CANADA

EFFECT OF HEAT TREATMENT ON THE CORROSION BEHAVIOUR OF TWO ZIRCONIUM-COPPER-MOLYBDENUM ALLOYS

C. F. DIXON AND H. M. SKELLY

EPARTMENT OF MINES AND
CHNICAL SURVEYS, OTTAWA

PHYSICAL METALLURGY DIVISION

MINES BRANCH

RESEARCH REPORT

R 183

Price 50¢

MARCH 1966

Available by mail from the Queen's Printer, Ottawa,
and at the following Canadian Government bookshops:

OTTAWA
Daly Building, Corner Mackenzie and Rideau

TORONTO
Mackenzie Building, 36 Adelaide St. East

MONTREAL
Aeterna-Vie Building, 1182 St. Catherine St. West

or through your bookseller

A deposit copy of this publication is also available
for reference in public libraries across Canada

Price 50 cents Cat. No. M38 -1/183

Price subject to change without notice

ROGER DUHAMEL, F.R.S.C.
Queen's Printer and Controller of Stationery
Ottawa, Canada
1966

Mines Branch Research Report R 183

EFFECT OF HEAT TREATMENT ON THE CORROSION BEHAVIOUR OF TWO ZIRCONIUM-COPPER-MOLYBDENUM ALLOYS

by

C.F. Dixon* and H.M. Skelly**

- - - - - -

ABSTRACT

The effect of heat treatment on the corrosion properties of Zr-1.0% Cu-1.5% Mo and Zr-0.5% Cu-0.5% Mo alloys was investigated.

The heat treatment found to give optimum corrosion resistance in steam was, for the Zr-1.0% Cu-1.5% Mo alloy, 1000°C (1830°F) for one hour, then water quench, followed by ageing at 500°C (930°F) for 32 hours; and, for the Zr-0.5% Cu-0.5% Mo alloy, 1000°C (1830°F) for one hour, water quench, then age at 500°C (930°F) for 24 hours.

Over-ageing of the alloys resulted in growth of the intermetallic phase particles, which then caused cracking of the corrosion film.

Preparation of an experimental alloy, namely Zr-3.0% Cu-4.5% Mo, which contained a larger percentage of the intermetallic phase, made it possible to identify, by X-ray diffraction methods, that phase as being a cubic structure with a unit cell of 4.999 A.

---

* Scientific Officer and ** Senior Scientific Officer, Nuclear and Powder Metallurgy Section, Physical Metallurgy Division, Mines Branch, Department of Mines and Technical Surveys, Ottawa, Canada.

Direction des mines

Rapport de recherches R 183

EFFET DU TRAITEMENT THERMIQUE SUR LA RÉSISTANCE À LA CORROSION DE DEUX ALLIAGES DE ZIRCONIUM-CUIVRE-MOLYBDÈNE

par

C. F. Dixon* et H. M. Skelly**

- - - - -

RÉSUMÉ

Les auteurs ont étudié l'effet du traitement thermique sur la résistance à la corrosion de deux alliages à composition suivante: Zr-1.0%Cu-1.5%Mo, et Zr-0.5%Cu-0.5%Mo.

Pour l'alliage Zr-1.0%Cu-1.5%Mo, le traitement thermique qui a donné la meilleure résistance à la corrosion dans la vapeur a consisté à le maintenir à 1,000°C (1830°F) pendant une heure, puis de lui faire subir la trempe dans l'eau, suivie d'un vieillissement à 500°C (930°F) pendant 32 heures; pour l'alliage Zr-0.5%Cu-0.5%Mo, le maintien à 1,000°C (1830°F) pendant une heure, la trempe dans l'eau, et le vieillissement à 500°C (930°F) pendant 24 heures.

Le survieillissement des alliages a donné lieu à la croissance des particules de la phase intermétallique, ce qui a causé le fendillement du film de corrosion.

L'emploi d'un alliage expérimental, Zr-3.0%Cu-4.5%Mo, comptant une plus forte proportion de phase intermétallique a permis de reconnaître, par la diffraction aux rayons-x, que cette phase est de réseau cubique ayant une arête de 4.999 A.

---

*Agent scientifique et **agent scientifique senior, section de la métallurgie nucléaire et des poudres, Division de la métallurgie physique, Direction des mines, ministère des Mines et des Relevés techniques, Ottawa, Canada.

