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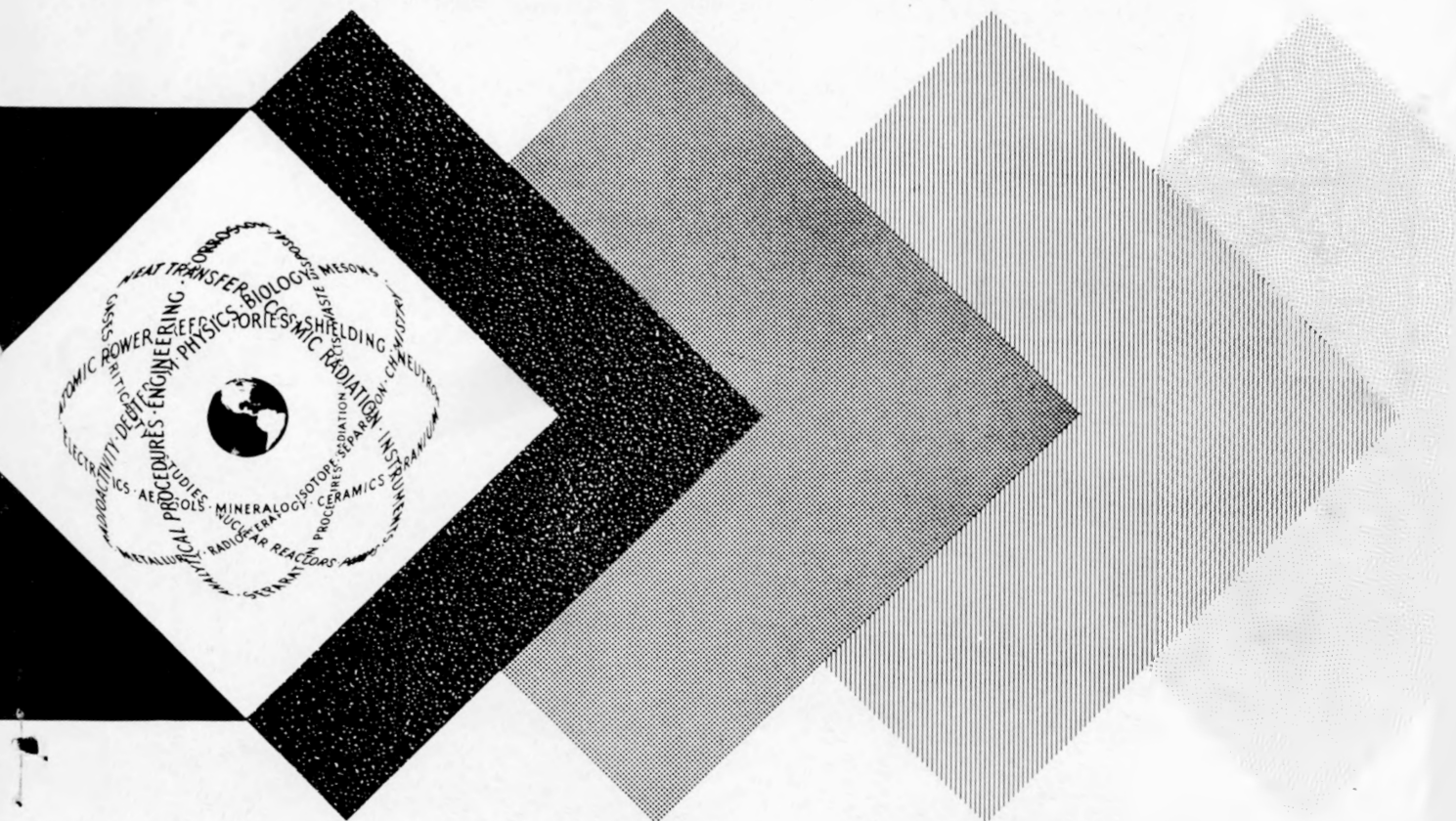
METALLURGY AND CERAMICS

CORROSION OF ZIRCONIUM ALLOYS IN 900 AND 1000°F STEAM

By
J. Paul Pemsler

March 15, 1960

Nuclear Metals, Inc.
Concord, Massachusetts



UNITED STATES ATOMIC ENERGY COMMISSION
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Nuclear Metals, Inc.
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TABLE OF CONTENTS

	<u>Page No.</u>
ABSTRACT	6
I INTRODUCTION	7
II EXPERIMENTAL	7
III RESULTS AND DISCUSSION	8
A. Zr-Ni-Cr Alloys	9
B. Zr-Ni-Fe Alloys	10
C. Zr-Fe-Cr Alloys	11
IV TABLES AND FIGURES	13

LIST OF TABLES AND FIGURES

	<u>Page No.</u>
TABLE I - Zirconium Ternary Alloy Compositions and Analysis	13
TABLE II - Rolling and Heat Treatment of the Alloys	14
FIGURE 1 - Corrosion of Zirconium Alloy NC-15 (0.6 ^w /o Ni-0.3 ^w /o Cr).	15
FIGURE 2 - Corrosion of Zirconium Alloy NC-16 (0.6 ^w /o Ni-0.3 ^w /o Fe).	16
FIGURE 3 - Corrosion of Zirconium Alloy NC-18 (0.6 ^w /o Ni-1.0 ^w /o Fe).	17
FIGURE 4 - Corrosion of Zirconium Alloy NC-21 (0.3 ^w /o Ni-1.0 ^w /o Cr).	18
FIGURE 5 - Corrosion of Zirconium Alloy NC-28 (0.6 ^w /o Fe-1.0 ^w /o Cr).	19
FIGURE 6 - Corrosion of Zirconium Alloy NC-29 (0.5 ^w /o Fe-0.3 ^w /o Cr).	20
FIGURE 7 - Corrosion of Zirconium Alloy NC-43 (0.3 ^w /o Ni-0.3 ^w /o Cr).	21
FIGURE 8 - Corrosion of Zirconium Alloy NC-44 (0.3 ^w /o Ni-0.3 ^w /o Fe).	22
FIGURE 9 - Corrosion of Zirconium Alloy NC-47 (1.0 ^w /o Fe-1.0 ^w /o Cr).	23
FIGURE 10 - Corrosion of Zirconium Alloy NC-48 (0.3 ^w /o Ni-1.0 ^w /o Fe).	24
FIGURE 11 - Anisotropic Corrosion of Sample NC-16 after 182 days in 900 ^o F (482 ^o C) steam.	25

LIST OF TABLES AND FIGURESPage No.

FIGURE 12 - Microcracks on Sample NC-28 after 155 days in
1000°F (538°C) steam.

26

ABSTRACT

Steam at 900 to 1000°F and 1500 psi is a very corrosive medium for zirconium alloys. Zircaloy-2 and Zircaloy-3 fail after a short time under these conditions. The presence of tin is highly detrimental to the corrosion resistance, while additions of chromium, nickel, and iron, both singly and in combination, extend the life of zirconium-base alloys at these temperatures. The results of the corrosion testing of eleven ternary alloys of zirconium with iron and nickel, nickel and chromium, and chromium and iron are presented. The effect of fabrication and heat treatment is discussed. Life expectancies of the order of two years in 900°F and six months in 1000°F steam before the commencement of spalling may be expected for some of the alloys.

