failed
3	X8001 Powder 96 B ₁₂ O ₃ Powder 4	Failed
4	X8001 Powder 96 SiO ₂ Powder 4	Passed
6	X8001 Powder 96 AlPO ₄ Powder 2 SiO ₂ Powder 2	Passed
7	X8001 Powder 100	Passed
8	X8001 Powder 96 As ₂ O ₃ Powder 2 AlPO ₄ Powder 2	Passed
9	X8001 Powder 96 $\alpha\text{-Al}_2\text{O}_3$ Powder 4	Passed

350°C water test. One other (#8), containing As_2O_3 and AlPO_4 , failed after 15 to 20 days at 290°C. The attack in this case proceeded from all the edges inward, causing perimeter swelling of the specimens. The other extrusions were tested for 35 to 56 days. In no case did the effluent pH or resistivity from the refreshed autoclaves indicate significant variation from values obtained in the testing of wrought alloys. For the purposes of discussion the results of the corrosion tests are divided into three groups.

In Fig. 1 the corrosion behavior of ANL extruded X8001 powder is compared with the previously mentioned extruded and cold-rolled powder product manufactured by Alcoa. Wrought X8001 is included for reference. The scatter of data prevented a determination of the rate law, so an average corrosion rate based on the period from 5 days to the end of the test was estimated. The intercepts of these average rate lines on the axis indicating the extent of corrosion were different for the three materials, but the slopes were quite similar. Subsequent to receipt of this first batch of Alcoa M457, a second lot of M457 was received from the Alcoa Research Laboratory. This material, whose mechanical history was unknown, failed by blistering in stringers during corrosion testing.

FIG.1 CORROSION OF ALUMINUM WROUGHT ALLOY VS POWDER PRODUCTS IN 290°C REFRESHED DISTILLED WATER

Corrosion results on extrusions containing 4 w/o SiO_2 and 4 w/o AlPO_4 , respectively, are plotted together in Fig. 2. The estimated corrosion rate was slightly greater for these samples than for the reference X8001.

The last group, containing 2 w/o SiO_2 -2 w/o AlPO_4 and 4 w/o $\alpha\text{Al}_2\text{O}_3$, corroded in a more desirable fashion (see Fig. 3). Scatter in the corrosion data was less than for the preceding alloys and the rate apparently decreased

with increasing time. For comparison a line of slope equal to 3.7 mdd (wrought X8001) is shown on the figure. At the end of 35 days the instantaneous corrosion rate (given by the slope of the curve) of the 2 w/o SiO_2 -2 w/o AlPO_4 powder product has diminished to about the reference rate and that of the 4 w/o $\alpha\text{-Al}_2\text{O}_3$ had become lower. Since Ex9 (4 w/o $\alpha\text{-Al}_2\text{O}_3$) appeared to be the most promising, a longer test was run. The data from this longer experiment confirmed the previous curve, but after about 65 days swelling of the sample edges in the extrusion direction was noted. The samples survived an additional 65 days but the edge swelling was very pronounced.

FIG. 2 CORROSION OF ALUMINUM POWDER PRODUCTS AT 290°C IN REFRESHED DISTILLED WATER

FIG. 3 CORROSION OF ALUMINUM POWDER EXTRUSIONS IN REFRESHED DISTILLED WATER AT 290°C

Relatively short corrosion tests in small static autoclaves were used to see if leaching of the "inhibitor" powder addition took place in the refreshed autoclave testing. From the similarity of the results of this type of exposure with those of exposure in the refreshed systems it was concluded that dilution of the test solution by continuous refreshment was not a vital factor in the corrosion behavior of the powder products.

Mechanical Properties

Data on the mechanical properties of X8001 wrought alloy and Alcoa M457 powder product are given in Table II. The increase in strength of the powder product at 316°C over that of the wrought alloy is a little more than two.