CONTENTS

	Page
Abstract	i
Résumé	ii
1. Introduction	1
2. Experimental Procedure	1
2.1 Alloy Preparation	1
2.2 Heat Treatment	2
2.3 Corrosion Testing	3
2.4 Corrosion Film Studies	3
2.4 X-ray Diffraction Analysis	3
3. Experimental Results	3
3.1 Corrosion Testing	3
3.2 Corrosion Film Studies	4
3.3 X-ray Diffraction Analysis	4
4. Discussion	5
4.1 Corrosion	5
4.2 Corrosion Film Examination	6
5. Conclusions	7
6. Acknowledgements	7
7. References	8
Figures 1-11	9-13

= =

TABLES

Page

No.

1. Materials Used 1

2. Arc Furnace Melts 2

FIGURES

1. Corrosion of Zr-1.0% Cu-1.5% Mo Alloy. Weight Gain After Corrosion Testing 400 Hours Vs. Ageing Time at 500°C (930°F) 9

2. Corrosion of Zr-0.5% Cu-0.5% Mo Alloy. Weight Gain After Corrosion Testing 330 Hours Vs. Ageing Time at 500°C (930°F) 10

3. Zr-0.5% Cu-0.5% Mo. H.T. 1000°C (1830°F), W.Q.; as-polished 11

4. Zr-0.5% Cu-0.5% Mo. H.T. 1000°C (1830°F), W.Q.; aged 8 hr at 500°C (930°F); as-polished 11

5. Zr-0.5% Cu-0.5% Mo. H.T. 1000°C (1830°F), W.Q.; aged 24 hr at 500°C (930°F); as-polished 11

6. Zr-0.5% Cu-0.5% Mo. H.T. 1000°C (1830°F), W.Q.; aged 100 hr at 500°C (930°F); as-polished 11

7. Zr-0.5% Cu-0.5% Mo. Annealed 700°C (1290°F); as-polished . . 12

8. Zr-0.5% Cu-0.5% Mo. H.T. 1000°C (1830°F), W.Q.; corrosion-tested 24 hr. 12

9. Zr-0.5% Cu-0.5% Mo. H.T. 1000°C (1830°F), W.Q.; aged 24 hr at 500°C (930°F); corrosion-tested 24 hr. 12

10. Zr-0.5% Cu-0.5% Mo. H.T. 1000°C (1830°F), W.Q.; aged 100 hr at 500°C (930°F); corrosion-tested 24 hr. 12

11. Zr-0.5% Cu-0.5% Mo. Annealed 1 hr 700°C (1290°F); corrosion-tested 24 hr. 13

1. INTRODUCTION

A program for the development of zirconium alloys for nuclear applications is being carried out in the Nuclear and Powder Metallurgy Section of the Physical Metallurgy Division of the Mines Branch, in Ottawa. Previous work in this program has shown that, for some zirconium alloys containing copper and molybdenum, there is considerable variation in the mechanical properties, the hydrogen pick-up and the corrosion behaviour, depending on the heat treatment applied [1].

The present report describes an investigation that was made to determine the heat treatments necessary for optimum corrosion resistance for Zr-1.0% Cu-1.5% Mo and Zr-0.5% Cu-0.5% Mo alloys in steam at 400 C° (750°F) and 1500 psi. The corrosion films that formed on the Zr-0.5% Cu-0.5% Mo alloy when in various heat-treated conditions were also examined. In an attempt to identify the intermetallic phase in these alloys, a Zr-3.0% Cu-4.5% Mo alloy was prepared and examined by X-ray diffraction.

2. EXPERIMENTAL PROCEDURE

2.1 Alloy Preparation

The materials used to prepare the alloys are listed in Table 1.

TABLE 1

Materials Used

Metal	Purity	Source
Zirconium Sponge	Reactor grade	Carborundum Metals Co.,
Copper	99.99%	American Metals Climax Inc.,
Molybdenum	99.5 %	Sylvania Electric Products Inc.,

The alloys were prepared in a laboratory-size, tungsten-arc furnace in which the metal charge was melted by striking an arc between a tungsten electrode and the charge contained in a water-cooled copper hearth. Melting was carried out in an argon atmosphere at a pressure of 350 mm mercury and each alloy was remelted four times to ensure homogeneity. The resultant ingot was cigar-shaped and weighed about 75 grams.

Table 2 lists the alloys that were prepared in the arc furnace. In addition to these laboratory-prepared alloys, tests were also carried out on Zr-1.0% Cu-1.5% Mo alloy sheet material obtained from Imperial Chemical Industries Limited (I.C.I.), Birmingham, England.

