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MINES BRANCH INVESTIGATION REPORT IR 61-31

OBSERVATIONS ON THE CORROSION OF ZIRCONIUM ALLOYS CONTAINING COPPER AND MOLYBDENUM

by

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PHYSICAL METALLURGY DIVISION

COPY NO. 16

APRIL 5, 1961

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SUMMARY OF RESULTS

Zirconium-copper-molybdenum alloys with additions of 0.25 wt% Sn and 0.25 wt% Fe were corrosion tested at 400°C (750°F) and 1500 psi.

The addition of the Sn and Fe had no beneficial effects on the corrosion resistance but quenching the alloys from the $\alpha + \beta$ phase region caused a change in the corrosion behaviour and greatly decreased the hydrogen pick-up during corrosion.

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INTRODUCTION

A program to study zirconium-base alloys containing 1.0 to 2.0 wt% copper with 1.5 to 2.5 wt% molybdenum for possible use in natural uranium fueled power reactors is being conducted in these laboratories. As part of this program a series of alloys was prepared for corrosion testing in steam at 400°C (750°F) and 1500 psi.

Additions of 0.25 wt% tin and 0.25 wt% iron were made to some Zr-Cu-Mo alloys and the corrosion behaviour of these alloys after heat treating at 750°C (1380°F) and 850°C (1560°F) was studied.

PROCEDURE

Preparation of Alloys

The materials used for preparing the alloys are listed in Table 1.

TABLE 1

MATERIALS USED

Material	Purity	Source
Zirconium Sponge	Reactor Grade	Carborundum Metals Co.
Copper	99.99%	OFHC
Molybdenum	99.5%	Sylvania Electric Products Inst.
Tin	99.98%	Vulcan's Electrolytic (Chempur)
Iron	99.9%	A. D. MacKay Inc. (Electro)

The alloys listed in Table 2 were prepared as 75 gram buttons by arc melting in an argon atmosphere using a tungsten electrode and a cold copper hearth. Loose zirconium sponge pieces were first melted in a 2¼ inch circular mould to convert from sponge to solid metal buttons, then the copper, molybdenum, tin and iron were added in one remelting operation followed by at least two remelts to insure homogeneity. The last two melts were made in a "cigar"-shaped cavity which produced an ingot (approximately 1/2 inch diameter and 3 inches long) suitable for swaging.

TABLE 2

ANALYSES OF MELTS

Melt	Mo	Cu	Fe	Sn	N_2
CE	1.96	1.27	-	-	0.002
BN	1.47	1.02	0.32	-	<0.001
BP	1.41	1.02	0.29	0.23	<0.001
BQ	1.53	1.57	-	0.25	<0.001
BR	1.49	1.54	0.28	-	<0.001
BZ	1.50	1.51	0.28	0.23	<0.001

Test Methods

The cigar -shaped ingots were hot swaged in air at 800°C (1470°F) into 0.35 inch diameter rods which were heated for 1 hour in Houghton 980 salt at 750°C (1380°F) and 850°C (1560°F), then quenched in water.

Corrosion samples $\frac{1}{4}$ inch in diameter and $\frac{3}{4}$ inch long were machined from the swaged rods. These samples were tested in an autoclave in steam at 400°C (750°F) and 1500 psi. They were removed periodically for weighing and the water changed after each weighing.

On completion of the corrosion tests, hydrogen determinations, X-ray analyses and metallographic examinations were done on the corroded samples. To put the hydrogen in solution and to remove hydride needles from the microstructure, the corroded samples were heated to 400°C (750°F) and then quenched in water.

Grain structures were revealed by electro-polishing in a solution containing 50 ml perchloric acid, 175 ml acetic acid and 100 ml ethylene glycol.

RESULTS

Corrosion

The graphs in Figures 1 to 6 (time vs weight gain) are the results of corrosion tests on the alloys in Table 2. The alloy CE contained no iron or tin and when heat treated at 750°C (1380°F) exhibited a high rate of corrosion (Figure 1).

Additions of iron and tin to the Zr-Cu-Mo alloys examined did not lower the corrosion rate (Figures 2 to 6). When the alloys were heat treated at 850°C (1560°F) their corrosion behaviour changed. The rate before breakaway was higher, but the rate after breakaway was lower than for the samples heat treated at 750°C (1380°F).

Samples heat treated at 750°C (1380°F) exhibited a white or grey corrosion film on first examination after 130 hours of testing. The film showed very little evidence of spalling after 1000 hours of testing for all the samples except those of alloy BN. The film on these samples spalled after 130 hours, consequently the testing of such specimens was terminated. This applied to any of the samples on which spalling was observed when examined.

On the first examination after 130 hours of testing, the samples heat treated at 850°C (1560°F) had developed a mottled appearance with the light and dark areas resembling a grain structure. The corrosion film showed some evidence of spalling on a few samples during testing and appeared to be caused by the formation of cracks chiefly at the boundaries between the light and dark areas. Figure 7 is a photograph of this film on a specimen of alloy BZ after 1000 hours of corrosion testing. Figure 8 is an electro-polished longitudinal section of the same sample. The microstructure of this sample after it had been quenched from 400°C (750°F) to remove the hydride needles is shown in Figure 9. A fine grain structure can be seen within the larger areas.