Table II
MECHANICAL PROPERTIES⁽¹⁾ OF X8001 AND M457

Temp, °C	Alloy	Tensile Strength, psi	Yield Strength, psi	Elong. in 2 in., %	After 100 Hr at Temp		
					Tensile Strength, psi	Yield Strength, psi	Elong. in 2 in., %
Room	X8001 (Forged Rod) (-F Temper)	20,800	18,700	20.5			
149					15,300	14,000	30.0
204					11,700	10,100	31.5
260					7,300	6,200	34.0
316					3,300	2,600	66.0
Room	X8001 (Extrusion) (-F Temper)	15,000	6,300	38.0			
316					3,300	2,800	84.0
427					1,500	1,200	81.0
Room	M457	22,400	12,700	30.0			
316					7,300	6,100	27.0
427					4,200	3,300	26.0

⁽¹⁾ Based on single lots of material.

Data supplied by Alcoa Research Laboratories (April 25, 1958).

Tensile tests were performed on three ANL powder extrusions by the Martin Company. The data are presented in Table III. Two of the extrusions were about equal in tensile strength, with the third (Ex. 1) consistently stronger.

Ultimate tensile strengths are compared in Fig. 4.

Table III

MECHANICAL PROPERTIES OF ANL POWDER EXTRUSIONS

Temperature, °C	Extrusion Number*	Ultimate Tensile Strength, psi (No Soaking at Temperature)	% Elongation in 1½ inches
Room	1	29500	40
	4	25750	35
	4	25700	40
93	1	24500	20
	4	23300	9
	4	22700	16
149	1	19900	33
	4	18150	23
	4	18300	15
204	1	14700	15
	9	12250	33
	9	12850	25
260	1	12150	23
	9	10600	27
	9	10500	20
316	1	9075	17
	9	7810	28
	9	8190	22

*No. 1. 4 w/o AlPO_4 + X80014. 4 w/o SiO_2 + X80019. 4 w/o Al_2O_3 + X8001

FIG. 4 ULTIMATE TENSILE STRENGTH OF ALUMINUM PRODUCTS AT VARIOUS TEMPERATURES

DISCUSSION

The variation in corrosion resistance of powder products obtained from Alcoa and the failure of an ANL extrusion by edge blistering suggest that production factors are extremely important. With so many possible variables in powder preparation and extrusion, it is considered encouraging that the initial efforts were largely successful.

The serious corrosion defect, namely, the swelling along the extrusion direction, is likely to yield to a change of production variables. Experience with wrought aluminum alloys has indicated that porosity is detrimental to good corrosion resistance. Steps to reduce porosity in powder extrusions might include vacuum drying and degassing of the powder, elimination of powder fines (extremely high surface-to-volume ratios increase adsorbed gas), and the use of larger reduction ratios in the extrusion of the billet.

It was noted that the main difference in corrosion behavior between the wrought alloy X8001 and extruded powdered X8001 (Fig. 1) was in the vertical displacement of the curves. The factors involved in the intercept of the corrosion curve are not clearly understood but probably are related to the sample preparation, the impurities in the distilled water, and the temperature during the first few hours of exposure. It is known that corrosion curves of wrought X8001 alloy tested at different times in different autoclaves have produced intercepts of 0.3 and 1.3 mg/cm². The slope from 5 to 30 days remained constant (~ 4 mdd) for these two tests.

It is believed that the reason for the corrosion failure of Ex2 (made from 1100 powder and Nicrobraz powder) was the relatively large distance between the Nicrobraz particles in the extruded sheet. Previous work* has shown that for a cathodic phase to be effective in wrought aluminum alloys it must be more finely distributed than was obtained in this powder product.

Some reduction of corrosion rate occurred with Ex6 and Ex9 but not to the extent previously obtained with dilute phosphoric acid. In this respect results were disappointing.

The mechanical properties of powder extrusions were improved by a factor of about two and one-half over wrought X8001 at 316°C. No attempt was made to optimize strength.

Aluminum powder products appear to have a future in the reactor field, but in critical corrosion applications more attention to production details will be required than is typical of the usual commercial product.

*Draley, J.E. and W.E.Ruther, "Experiments in Corrosion Mechanism: Aluminum at High Temperatures," ANL-5658 (April, 1957) pp. 8-12.