TABLE 2

Arc Furnace Melts

Melt Ident.	Composition (wt. %)		
	Cu	Mo	Zr
FN	0.5	0.5	Remainder
FM	0.5	0.5	"
FL	1.0	1.5	"
KU	3.0	4.5	"

The cigar-shaped ingots from melts FN and FM (both Zr-0.5% Cu-0.5% Mo) and melt FL (Zr-1.0% Cu-1.5% Mo) were hot-swaged in air at 700°C (1290°F) to rods of 0.35 in. diameter. The swaged rods from melts FN and FL were hot-rolled at 700°C (1290°F) to 0.20 in. thickness.

2.2 Heat Treatment

The rolled bars of the Zr-0.5% Cu-0.5% Mo and Zr-1.0% Cu-1.5% Mo alloys, the swaged rod of the Zr-0.5% Cu-0.5% Mo alloy, and the I.C.I. sheet material (Zr-1.0% Cu-1.5% Mo) were all vacuum-sealed in quartz, heated at 1000°C (1830°F) for one hour, and water-quenched; the alloys were then aged in air at 500°C (930°F) for times of up to 100 hours. The Zr-3.0% Cu-4.5% Mo alloy ingot was heat-treated in a similar manner, but aged for periods of 24 and 100

hours. In addition, a sample of the swaged Zr-0.5% Cu-0.5% Mo alloy was annealed at 700°C (1290°F) for one hour, sealed under vacuum in quartz.

2.3 Corrosion Testing

Corrosion specimens, 1 in. x 5/16 in. x 5/64 in., for weight gain determinations, were machined from the heat-treated, rolled bars of the Zr-0.5% Cu-0.5% Mo and Zr-1.0% Cu-1.5% Mo alloys and from the heat-treated samples of the I.C.I. sheet material (Zr-1.0% Cu-1.5% Mo alloy). The corrosion specimens were tested in an autoclave in steam at 400°C (750°F) and 1500 psi, and were removed periodically for weighing. The water was changed after each weighing.

2.4 Corrosion Film Studies

For corrosion film studies, specimens one inch in length were cut from the heat-treated, swaged rods of the Zr-0.5% Cu-0.5% Mo alloy. One end of each specimen was polished, first on silicon carbide paper to 600 grit and then with Linde "A" compound on microcloth. This was followed by chemical polishing in a solution containing 45 parts nitric acid, 45 parts distilled water, and 8 to 10 parts hydrofluoric acid. Electron micrographs were taken of the as-polished surfaces of specimens of the Zr-0.5% Cu-0.5% Mo alloy in the following conditions: (a) water-quenched after one hour at 1000°C (1830°F); (b) aged at 500°C (930°F) for 8, 24 and 100 hours; and (c) annealed at 700°C (1290°F) for one hour. Electron micrographs were also taken of the corrosion film on all the above specimens, after corrosion testing for 1, 8, 24 and 100 hours.

2.5 X-ray Diffraction Analysis

To identify the intermetallics, X-ray diffraction analyses were carried out on as-polished surfaces of the Zr-0.5% Cu-0.5% Mo, Zr-1.0% Cu-1.5% Mo and Zr-3.0% Cu-4.5% Mo alloys after quenching from 1000°C (1830°F), and also after quenching from 1000°C (1830°F) followed by ageing at 500°C (930°F) for 24 hours and 100 hours.

3. EXPERIMENTAL RESULTS

3.1 Corrosion Testing

The results of corrosion-testing the Zr-1.0% Cu-1.5% Mo and Zr-0.5% Cu-0.5% Mo alloys are shown in Figures 1 and 2, which are plots of weight gain versus time of ageing at 500°C (930°F).

Figure 1 gives the corrosion results for the Zr-1.0% Cu-1.5% Mo alloy (both the laboratory-prepared alloy and the I.C.I. sheet material). From this graph it can be seen that the weight gain due to corrosion varies considerably with ageing time, being large for specimens aged for one hour and 88 hours, and at a minimum of 40 mg/dm^2 for specimens aged for 32 hours.

The corrosion results plotted in Figure 2 show that the weight gains for the Zr-0.5% Cu-0.5% Mo alloy were also related to ageing time, with large weight gains being recorded for specimens aged for one hour and 70 hours, and a minimum (50 mg/dm^2) occurring with an ageing time of 24 hours.