I. INTRODUCTION

Zirconium-base alloys were developed for use in nuclear reactors at temperatures below the critical temperature of water, 706°F (374°C). The behavior of these alloys in steam at 750°F (399°C) and 1500 psi does not necessarily correlate with results in water below the critical temperature. Previous work in this laboratory¹ demonstrated that steam at 900°F (482°C) is a very corrosive medium for zirconium alloys. The presence of tin was highly detrimental to the corrosion resistance of zirconium alloys and the tin-containing alloys Zircaloy-2 and Zircaloy-3 failed rapidly in 900°F (482°C) steam. Additions of nickel, chromium, and iron extended the life of zirconium to as long as sixty days before spalling commenced at the edges. Quenching from the beta phase impaired the corrosion resistance of nickel and chromium-containing alloys and extended the life of iron-containing alloys and the Zircaloys.

Subsequent work demonstrated that, if sharp edges and corners where spalling initiates were eliminated, sample lifetimes before the onset of spalling could be greatly increased; an ellipsoidal specimen of Zr - 0.6 w/o Ni still in test has survived 535 days exposure to 900°F (482°C) steam at 1500 psi and has gained 595 mg/cm² with no visible sign of spalling.

This work describes a continuation of the investigation of the corrosion behavior of zirconium alloys in 900°F (482°C) and 1000°F (538°C) steam. Ternary alloys of zirconium with nickel, chromium, and iron were studied.

II. EXPERIMENTAL

Alloys were fabricated with Westinghouse Grade I crystal bar zirconium. Twelve 3-inch diameter, 4 to 5-lb castings were melted by Nuclear Materials and Equipment Corporation, Apollo, Pennsylvania. The alloys were double arc-melted in a vacuum with a consumable electrode. Their nominal compositions and results of chemical analysis are given in Table I.

1. J. Paul Pemsler, "The Corrosion of Zirconium Alloys in 900°F Steam", Report No. NMI-1208 (1958).

The melts were subsequently encased in mild steel containers and hot rolled at 900°C (beta phase) to approximately one-half their original thickness. A single alloy, NC-16, was rolled in the alpha phase at 790°C. Portions of the eleven beta-rolled alloys were rerolled at 790°C in an attempt to regain the alpha structure.

The beta-rolled alloys were wrapped in tantalum foil, sealed in an evacuated quartz tube, and given one of the following heat treatments:

1. one hour at 950°C and furnace cool,
2. one hour at 950°C and water quench,
3. one hour at 950°C and furnace cool, followed by one hour at 800°C and furnace cool, and
4. one hour at 950°C and water quench, followed by one hour at 800°C and furnace cool.

Heat treatments 1 and 2 were designed to affect the size and distribution of second-phase intermetallics present in these alloys, while treatments 3 and 4 tested the effects of a stress-relief anneal (subsequent to cooling through the transformation temperature). The alloys rerolled in the alpha phase were given a further heat treatment:

5. six hours at 800°C and furnace cooled.

To eliminate effects of sharp edges, all samples were machined to spheres. Beta-rolled samples and NC-16 were machined to 1/2-inch diameter spheres; twice-rolled specimens were machined to spheres of about 5/16-inch diameter. Specimens were etched for 2-1/2 minutes in a bath of 50 vol. % concentrated HNO₃, 5 vol % concentrated HF, and 45 vol. % H₂O. Corrosion tests were carried out in dry steam in stainless steel autoclaves at 900°F (482°C) and 1000°F (538°C) steam and 1500 psi. Specimens were examined with a microscope at 45 diameters magnification after each weighing.

III. RESULTS AND DISCUSSION

Table II lists the various rolling conditions and heat treatments the alloys underwent, along with the symbol used to designate this treatment in the results presented in Figs. 1 through 10. As indicated, open

symbols represent corrosion data in 900°F (482°C) steam, and filled symbols represent corrosion in 1000°F (538°C) steam.

All samples of NC-20 showed white oxide after their initial exposure in the corrosion environment. Since these results cannot be explained in terms of the alloy composition, it is assumed that the alloy is contaminated or segregated. The weight gains of sample NC-17 are higher than would be anticipated on the basis of its alloy composition, and this can be traced to a high nitrogen content (92 ppm for NC-17 compared with 25-50 ppm for other samples). For the above reasons, data on NC-17 and NC-20 are not reported.

Even though corrosion data on the remaining ten alloys are as yet incomplete, and only a small number of samples of each alloy have been tested, the following generalizations may be drawn from the data.

A. Zr-Ni-Cr Alloys

Samples of alloy NC-15 exhibited superior corrosion resistance in both 900°F (482°C) and 1000°F (538°C) steam when the beta-rolled alloys were water-quenched from the beta phase compared with samples furnace-cooled from the beta phase. Alloys rerolled in the alpha phase showed corrosion resistance equivalent to that of the water-quenched samples. No change in corrosion resistance was observed when beta-rolled samples were given stress-relief anneals.

Samples of alloy NC-21, furnace cooled from the beta phase, appeared initially to have superior corrosion resistance compared with water-quenched samples. However, after increased exposure to the corrosion environment, a reversal was noted, wherein water-quenched samples exhibited superior corrosion resistance. In 900°F (482°C) steam, samples rerolled in the alpha phase showed poor corrosion resistance, while at 1000°F (538°C) steam, the alpha reroll appeared to be beneficial. In 900°F (482°C) steam, the stress-relief anneal did not change the corrosion behavior of the samples. In 1000°F (538°C) steam, however, the stress-relief anneal benefited water-quenched samples and resulted in spalling of furnace-cooled samples after seventy days.

In samples of alloy NC-43, water-quenching from the beta phase was superior to furnace-cooling from the beta phase as a heat treatment. Re-rolling in the alpha phase, and, apparently, annealing for stress relief, were detrimental to corrosion resistance of these alloys.

In the Zr-Ni-Cr ternary alloys, water-quenching of the beta-rolled material results in superior corrosion behavior compared with furnace-cooling the samples. Re-rolling in the alpha phase does not change the corrosion resistance of alloys with appreciable nickel content, but is detrimental to the resistance of those with low nickel content. Stress-relief anneals do not affect samples with high alloy content, but are detrimental to the resistance of alloys with low nickel and low chromium content.

B. Zr-Ni-Fe Alloys

In sample NC-18, water quenching of beta-rolled alloys from the beta phase resulted in superior corrosion behavior compared with furnace cooling from the beta phase. Re-rolling in the alpha phase was detrimental to the corrosion resistance. Stress-relief anneals were detrimental to corrosion behavior in 900^oF (482^oC) steam and beneficial to corrosion resistance in 1000^oF steam of beta-rolled, water-quenched alloys.

In sample NC-16, all samples were rolled in the alpha phase. Water-quenching, from the beta phase, of the alpha-rolled material resulted in superior corrosion performance compared with that obtained by furnace-cooling from these temperatures. Annealing of samples in the alpha phase resulted in poor corrosion behavior. Stress-relief anneals on the beta-treated material were detrimental to corrosion behavior.

In sample NC-44, water-quenched samples resulted in superior corrosion behavior compared with furnace-cooled samples. Alpha re-rolling was detrimental and stress-relief anneals beneficial to the corrosion behavior of samples water-quenched from the beta phase.

In sample NC-48, water-quenching was again superior to furnace-cooling as a precorrosion treatment for beta-rolled alloys. Alpha re-rolling of samples was detrimental to their corrosion behavior. The stress-relief anneals caused no change in the corrosion behavior of

samples in 900°F (482°C) steam and proved somewhat beneficial to water-quenched samples in 1000°F (538°C) steam.

In Zr-Ni-Fe alloys, water-quenching from the beta phase was superior to furnace-cooling from these temperatures, and alpha rerolling was detrimental to the corrosion behavior of the alloys. The stress-relief anneal was detrimental to the corrosion behavior of high-nickel alloys and beneficial to water-quenched samples of low nickel content.