The thicknesses of the corrosion films on the samples heat treated at 750°C (1380°F) and 850°C (1560°F) were 0.0052 inches and 0.0037 inches respectively. These samples were selected for examination because they were typical of the other alloys and the corrosion film was adherent after 1000 hours in both conditions of heat treatment.

Hydrogen Pick-Up

The hydrogen content of samples of alloy BZ heat treated at 750°C (1380°F) increased from 50 ppm before corrosion testing to 730 ppm after 1000 hours of testing. This corresponds to 28% of the stoichiometric hydrogen released during corrosion. The hydrogen content of the same alloy heat treated at 850°C (1560°F) increased from 100 ppm before corrosion testing to 200 ppm after corrosion testing for 1000 hours. This represents only 8% of the hydrogen released.

Samples of alloy BR were also analysed for hydrogen and showed similar results. Hydrogen picked up on corrosion by samples of this alloy heat treated at 750°C (1380°F) was 32% of the available hydrogen as compared to 11% for the samples heat treated at 850°C (1560°F)

Alloy Structure

X-ray analyses of samples of alloy BZ heat treated at 750°C (1380°F) and before corrosion testing showed the presence of α, ω, Zr_2Cu and $ZrMo_2$ phases. Figure 10 is a photomicrograph of this structure. X-ray analysis after corrosion testing for 1000 hours showed the presence of α, Zr_2Cu and $ZrMo_2$ phases.

X-ray analysis of the same alloy heat treated at 850°C (1560°F) before corrosion testing showed only the α' phase but photomicrographs of this structure (Figure 11) shows some equilibrium α. The lines of the α phase on X-ray analysis were overshadowed by broad diffused lines of the α' phase. Figure 11 also shows the outline of a coarse grain structure.

X-ray analysis by diffraction and microbeam techniques of the corroded samples of alloy BZ heat treated at 850°C (1560°F) showed a random orientated α phase in a matrix of β and ω phases which had similar orientations within the light and dark areas.

DISCUSSION

The corrosion rates of the alloys examined were approximately ten times greater than that of zircaloy-2 tested at the same temperature and pressure (1) and the additions of tin and iron had no effect on reducing this. Varying the heat treatment, however, did affect the corrosion rate as well as the type of corrosion film formed and also reduced the amount of hydrogen absorbed during corrosion.

Corrosion

The structure of the alloys heat treated at 750°C (1380°F) and before corrosion testing consisted of α, ω, Zr_2Cu and $ZrMo_2$ phases. On ageing during corrosion the ω disappeared and the structure consisted of α, Zr_2Cu and $ZrMo_2$ phases.

The grey corrosion film on these samples was similar to the film usually associated with post-transition corrosion of zirconium alloys.

The structure of samples heat treated at 850°C (1560°F) and before corrosion testing, indicated that the samples were quenched from the $\alpha + \beta$ phase region. The equilibrium α phase existing at this temperature remained on quenching and the β phase transformed martensitically into α'. During corrosion testing the samples evidently aged, X-ray analysis showing that the structure transformed from $\alpha' + \alpha$ to $\alpha + \beta + \omega$

This structure was made up of groups of grains and it is possible that these groups were the outline of the β grains that had been present when the samples were originally heated to 850°C (1560°F).

The α phase that was formed during the ageing had random orientation but the β and ω formed from the α' had similar orientations within each group of grains.

It appears that the β and ω phases had anisotropic corrosion properties which resulted in each group of grains corroding at a rate depending on their particular orientation. Some groups with a high corrosion rate proceeded to transition rapidly and formed a white film while other groups having β and ω grains with different orientations had a lower corrosion rate and formed black films.

The cracks which occurred between the light and dark areas can be explained as being caused by stresses resulting from the different rate of film growth on adjacent groups of grains.

Hydrogen Pick-Up

The hydrogen pick-up for the alloys heat treated at 750°C (1380°F) was what might be expected during the corrosion of zirconium alloys at 400°C (750°F) and 1500 psi. Zircaloy-2 under these conditions will absorb in the order of 20% to 45% (2) of the hydrogen produced by the corrosion reaction.

Berry et al (3) suggest that the hydrogen absorbed in zirconium alloys during corrosion is that which is produced in the corrosion reaction, and Mallett and Albrecht (4), show the corrosion reaction takes place at the metal oxide interface. It is suggested from the results of the present investigation that in the alloys heat treated at 750°C (1380°F), second phase intermetallic particles dissolved this hydrogen formed at the metal surface and acted as diffusion paths. This theory is postulated by Berry et al (3) for zirconium alloys containing nickel.

The samples heat treated at 750°C (1380°F) may have contained other intermetallic compounds in addition to Zr_2Cu and $ZrMo_2$ but in amounts too small to be detected by X-ray diffraction. It is reasonable to expect the tin and iron and any residual elements might combine with zirconium as well as with each other to form intermetallic compounds.

Not all intermetallics would be diffusion pathways for hydrogen. In fact Berry et al (3) showed that antimony, chromium or iron in zirconium decreased the hydrogen pick-up during corrosion. However, in the alloys examined in this investigation those intermetallic compounds that acted as diffusion pathways apparently exhibited the greater influence.