3.2 Corrosion Film Studies

Electron micrographs of the as-polished ends of the swaged specimens of the Zr-0.5% Cu-0.5% Mo alloy, after ageing for 0, 8, 24 and 100 hours and after annealing, are shown in Figures 3, 4, 5, 6 and 7, respectively. From Figure 3 it can be seen that there were very few intermetallics in the specimen quenched from 1000°C (1830°F). Also, as ageing proceeded, the size of the intermetallic particles increased continuously and their number increased initially and then decreased (compare Figures 3, 4, 5 and 6). The annealed specimens exhibited the largest intermetallics (Figure 7).

As corrosion proceeded, the zirconium oxide corrosion film remained adherent on the specimens quenched from 1000°C (1830°F) and on the specimens aged for 24 hours, both of which contained fine intermetallics (see Figures 8 and 9, respectively). However, in the case of the specimens containing large intermetallics, i.e., those aged for 100 hours (Figure 6) and those annealed (Figure 7), the corrosion film broke up as a result of cracking around the intermetallics, as shown in Figures 10 and 11 respectively.

3.3 X-ray Diffraction Analysis

X-ray diffraction analysis of the Zr-0.5% Cu-0.5% Mo and Zr-1.0% Cu-1.5% Mo alloys showed the presence of alpha-zirconium only; but analysis of the Zr-3.0% Cu-4.5% Mo alloy showed, in addition to the alpha-zirconium, lines that were tentatively identified as a cubic phase with spacings as follows:

hkl	d(A)
111	2.883
200	2.499
220	1.767
222	1.443
420	1.118
422	1.020

The above values were the same for specimens of the Zr-3% Cu-4.5% Mo alloy aged for 24 hours and 100 hours, but the lines were not present in specimens quenched from 1000°C (1830°F).

4. DISCUSSION

4.1 Corrosion

In a previous report [1] it was shown that the corrosion behaviour of the Zr-1.0% Cu-1.5% Mo alloy varied with the heat treatment. The present investigation has determined more precisely the heat treatment that gives the optimum corrosion resistance; namely, heating at 1000°C (1830°F) for one hour, followed by water-quenching and then ageing at 500°C (930°F) for 32 hours. Figure 1 shows that the weight gain varies by a factor of 20, depending on the ageing time.

The present work also shows that the corrosion behaviour of the Zr-0.5% Cu-0.5% Mo alloy varies with heat treatment, and that a minimum weight gain for this alloy is obtained after ageing at 500°C (930°F) for 24 hours.

In both the Zr-1.0% Cu-1.5% Mo and Zr-0.5% Cu-0.5% Mo alloys, the improvement in corrosion resistance with ageing time is reversed after

an optimum ageing time is reached.

The short corrosion times (400 hours and 330 hours) used in determining the curves in Figures 1 and 2 were found necessary because the corrosion film on some of the specimens, particularly those exhibiting large weight gains, began to spall if the tests were continued for longer times.

4.2 Corrosion Film Examination

The oxide film that forms on zirconium and its alloys during corrosion has been shown to be an anion deficit semiconductor, with corrosion occurring by oxygen diffusing through the film and then reacting at the oxide/metal interface [2].

According to the Hauffe theory for the oxidation of semiconductors with anion holes, the addition of alloying elements with a higher valence than zirconium would decrease the number of oxygen ion defects, retard the diffusion of oxygen, and reduce the corrosion rate. Conversely, alloying elements with a lower valence than zirconium would increase the number of anion holes and increase the corrosion rate. Because an important condition for the Hauffe theory to apply is that the alloying elements must be in solid solution in the zirconium in order to share in the film formation, this theory does not apply when intermetallics are present and, in such a circumstance, the properties of the intermetallics would have to be considered in relation to those of the zirconium matrix.

It would appear, from the electron micrograph in Figure 3, that the copper and the molybdenum were held in solid solution on quenching the Zr-0.5% Cu-0.5% Mo alloy from 1000°C (1830°F). In this situation the Hauffe theory would apply and it can be concluded, from the high corrosion rate of the quenched specimens of both the Zr-0.5% Cu-0.5% Mo and Zr-1.0% Cu-1.5% Mo alloys, that the valence value of the alloys due to the copper and molybdenum being in solid solution was not favourable for good corrosion resistance.