C. Zr-Fe-Cr Alloys

Samples of NC-47, furnace-cooled from the beta phase, were initially equivalent to water-quenched samples in their corrosion behavior in 900°F (482°C) steam. Upon prolonged exposure, however, furnace-cooled samples exhibited better resistance than water-quenched samples. In 1000°F (538°C) steam, water-quenched samples were more resistant than furnace-cooled samples. Alpha-rerolled samples behaved similarly to water-quenched samples at both temperatures. The stress-relief anneal was detrimental to the corrosion behavior of furnace-cooled samples and did not change the behavior of water-quenched samples in 900°F (482°C) steam. The stress-relief anneal was beneficial to water-quenched samples in 1000°F (538°C) steam.

Samples of alloy NC-28, whether furnace-cooled or water-quenched from the beta phase, or given the additional alpha rolling, exhibited equivalent corrosion resistance in 900°F (482°C) steam. In 1000°F (538°C) steam, however, water-quenched samples exhibited superior resistance compared with furnace-cooled samples. Samples rerolled in the alpha phase are even more corrosion resistant than water-quenched samples. The stress-relief anneal appeared detrimental to the corrosion behavior of water-quenched alloys in 900°F (482°C) steam and beneficial to their behavior in 1000°F (538°C) steam.

In alloy NC-29, samples water-quenched from the beta phase showed superior resistance compared with those furnace-cooled from the beta phase. Rerolling samples in the alpha phase improved their corrosion resistance in 900°F (482°C) steam and did not change their behavior in 1000°F (538°C) steam. No change was noted on stress-relief annealing the samples.

In the Zr-Fe-Cr alloys, those alloys high in both iron and chromium have equivalent corrosion resistance in 900^oF (482^oC) steam whether furnace-cooled or water-quenched from the beta phase, except for the 1 w/o Fe - 1 w/o Cr alloys which, when water-quenched, undergo accelerated corrosion after about seventy days. For beta-rolled alloys with low chromium content, water-quenching from the beta phase is definitely superior to furnace-cooling from the beta phase. Rerolling in the alpha phase resulted in samples with corrosion behavior equivalent to that of the water-quenched samples of alloys rolled in the beta phase. Stress-relief anneals had little effect on improving the corrosion resistance of these Zr-Fe-Cr alloys.

Microscopic examination of the alloys after each weighing revealed that the corrosion process is anisotropic. The thickness of the oxide layer varied greatly from grain to grain in a single sample; some grains still exhibited a black tarnish film while other neighboring grains possessed much thicker glazed oxide, as shown in Fig. 11. Alloys containing iron developed tan oxide on some grains after achieving appreciable weight gains.

Many of the samples developed cracks in the oxide film after prolonged exposure (see Fig. 12), although a considerable number of samples which have undergone corrosion testing up to 180 days show no visible signs of cracking of the oxide. In some cases, it appears that accelerated corrosion follows the appearance of these microcracks, but in other cases no correlation is apparent. Disintegration or spalling did not necessarily follow accelerated corrosion after the appearance of microcracks. Some samples have survived an additional 100 days in 1000^oF steam and still show no evidence of spalling.

On the basis of accumulated exposure to the corrosion environment at the time of writing this paper, it appears that the more resistant alloys will survive for over six months in 1000^oF steam and from one to two years in 900^oF steam.

IV. TABLES AND FIGURESTable IZirconium Ternary Alloy Compositions and Analysis

Alloy	Nominal Composition (w/o)	Analysis of Ingot (w/o)	
		Top	Bottom
NC-15	0.6 Ni	0.67	0.58
	0.3 Cr	0.33	0.35
NC-16	0.6 Ni	0.62	0.76
	0.3 Fe	0.32	0.45
NC-17	0.6 Ni	0.55	0.60
	1.0 Cr	0.97	1.10
NC-18	0.6 Ni	0.54	0.69
	1.0 Fe	1.28	1.05
NC-20	0.6 Ni	0.58	0.61
	0.6 Fe	0.62	0.63
NC-21	1.0 Cr	1.13	1.30
	0.3 Ni	0.33	0.33
NC-28	1.0 Cr		
	0.6 Fe		
NC-29	0.3 Cr		
	0.5 Fe		
NC-43	0.3 Cr		
	0.3 Ni		
NC-44	0.3 Ni		
	0.5 Fe		
NC-47	1.0 Cr		
	1.0 Fe		
NC-48	0.3 Ni		
	1.0 Fe		

Table II

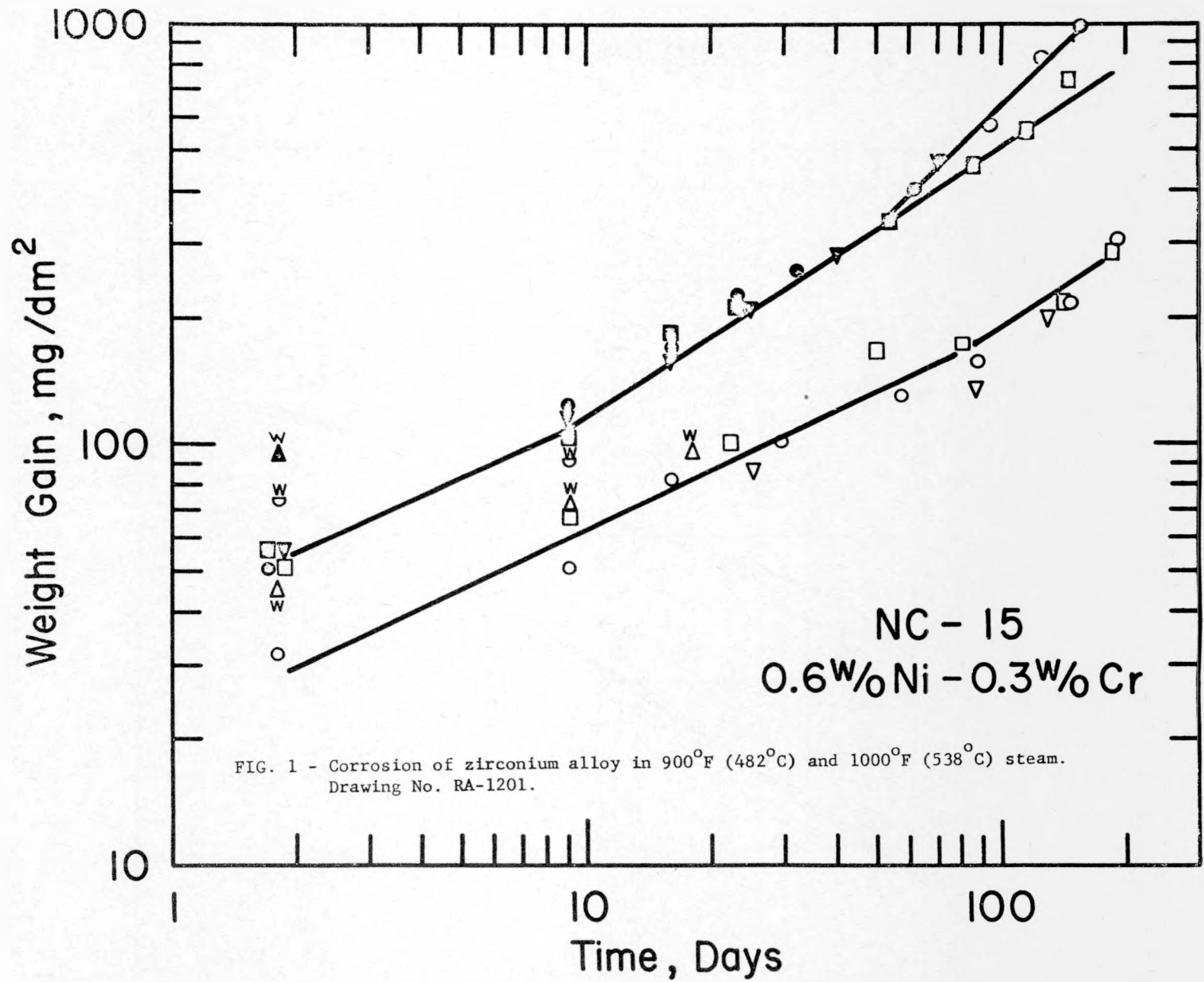
Rolling and Heat Treatment of the Alloys