When the samples were quenched from 850°C (1560°F) the alloying elements were retained in solid solution thus removing these diffusion pathways and a greater proportion of the hydrogen produced during corrosion diffused into the outer environment or, as in the case with the corrosion of high purity crystal bar zirconium, formed a hydride layer at the metal oxide interface.(3)

Because the hydrogen content was determined after "breakaway" there may have been some micro-spalling of the films that was not noticed. This would effect the calculation of the available hydrogen produced by the corrosion reaction. If the film did spall there would be more hydrogen available than was calculated from the weight gains so the percentage absorbed would be lower. However, it was the film on the samples heat treated at 850°C (1560°F) that showed the greatest tendency to spall, so the difference in hydrogen pick-up appears to be real and any micro-spalling, if it occurred, would make the difference still greater.

CONCLUSIONS

1. The alloys examined have a high corrosion rate in steam at 400°C (750°F) and 1500 psi.
2. Additions of iron and tin in the Zr-Cu-Mo alloys examined had no beneficial effect on the corrosion rate.
3. Samples heat treated at 750°C (1380°F) corroded as would be expected of zirconium alloys and the amount of hydrogen pick-up was also typical.
4. Quenching from the $\alpha+\beta$ phase region at 850°C (1560°F) reduced the hydrogen pick-up to as low as 8% of the hydrogen produced in the corrosion reaction. This was associated with the absence of intermetallic compounds in the structure of the samples quenched from 850°C (1560°F)
5. Quenching from 850°C (1560°F) also caused a change in the corrosion behaviour and resulted in the formation of a mottled corrosion film which may have been caused by the anisotropic corrosion properties of the β and ω phases.

ACKNOWLEDGEMENT

This work was performed under the general direction of Mr. N. S. Spence, Head of the Nuclear Metallurgy Section.

The production of alloy melts, heat treatment, preparation of metallographic specimens and corrosion testing were performed by W. Hutchirgs and W. Koops. X-ray diffraction examinations were done by Mrs. S. J. Basinski, Metal Physics Section, whose assistance in interpreting the data, is acknowledged.

