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STATISTICAL TECHNIQUES AND ANALYSIS IN CORROSION MEASUREMENTS OF Zr ALLOYS IN TERPHENYLS

by

G.C. IMARISIO and M. COCCHI

1966

ORGEL Program

Joint Nuclear Research Center
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Physical Chemistry
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SUMMARY

The scope of this paper is to describe the theoretical criteria and the experimental procedures adopted to investigate the agents that cause corrosion of Zr-alloys in terphenyls; this work represents a first approach to this, indeed complex, problem. Further results are about to be obtained.

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Scope of the research

The interest in zirconium alloys as a structural material for use in high temperature terphenyl in the Orgel reactor has been always increasing because of the very interesting possibilities offered by these alloys. In fact their low neutron cross section and good mechanical properties are well known, so that if their corrosion in terphenyl were found to be reasonable, very good use could be made of the above mentioned valuable properties.

At the beginning of this research program only a few corrosion data of zirconium alloys in terphenyls were available and mostly negative or (1,2) contradictory.

Successive more promising results (3) led us to begin an extensive research program on the corrosion behaviour of the zirconium alloys in terphenyls at high temperature.

As a working hypothesis it was assumed that the water dissolved in the organic at the working temperature (around 400°C) should behave almost like steam at the same partial pressure and temperature.

On this tentative basis the choice of alloys was restricted to those developed for water or steam service, whose corrosion behaviour in steam was already well known. Zircaloy-2 and Zr-3Nb-1Sn were finally chosen for the measurements.

Statistical planning

Taking into account the high number of variables involved and the lack of information "a priori" about the possible effects of them,

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a statistical planning was chosen. More precisely, for purpose of investigating all possible combinations of experimental factors we preferred a factorial experiment. We should point out that an experiment which has been designed in this manner may yield more information than an experiment of the same size but designed on the classical principles, because the possible interactions between the experimental factors are explored (4,5).

The oxygen weight gain (due to oxidation) and the hydrogen pick-up (hydriding) were considered as the measurable effects of the corrosion; therefore we had, arranged in the same experimental design, two groups of measures. Of course, each different corrosion effect was intended to confirm each other; moreover they would have constituted an excellent test of comparison for proving the correctness of the experimental measurements.

The factors that we chose as probably significant in corrosion were:

A - water concentration
C - temperature of the liquid
D - time of exposure
E - chlorine concentration
F - surface condition

We remark that these five factors were selected after some preliminary tests had excluded the significant influence on corrosion of other factors (such as the hydrogen concentration).

Levels of the variables

Among the factors that we considered, particular attention was devoted to D, the time of exposure; in fact, the measure of distinguishably different effects of it on corrosion needs very long experiments; we may say, at least some months. Also for this reason, that is for the purpose of avoiding long and expensive research towards what were, perhaps, wrong directions, we preferred to do, in this first phase, a not very complex experimental design, that is with a low number of levels. It is clear that in this manner we should not have reached an exact understanding of the phenomenon, in particular no response surface (probably not linear) could have been drawn. On the other hand, a quick realization of this first phase would have allowed us to direct more efficiently our research once we had gained experience about the real influence of the factors.

Moreover it was reasonable to think that at least a part of the measures made in this first work could have been utilized also in successive designs; at least for a better estimating of the average of the samples.

Finally we fixed two levels for every factor. They were chosen as follows

	1st lev.	2nd lev.
A	20 - 30	60 - 80 ppm
C	380 (Zr-2) 360 (Zr-Nb-Sn)	420 (Zr-2) °C 400 (Zr-Nb-Sn) °C
D	15	30 days
E	0.2 - 0.4	1.5 - 2 ppm
F	pickled	preoxidized

In the following table 1 is summarized the complete factorial design:

Table 1

N° of the exp.	Treatment comb.	Levels of the factors ΔP ΔH				
		A	C	D	E	F
3	(1)	−	−	−	−	−
2	a	+	−	−	−	−
5	c	−	+	−	−	−
8	ac	+	+	−	−	−
9	d	−	−	+	−	−
13	ad	+	−	+	−	−
15	cd	−	+	+	−	−
14	acd	+	+	+	−	−
1	e	−	−	−	+	−
4	ae	+	−	−	+	−
7	ce	−	+	−	+	−
6	ace	+	+	−	+	−
11	de	−	−	+	+	−
10	ade	+	−	+	+	−
12	cde	−	+	+	+	−
16	acde	+	+	+	+	−
3*	f	−	−	−	−	+
2*	af	+	−	−	−	+
5*	cf	−	+	−	−	+
8*	acf	+	+	−	−	+
9*	df	−	−	+	−	+
13*	adf	+	−	+	−	+
15*	cdf	−	+	+	−	+
14*	acdf	+	+	+	−	+
1*	ef	−	−	−	+	+
4*	aef	+	−	−	+	+
7*	cef	−	+	−	+	+
6*	acef	+	+	−	+	+
11*	def	−	−	+	+	+
10*	adef	+	−	+	+	+
12*	cdef	−	+	+	+	+
16*	acdef	+	+	+	+	+

In the first column are control codes; ΔP e ΔH are respectively the weight gain for oxydation and the hydrogen pick-up.