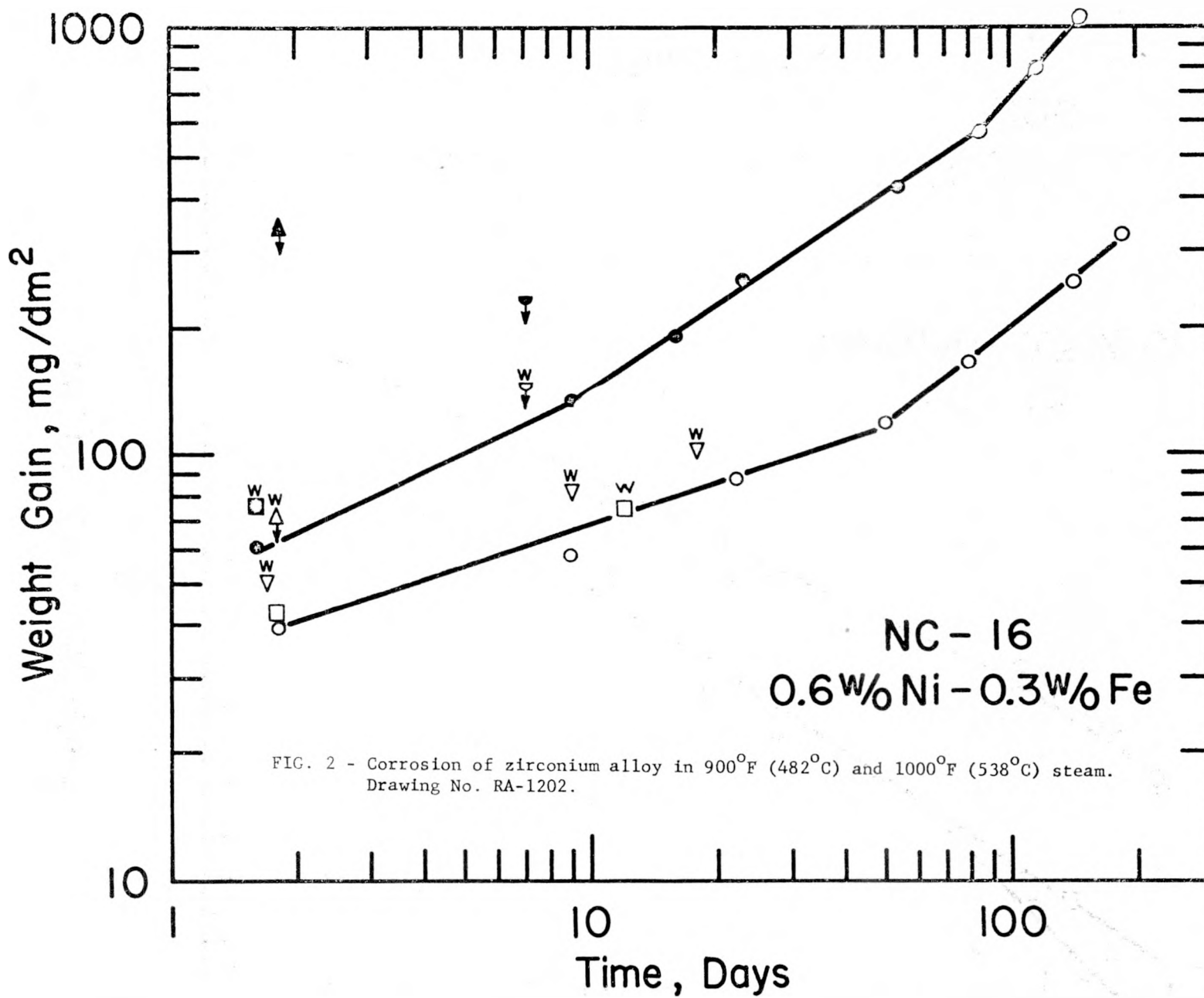
(Refer to Figs 1 through 10)*

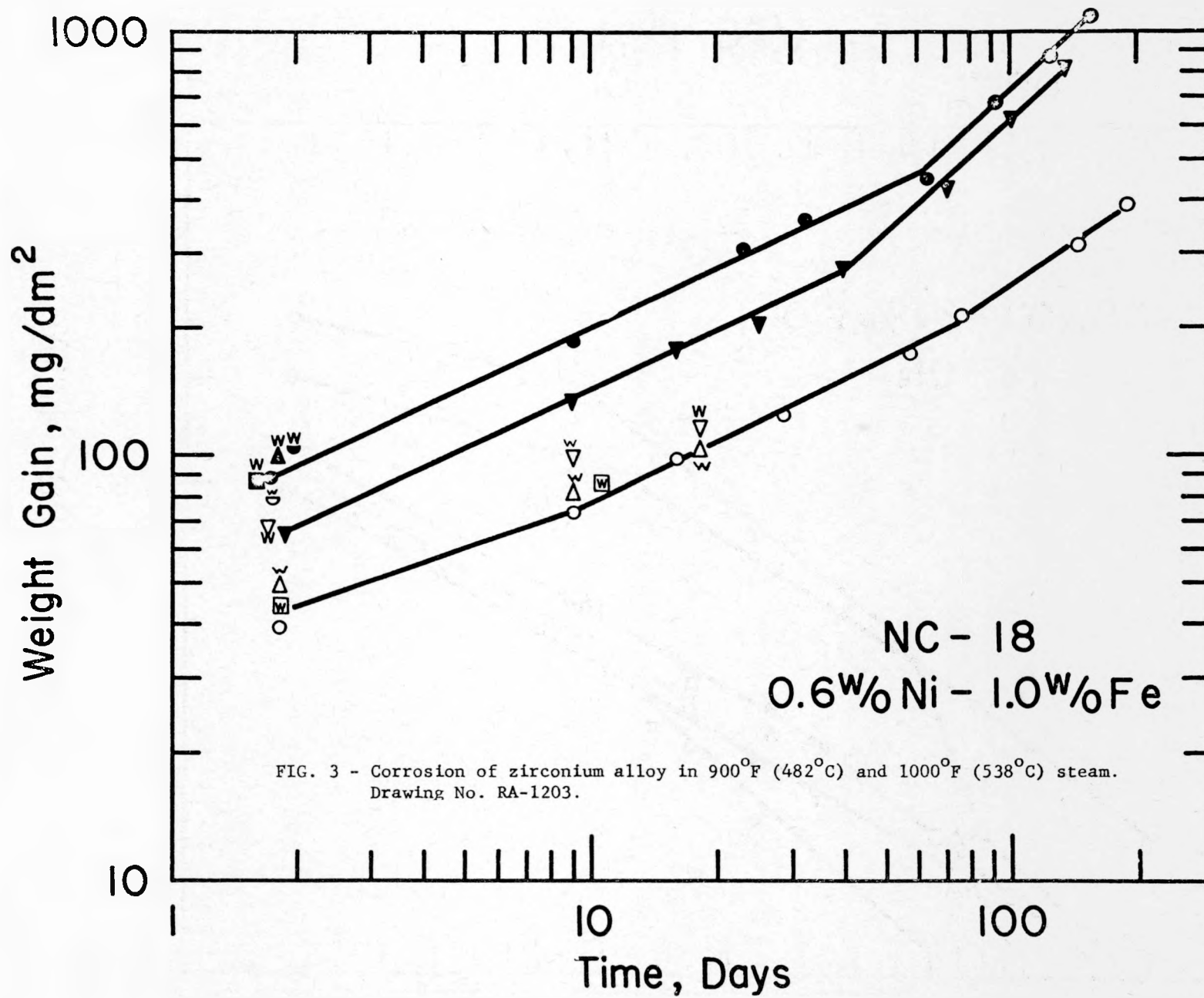
900°F Corrosion Test	1000°F Corrosion Test	Treatment
○	●	Beta rolled; 950°C 1 hr, water-quenched
△	▲	Beta rolled; 950°C 1 hr, furnace-cooled
◐	◑	Beta rolled; 950°C 1 hr, furnace-cooled followed by 1 hr 800°C, furnace-cooled
▽	▼	Beta rolled; 950°C 1 hr, water-quenched followed by 1 hr 800°C, furnace-cooled
□**	■**	Beta rolled; alpha rerolled, 800°C 6 hr, furnace-cooled