As the intermetallics begin to precipitate in a finely-divided form, the corrosion resistance improves and, as was mentioned above, the Hauffe theory does not apply; the reason for the improved corrosion resistance at this stage is not known, but it appears to be related to the presence of finely-divided intermetallics. When these intermetallics reach a certain size they begin to produce cracking in the corrosion film and the corrosion rate increases. Figures 10 and 11 illustrate the cracking in the corrosion film adjacent to the large particles of intermetallics in the Zr-0.5% Cu-0.5% Mo alloy specimens that had been aged for 100 hours (Figure 10) or had been annealed (Figure 11) prior to corrosion testing. These electron micrographs can be compared with Figure 9, which shows the adherent film on a specimen of the same alloy aged for 24 hours and then corrosion-tested for the same

time.

Attempts to identify the precipitated intermetallics in the Zr-0.5% Cu-0.5% Mo and Zr-1.0% Cu-1.5% Mo alloys by X-ray diffraction methods were not successful, because of the small amount of intermetallics present. However, by increasing the copper to 3% and the molybdenum to 4.5% (melt KU), there were sufficient intermetallics present to identify a cubic phase with a unit cell that was calculated to be 4.999A. Identification of such a phase has not been reported in the literature.

5. CONCLUSIONS

1. Weight gains during corrosion testing of a Zr-1.0% Cu-1.5% Mo alloy varied by a factor of 20, depending on the heat treatment. Minimum weight gains (40 mg/dm^2) for specimens corrosion-tested in steam at 400°C (750°F) and 1500 psi for 400 hours were obtained by heat treating at 1000°C (1830°F) for one hour, water-quenching, and ageing in air at 500°C (930°F) for 32 hours.

2. Weight gains during corrosion of a Zr-0.5% Cu-0.5% Mo alloy were also shown to depend on the heat treatment. The treatment found to give minimum weight gain (50 mg/dm^2) was to heat at 1000°C (1830°F) for one hour, water-quench, and then age in air at 500°C (930°F) for 24 hours.

3. Over-ageing of the Zr-0.5% Cu-0.5% Mo and Zr-1.0% Cu-1.5% Mo alloys resulted in the formation of large intermetallics that caused cracking in the corrosion film and an acceleration in the corrosion rate.

4. The intermetallic phase in a Zr-3.0% Cu-4.5% Mo alloy was found to be a cubic structure with a unit cell of 4.999A.

6. ACKNOWLEDGEMENTS

The authors wish to thank Miss J. Ng-Yelim and Dr. C.M. Mitchell, both of the Metal Physics Section, Physical Metallurgy Division, for assistance with the electron microscopy and X-ray diffraction analyses, respectively.

7. REFERENCES

1. C.F. Dixon, "Influence of Transformation Reactions on Mechanical Properties and Corrosion Behaviour of Zirconium-Copper-Molybdenum Alloys". Mines Branch Investigation Report IR 62-3 (1962).

2. M.E. Straumanis, W.J. James and W.C. Custead, "The Difference Effect and Anodic Behaviour of Zirconium Dissolving in Hydrofluoric Acid". J. Electrochem. Soc. 107 (6), 502-506 (1960).