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CFD/gm

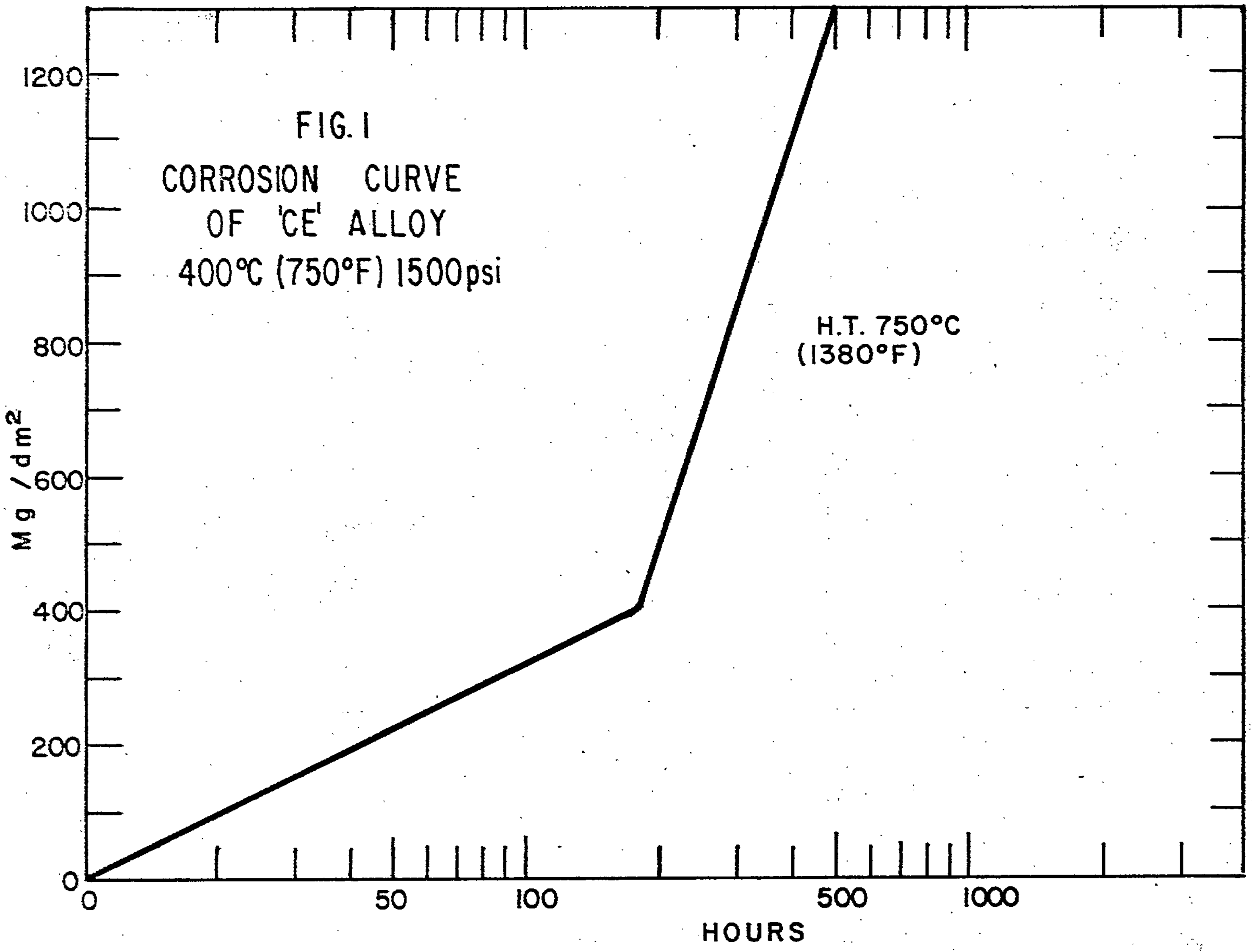


FIG. I

CORROSION CURVE OF 'CE' ALLOY 400°C (750°F) 1500psi

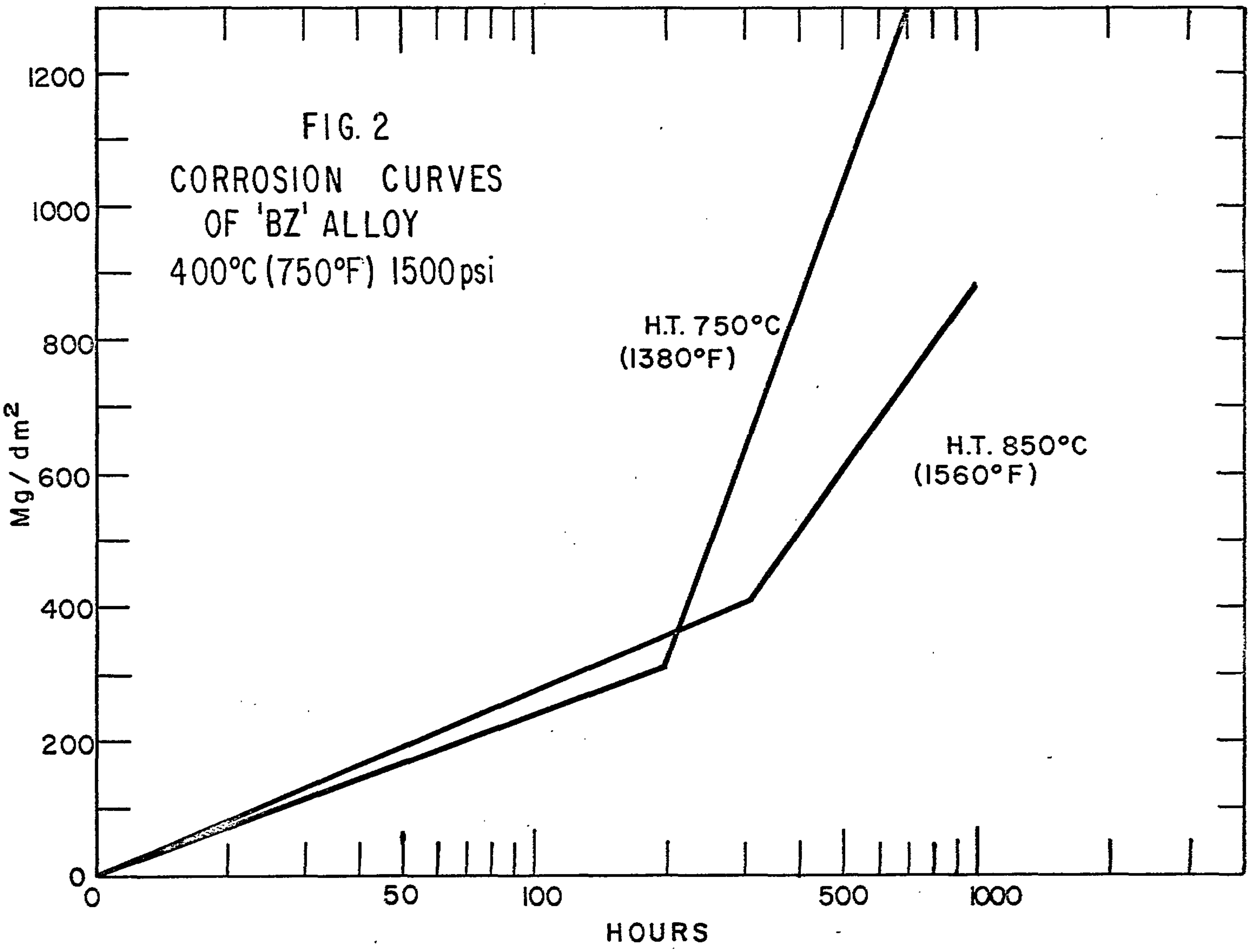


FIG. 2

CORROSION CURVES OF 'BZ' ALLOY

400°C (750°F) 1500 psi