* In these figures, the symbol "W" refers to the appearance of white oxide on the sample.

** Except sample NC-16 when it represents 800°C 1 hr, furnace-cooled.







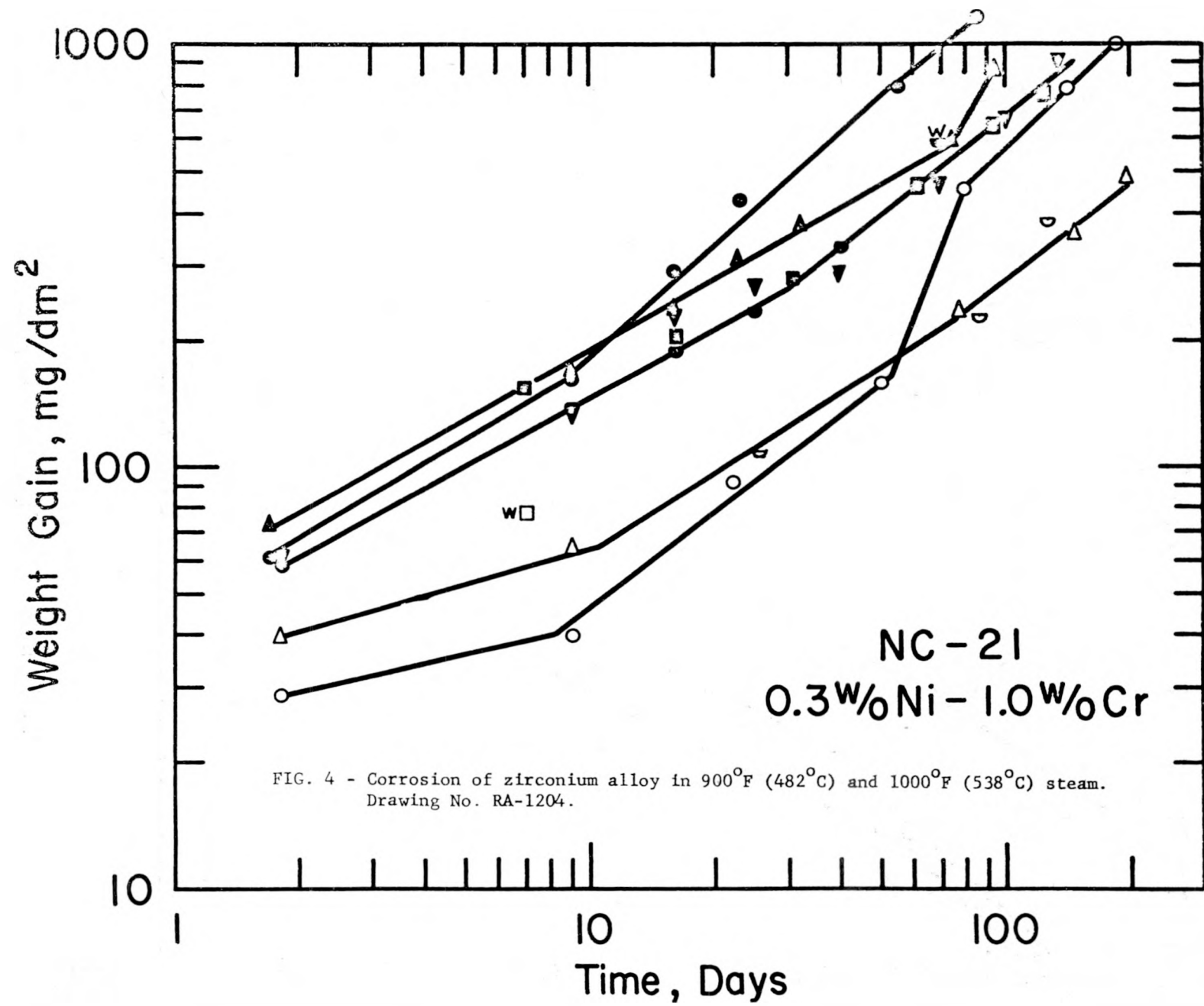
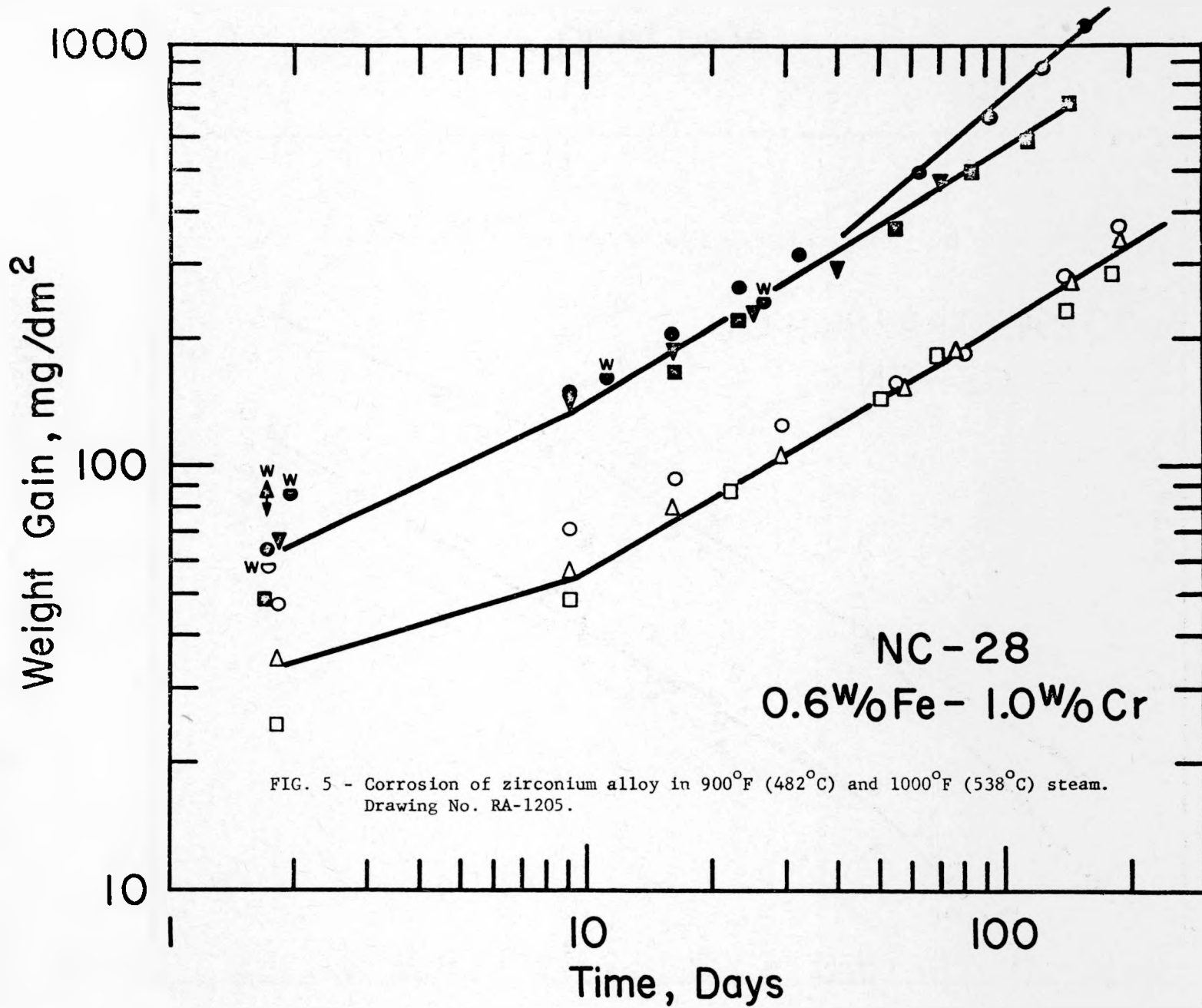
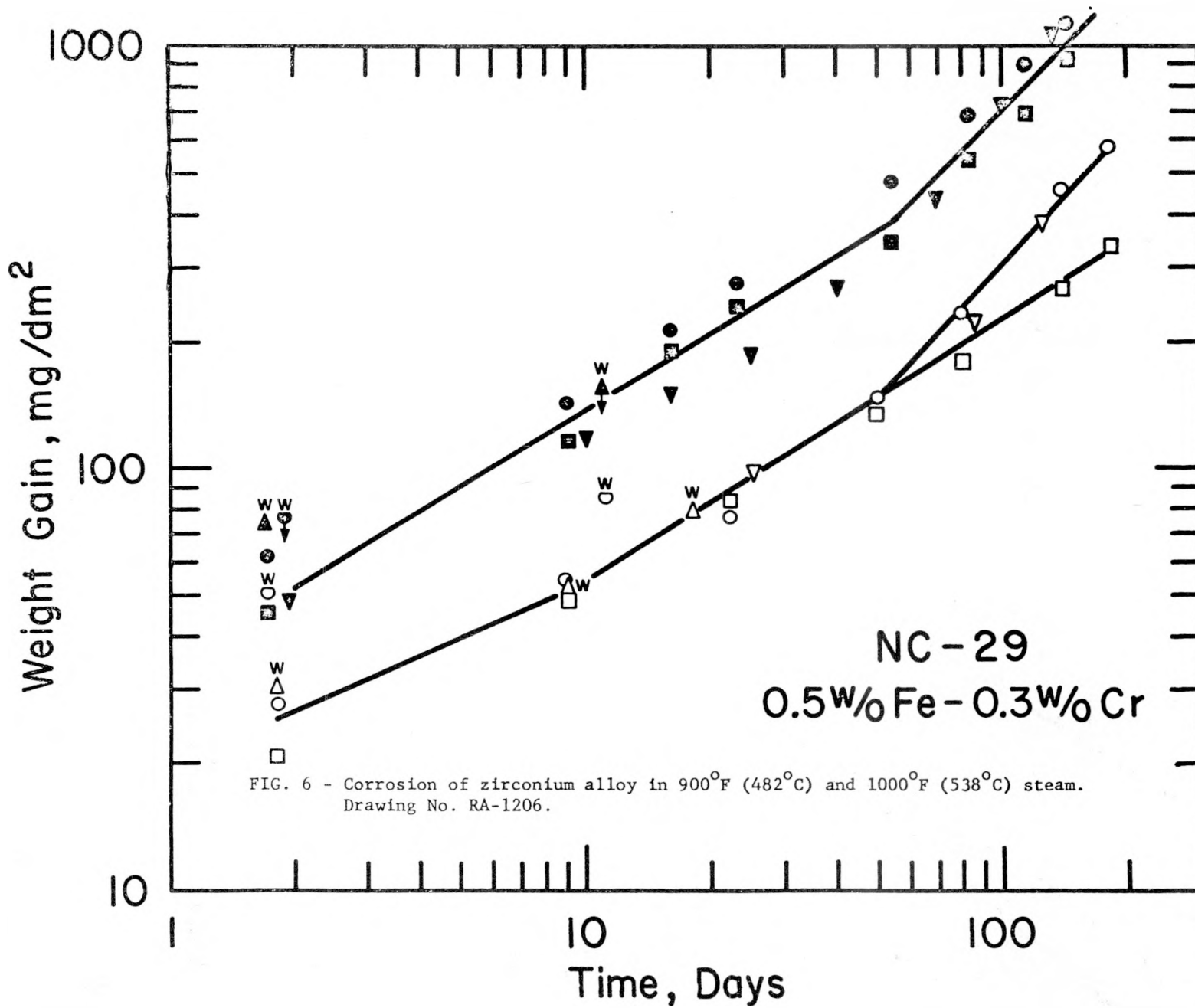