- = = -

CFD:HMS:(PES):lc

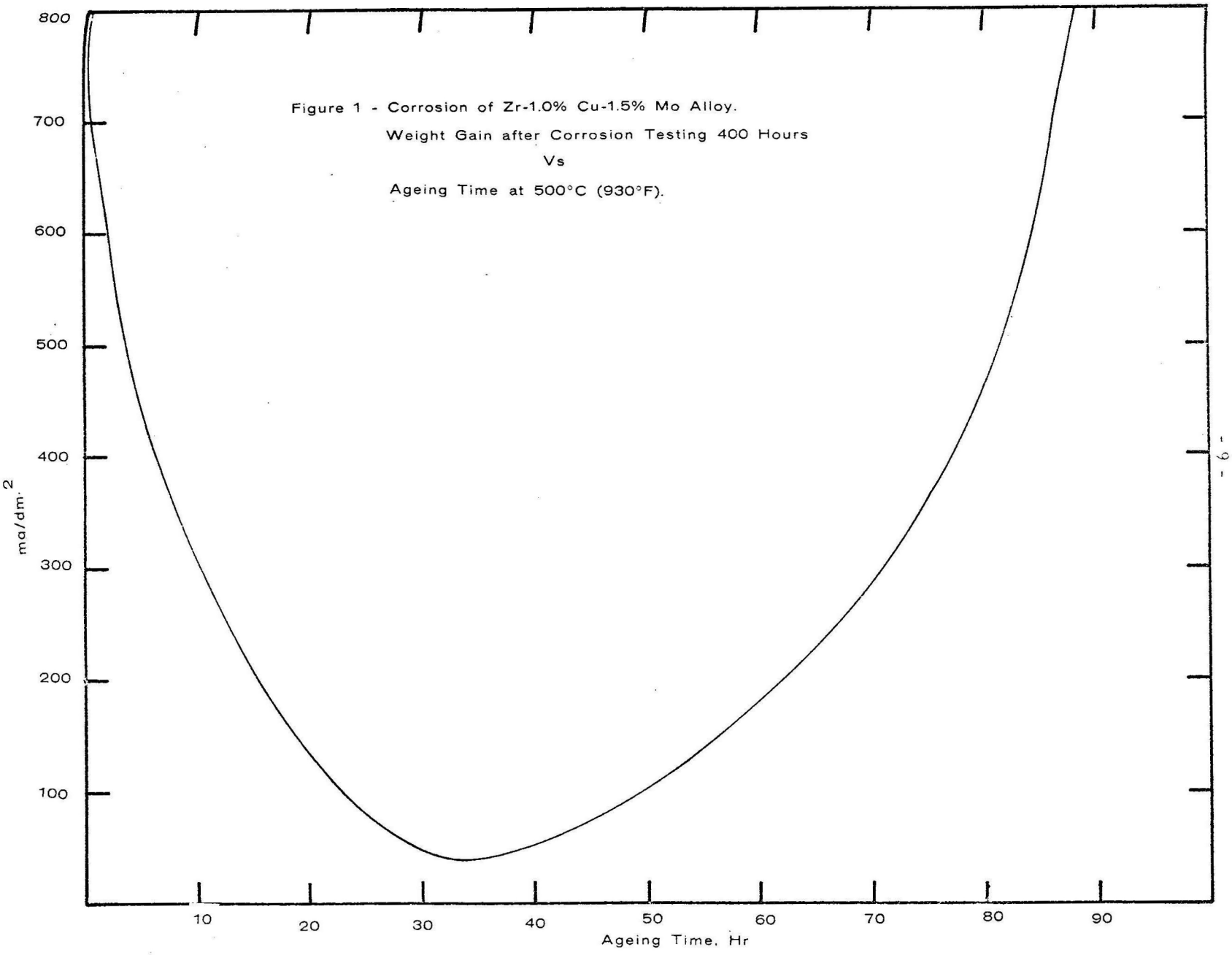


Figure 1 - Corrosion of Zr-1.0% Cu-1.5% Mo Alloy.
Weight Gain after Corrosion Testing 400 Hours
Vs
Ageing Time at 500°C (930°F).