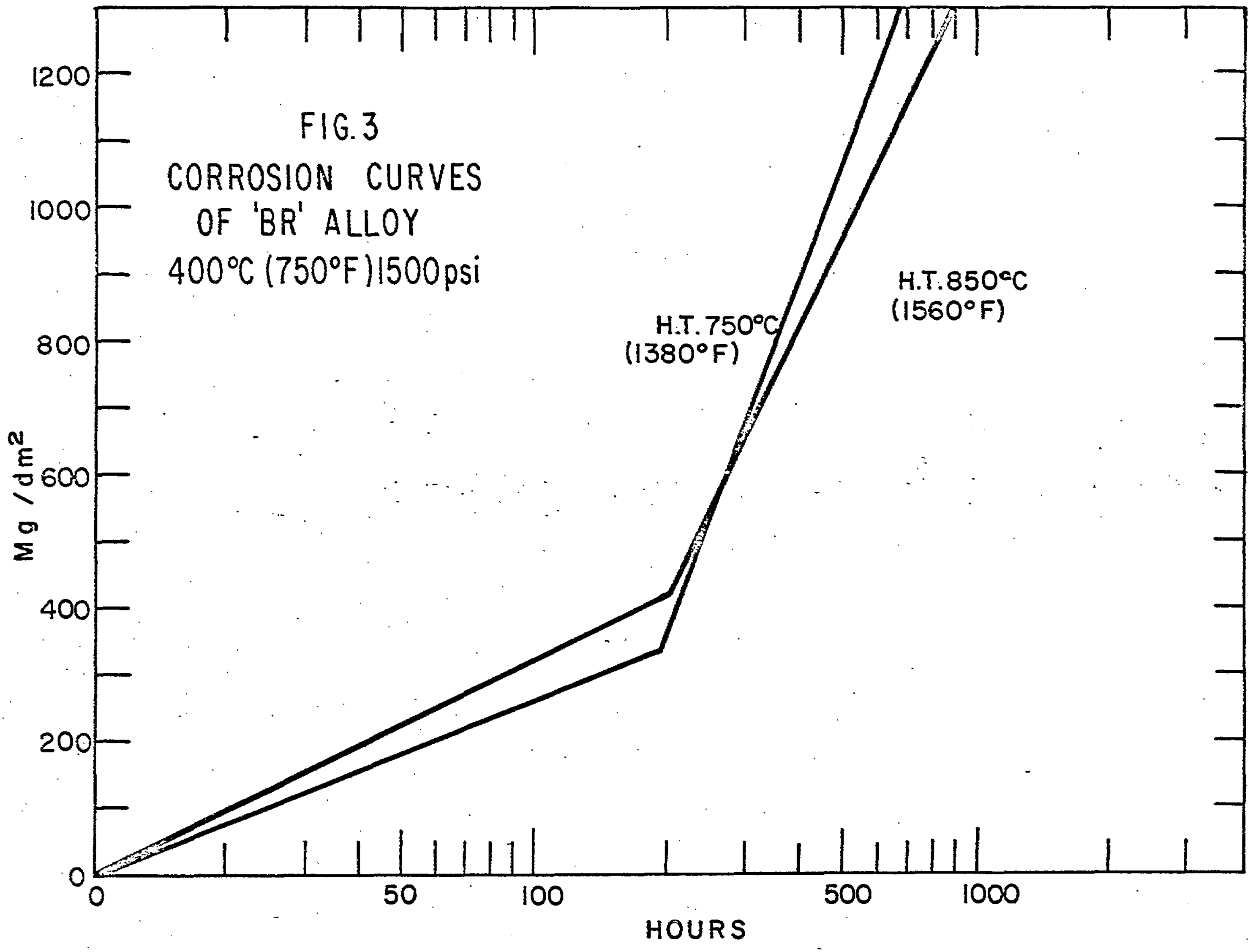


FIG. 3
CORROSION CURVES
OF 'BR' ALLOY
400°C (750°F) 1500 psi

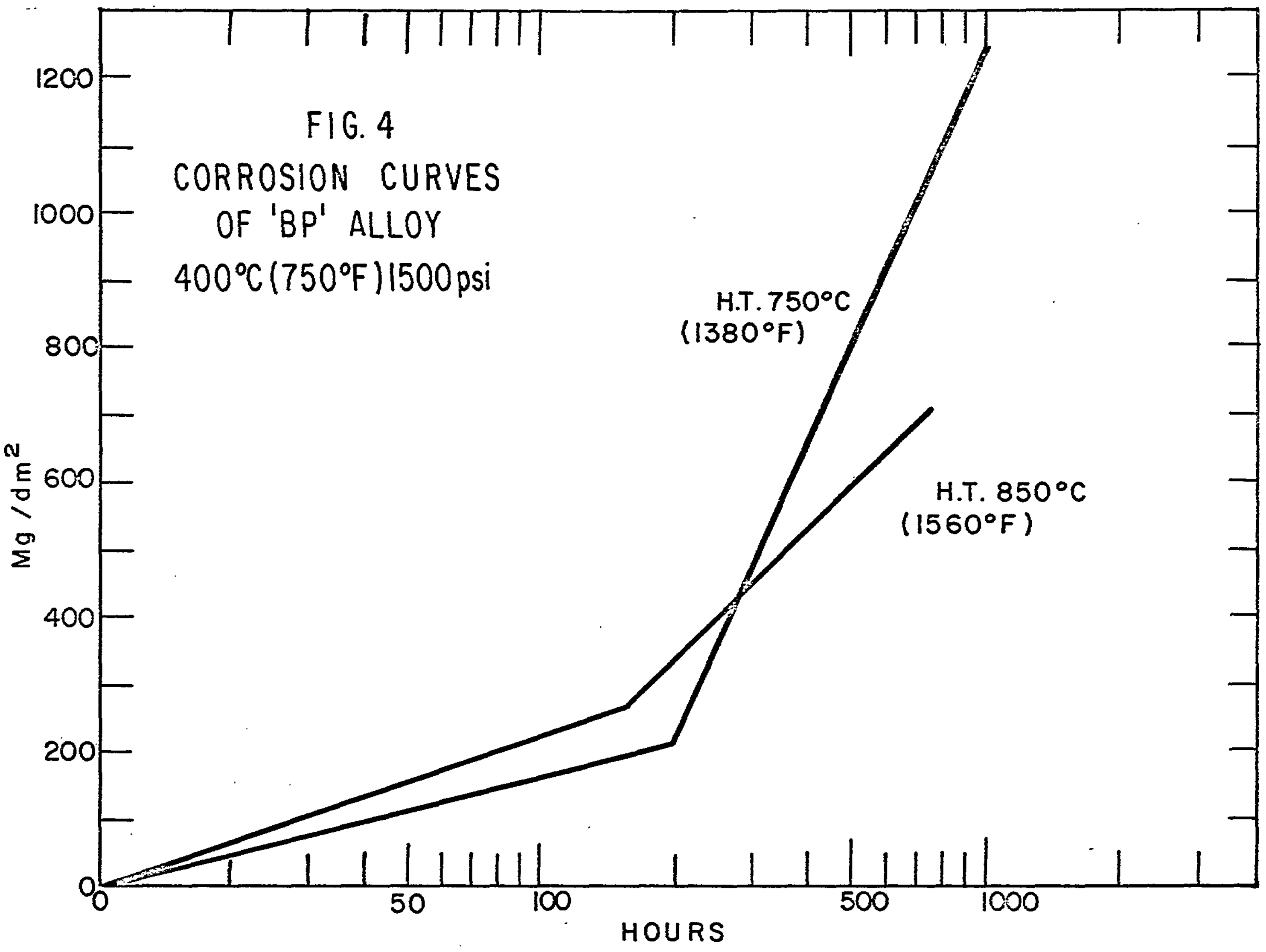


FIG. 4
CORROSION CURVES
OF 'BP' ALLOY
400°C (750°F) 1500 psi

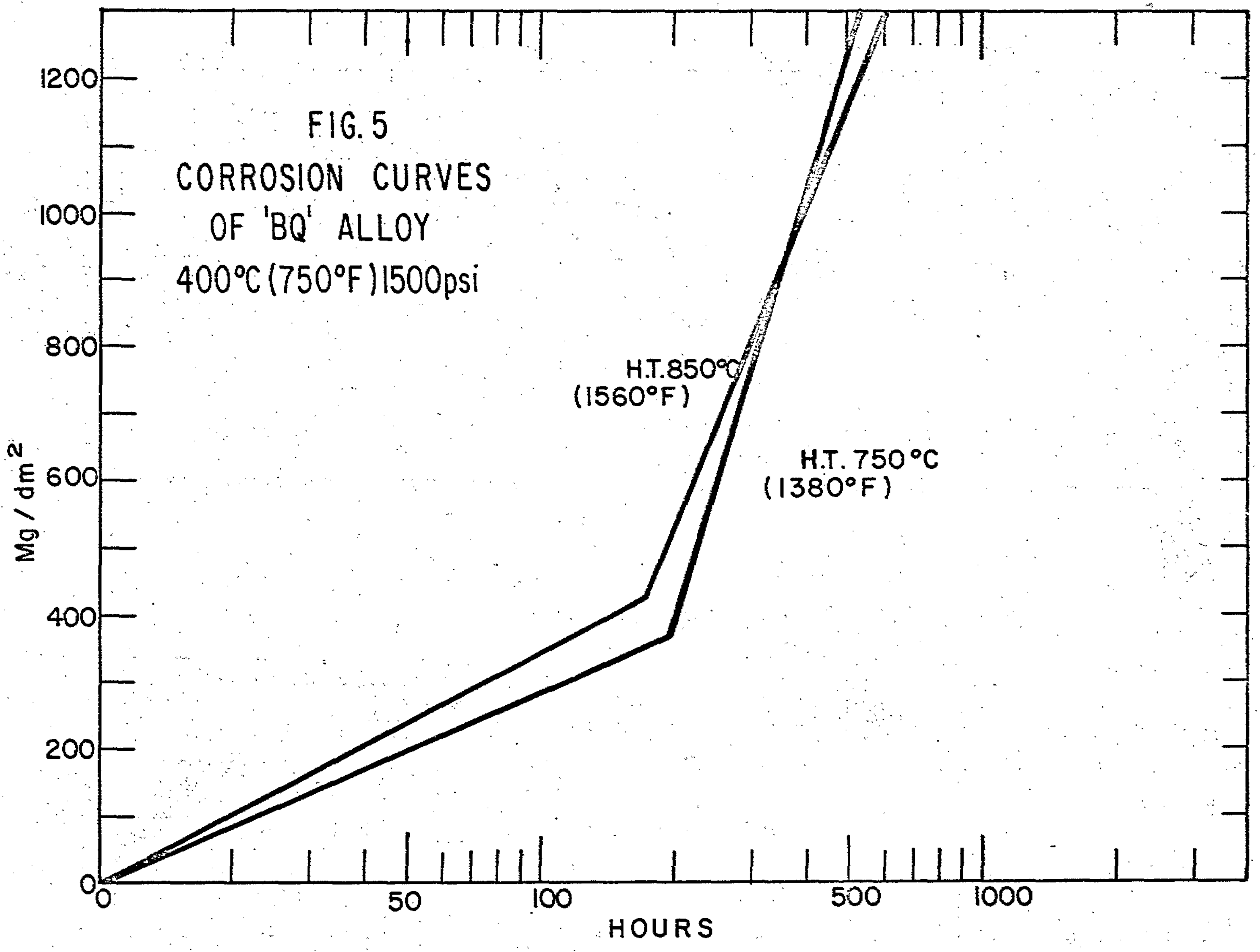


FIG. 5
CORROSION CURVES
OF 'BQ' ALLOY