FIG. 4 - Corrosion of zirconium alloy in 900°F (482°C) and 1000°F (538°C) steam.
Drawing No. RA-1204.





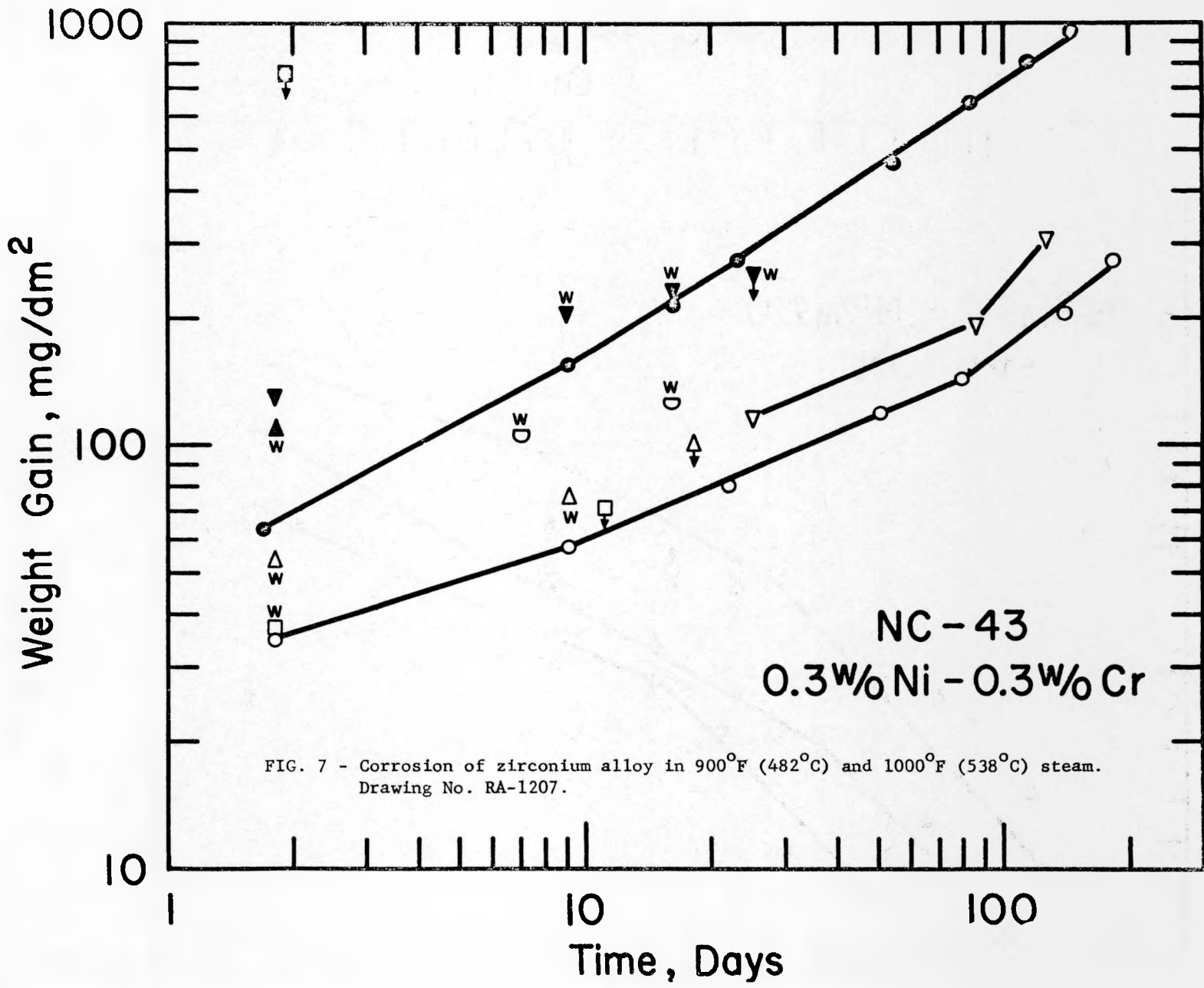
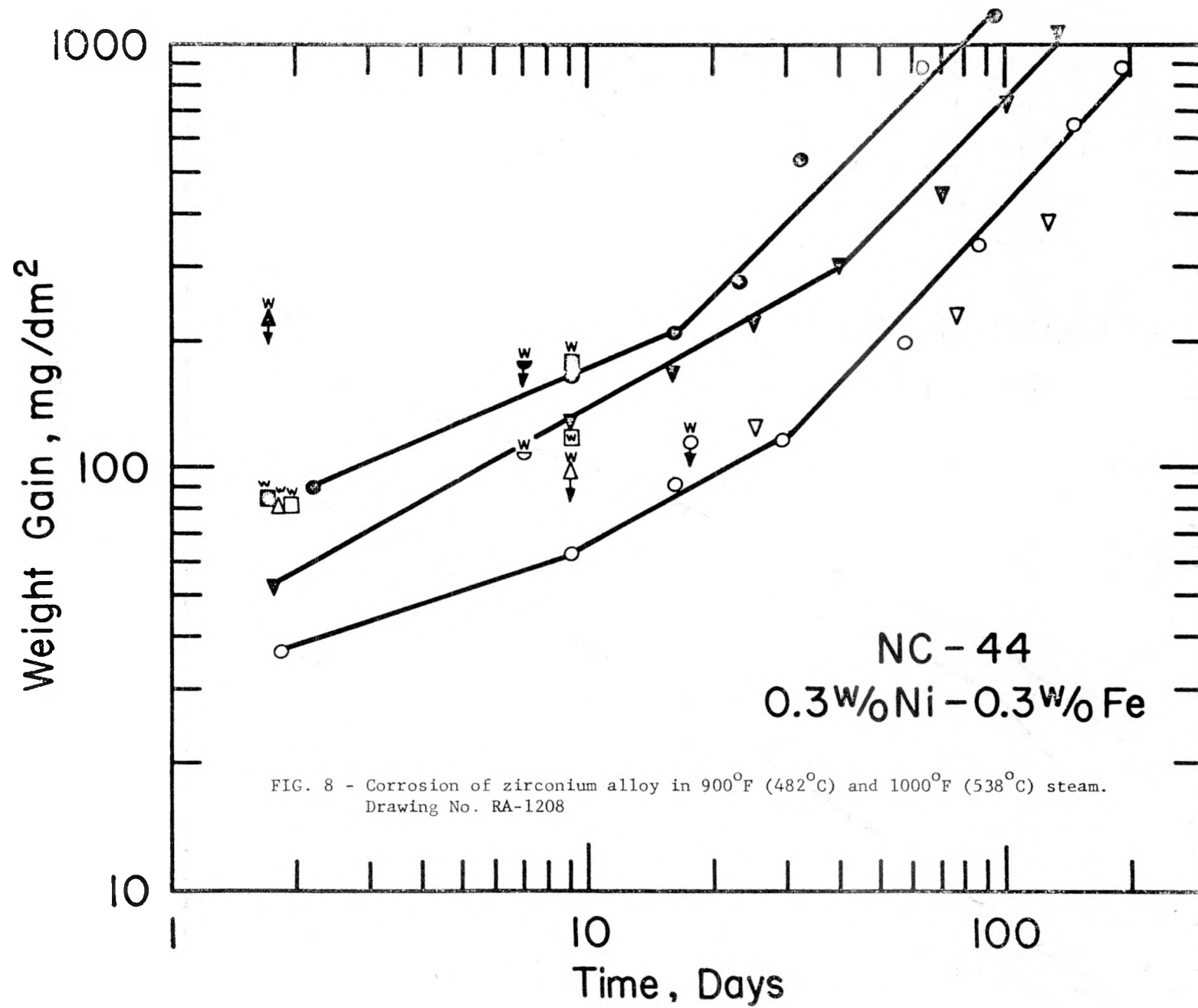
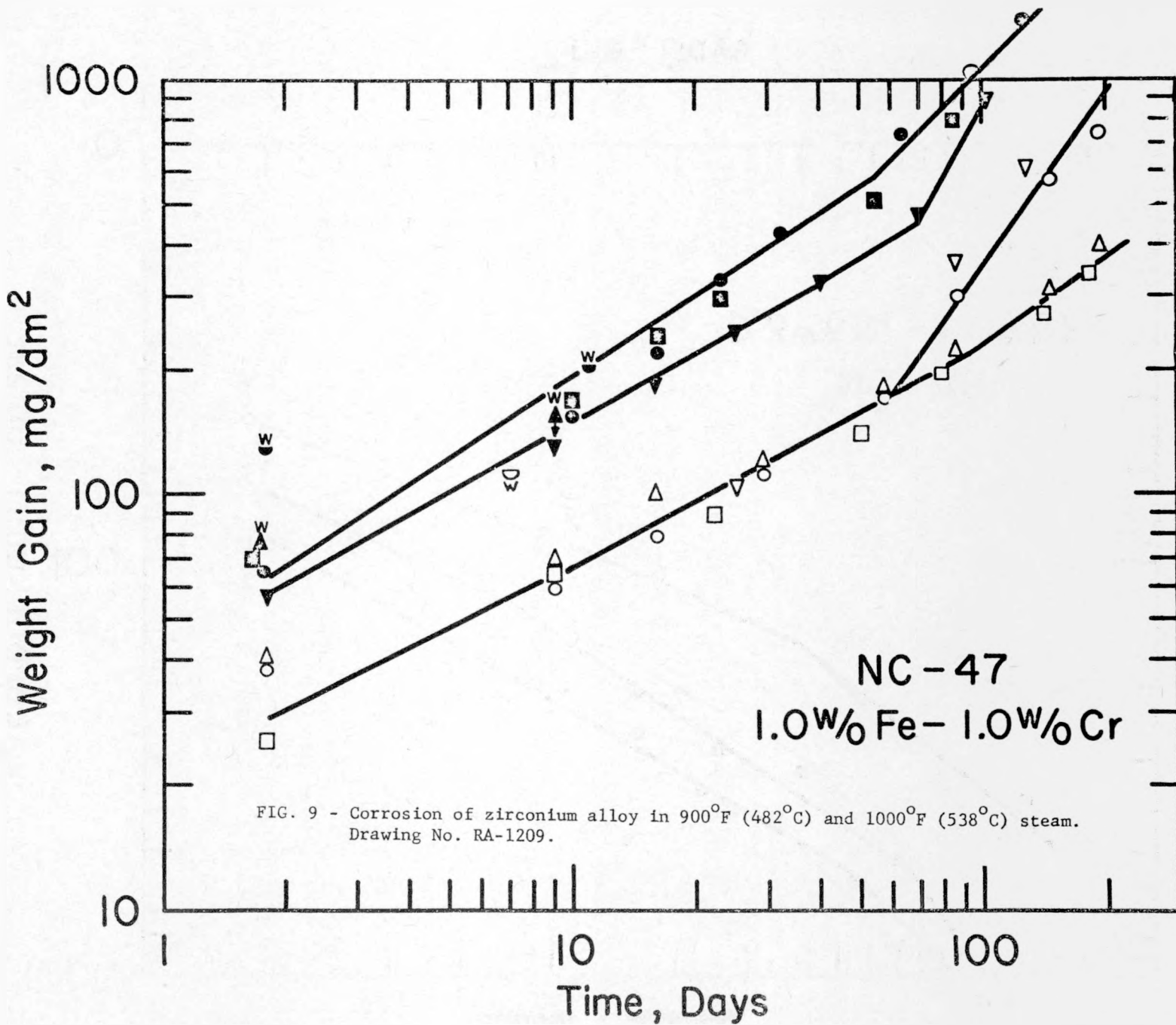
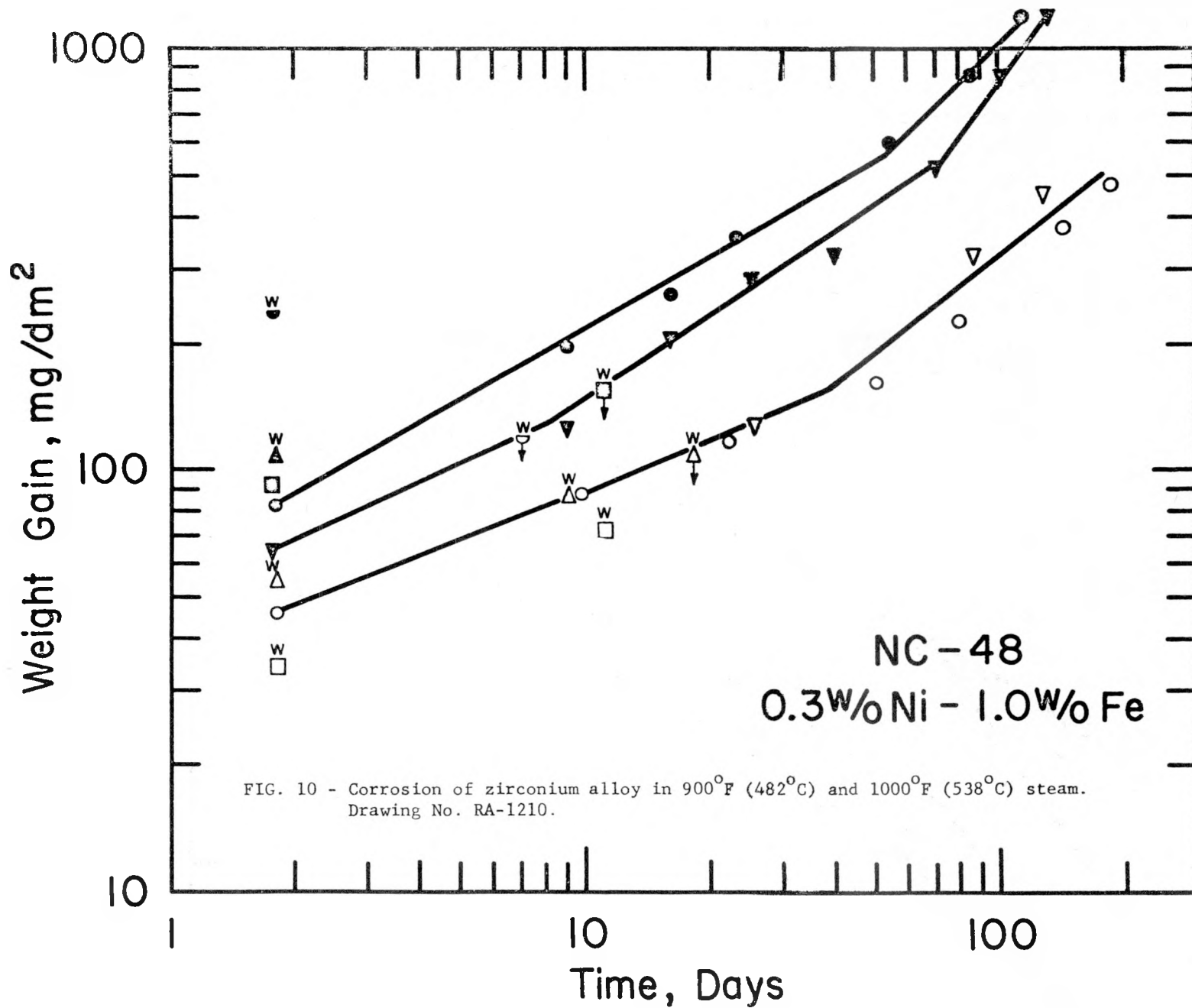
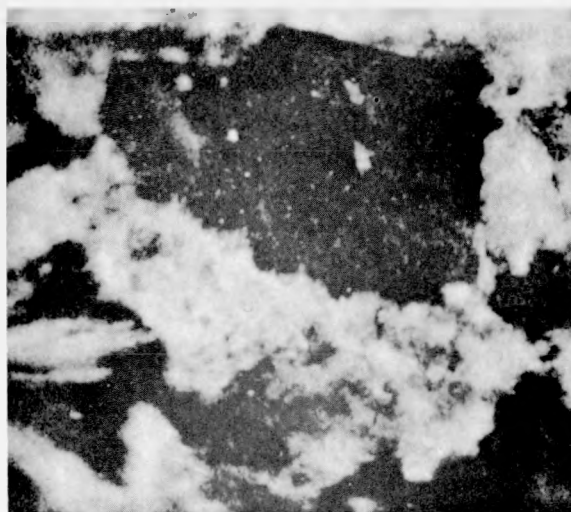


FIG. 7 - Corrosion of zirconium alloy in 900°F (482°C) and 1000°F (538°C) steam.
 Drawing No. RA-1207.









50X

RF-7006

FIG 11 - Anisotropic corrosion of
Sample NC-16 after 182 days
in 900°F (482°C) steam



50X

RF-7001

FIG 12 - Microcracks on sample NC-28
after 155 days in 1000°F (538°C)
steam The thin microcracks are
visible in the center of the pic-
ture; other heavier lines are
grain boundaries