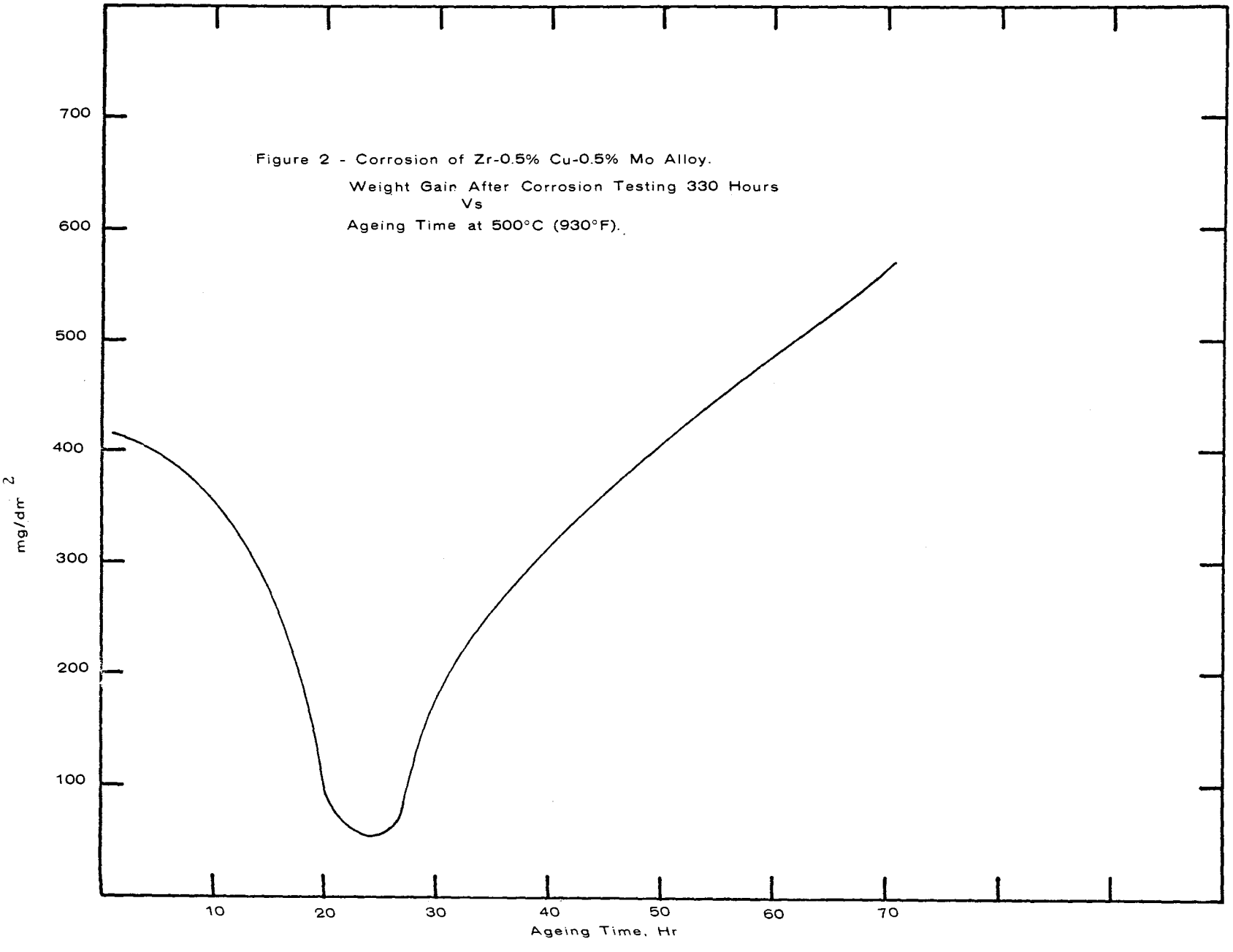
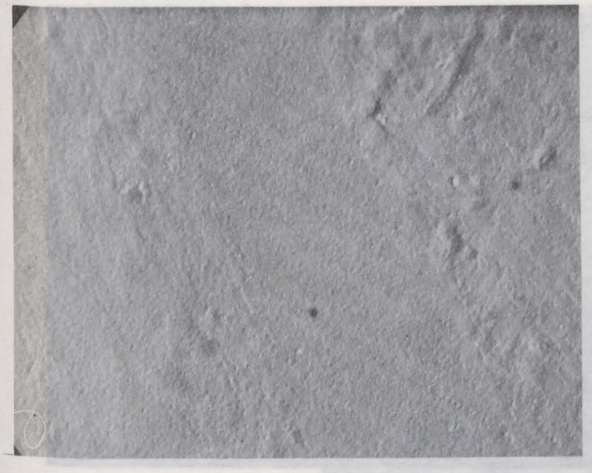


Figure 2 - Corrosion of Zr-0.5% Cu-0.5% Mo Alloy.
Weight Gain After Corrosion Testing 330 Hours
Vs
Ageing Time at 500°C (930°F).



X10,000

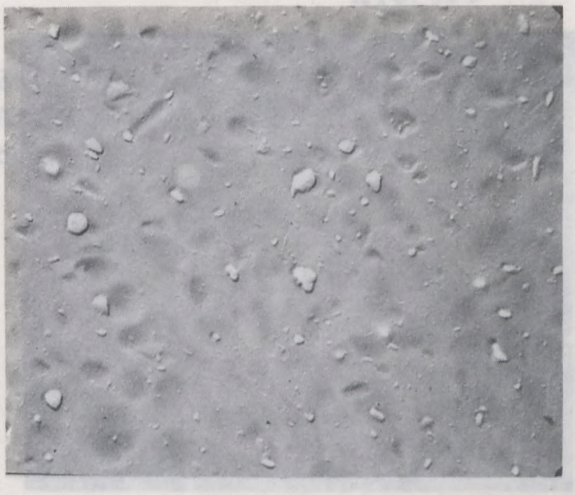
Figure 3 - Zr-0.5% Cu-0.5% Mo. H.T. 1000°C (1830°F), W.Q.; as-polished.