400°C (750°F) 1500psi

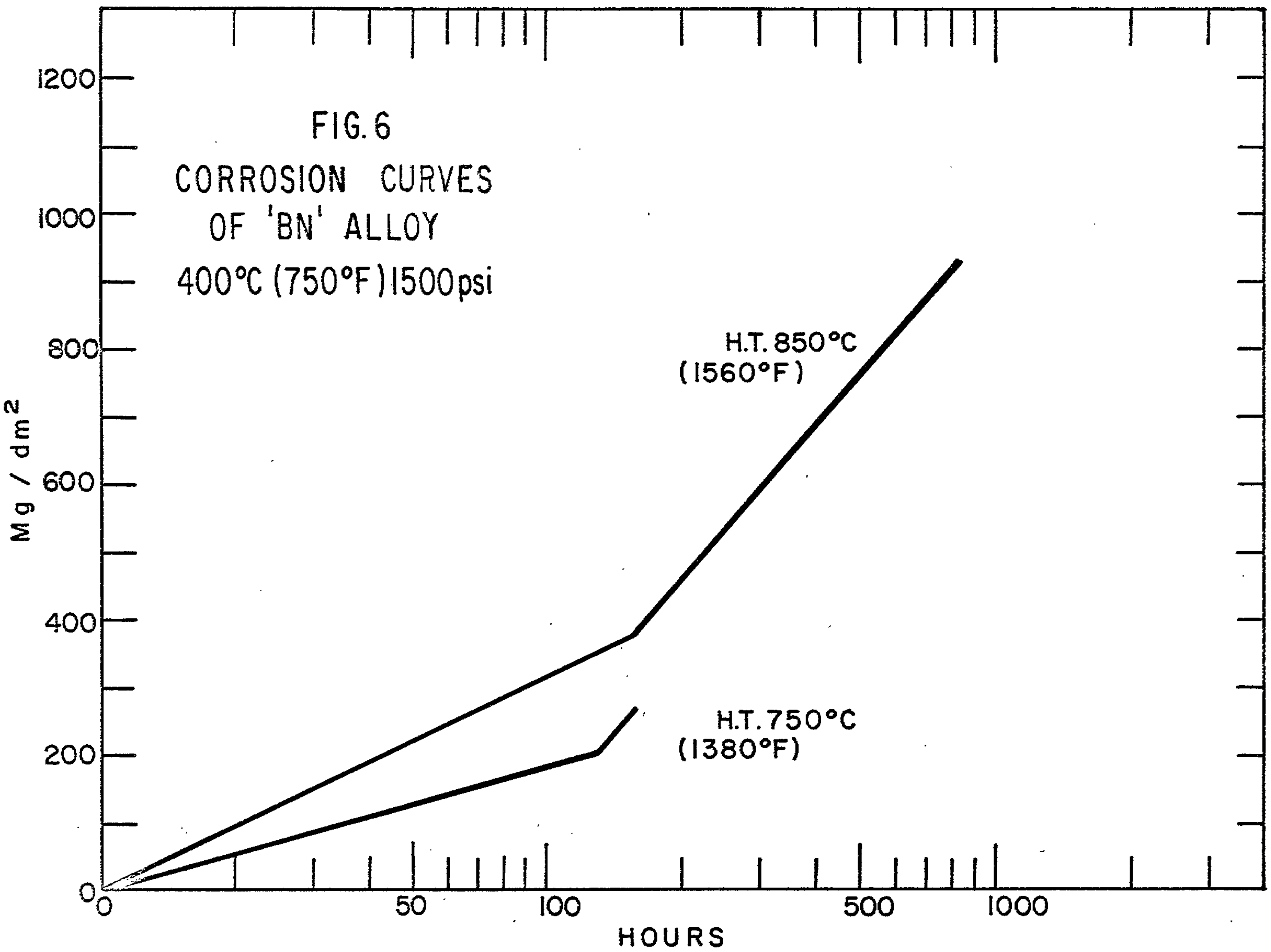


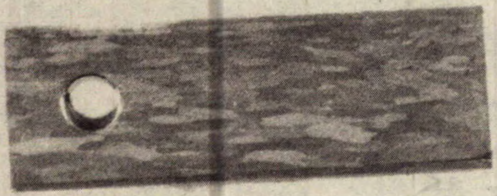
FIG. 6

CORROSION CURVES OF 'BN' ALLOY

400°C (750°F) 1500psi

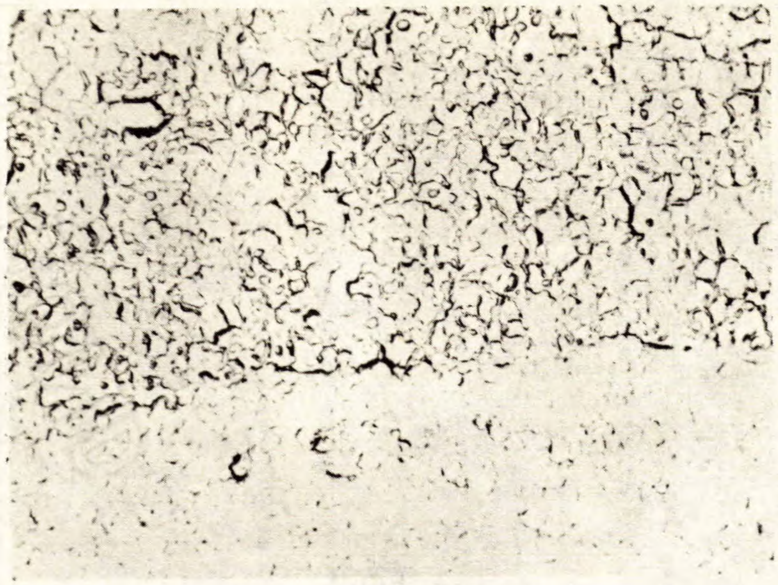
(3X)

Figure 7 - BZ Alloy
Heat Treated 850°C (1560°F)
Corrosion Film
1000 Hours 400°C (750°F) 1500 psi.



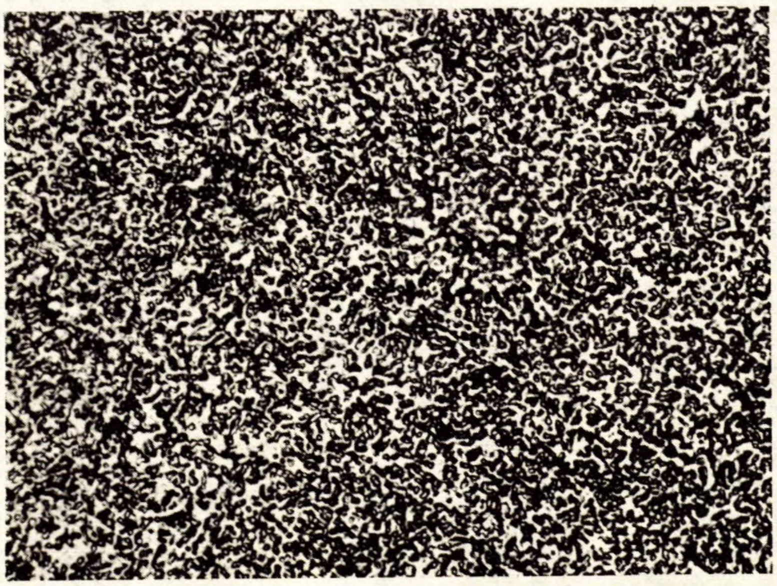
(3X)

Figure 8 - BZ Alloy
Heat Treated 850°C (1560°F)
Longitudinal Section
1000 Hours 400°C (750°F) 1500 psi
Electro-Polished



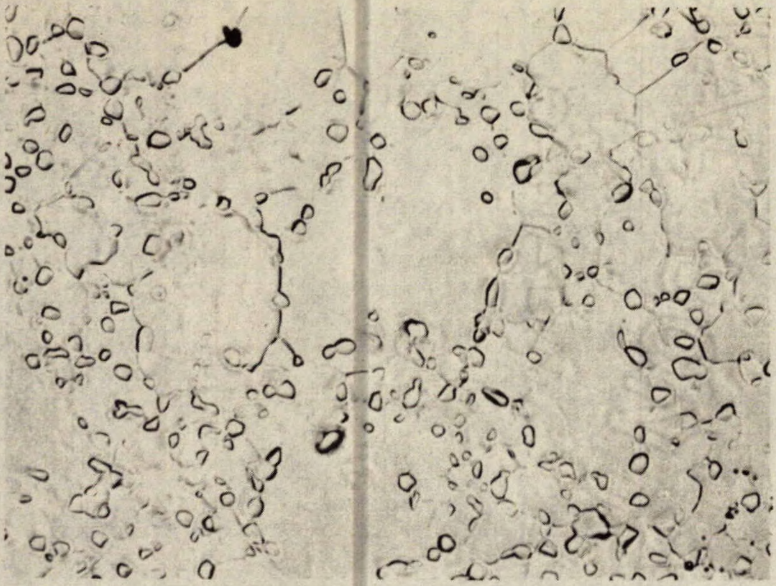
(750X)

Figure 9 - BZ Alloy
Heat Treated 850°C (1560°F)
Corrosion Tested 1000 Hrs.
Longitudinal Section, Electro-Polished



(750X)

Figure 10 - BZ Alloy
Heat Treated 750°C (1380°F)
Cross Section, Electro-Polished



(750X)

Figure 11 - BZ Alloy
Heat Treated 850°C (1560°F)
Cross Section, Electro-Polished