X10,000

Figure 4 - Zr-0.5% Cu-0.5% Mo. H.T. 1000°C (1830°F), W.Q.; aged 8 hr at 500°C (930°F); as-polished.

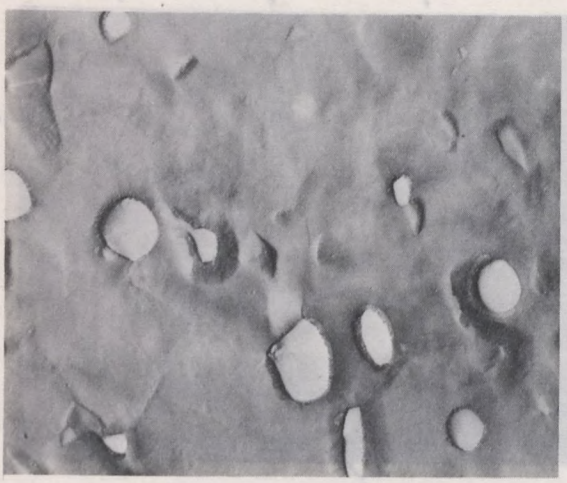
X10,000

Figure 5 - Zr-0.5% Cu-0.5% Mo. H.T. 1000°C (1830°F), W.Q.; aged 24 hr at 500°C (930°F); as-polished.



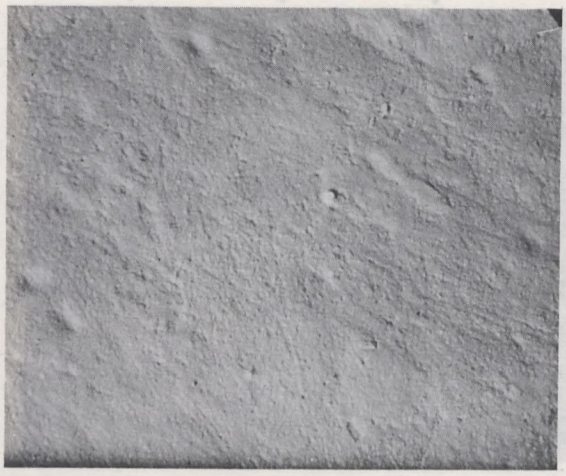
X10,000

Figure 6 - Zr-0.5% Cu-0.5% Mo. H.T. 1000°C (1830°F), W.Q.; aged 100 hr at 500°C (930°F); as-polished.



X10,000

Figure 7 - Zr-0.5% Cu-0.5% Mo. Annealed 700°C (1290°F); as-polished.



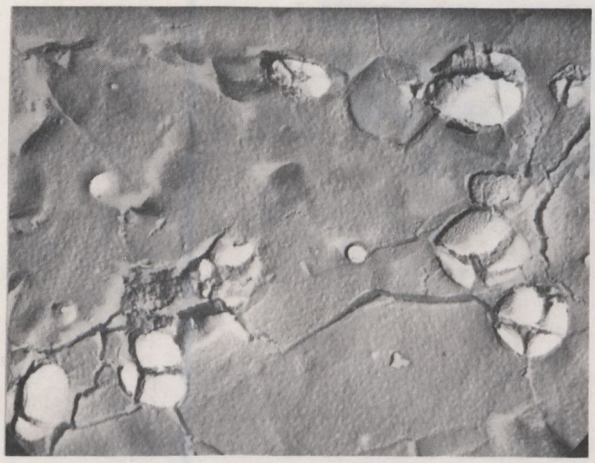
X10,000

Figure 8 - Zr-0.5% Cu-0.5% Mo. H.T. 1000°C (1830°F), W.Q.; corrosion-tested 24 hr.

X10,000

Figure 9 - Zr-0.5% Cu-0.5% Mo. H.T. 1000°C (1830°F), W.Q.; aged 24 hr at 500°C (930°F); corrosion-tested 24 hr.

Figure 10 - Zr-0.5% Cu-0.5% Mo. H.T. 1000°C (1830°F), W.Q.; aged 100 hr at 500°C (930°F); corrosion-tested 24 hr.



X10,000

Figure 11 - Zr-0.5% Cu-0.5% Mo.
Annealed 1 hr 700°C (1290°F);
corrosion-tested 24 hr.