In the above table ΔP and ΔH are to be intended as mean values of the measures obtained from nine replicates per sample. This number is related, of course, to the physical dimensions of the installations.

Corrosion facilities

A high number of corrosion parameters requires a strict control during the corrosion exposure in terphenyl as previously mentioned. For this reason special corrosion equipment had to be provided. Circulation of the liquid appeared necessary so that loops were chosen as corrosion apparatus. To avoid the troubles given by pumps, thermal circulation was chosen. The low circulation speed given by this method is of minor concern for corrosion work, because corrosion of Zr-alloys is rarely affected by the speed of the corroding medium, at least for reasonable speeds.

The maximum performances of the thermosiphon loops are:

temperature	$\leq 420^{\circ}C$
pressure	≤ 25 kg/cm^2
speed of liquid	≤ 10 cm/sec.

The temperature is constant within $\pm 3^{\circ}C$. The water concentration in the terphenyl is kept constant by continuously bubbling wet nitrogen in the circulating terphenyl. The nitrogen is previously saturated with

water kept at a constant temperature in a thermostat. The chlorinated impurities are added discontinuously to the circulating terphenyl as high-chlorine terphenyl. It is more likely that the chlorinated compounds added in this way are more similar to those contained as an impurity in the received terphenyl.

Analytical controls are routinely done on all the important parameters.

Two test sections are provided for each loop at the two temperatures of the thermosiphon. Each test section can accommodate 18 corrosion samples 2 cm by 9.5 cm.

Eight loops had to be constructed (6) to meet the needs of the previously described program.

The operation of the whole facility has been made automatic for continuous work with a minimum of surveillance.

Experimental procedures

The samples of the two alloys were marked and cut from the sheets of metal. A full anneal and pickling was done before the exposure in the terphenyl. Some of the samples were preoxidized in dry oxygen at the same temperature of the subsequent experiment. Blanks were provided for the measurement of the initial hydrogen content. Special care was taken to assure true representative blanks.

A random choice of the samples assigned to each experiment was done in order to avoid any biasing due to small alloy differences.

The control of the experimental parameters was as good as possible (7): only the chlorine concentration was in fact not always constant because of the slowness of the analytical method and of the relatively fast change of the chlorine concentration with time.

The overall corrosion reaction between water and zirconium alloys is

$$Zr + 2H_2O \longrightarrow ZrO_2 + 2H_2 \qquad (1)$$

A certain percentage of the hydrogen developed by the above reaction enters the metal and reacts to form zirconium hydride. Eventually the hydride concentration exceeds the solubility at the working temperature and the hydride precipitates. The resulting fragilization of the metal impairs its mechanical properties to a great extent.

Both the oxide thickness and hydrogen pick-up are then of interest for reactor designers to assess the maximum performance of the alloys for in-reactor-use.

The oxide thickness was measured after the corrosion in terphenyl by the weight gains for unit surface of the samples. No weight gain was measurable, of course, for the spalled samples.

The hydrogen pick-up was obtained from the difference between the hydrogen content of the samples after and before the exposure. Blanks were needed for these measurements because the analysis is destructive (vacuum extraction at high temperature).

The expected precision of the measurement of the above data depends on the precision of the single measurements, which are as

follows:

length	±	0.01 cm
weight	±	0.1 mg
time	±	30 min. (due to heating and cooling

times for the loops).

Hydrogen concentration ± 5 % (for values ≥ 10 ppm).

The hydrogen content of the blanks was almost always constant; this fact seems to confirm that the procedure adopted for the sample processing is reasonably correct.

Data processing procedures

The experimental results of analysis obtained according to the scheme of the table 1) were treated using a 7090 IBM computer.

A FORTRAN-IV program specially made for such types of problems was utilized (3). We shall not describe it in detail; we only note that is was realized using the classical method of Yates because:

a) it is the quickest when all or most of the factorial effects are wanted for study,
b) it gives the opportunity of a general calculation check, very suitable in an automatic procedure.

Finally the simple effects of the factors, the mean effects and the interactions up to the fourth order were obtained. Tests of significance for all the effects were made.

Analysis of the results

The treatment of the corrosion results has been done on the hydrogen pick-up only; in fact some of the weight gain measurements were impossible because of the spalling of the samples; indeed, in certain conditions the total corrosion observed was very high.

Tables 2 and 3 report the essential data of the Yates method of statistical analysis of the whole set of experimental data. Double asterisk denotes significance at the 1 % level of the F-test. Single asterisk denotes significance at the 5 % level.

The following conclusions may be drawn:

The factors time
temperature
chlorine concentration

and their interactions are all significant for both the alloys, while the surface treatment seems to have negligible effects. The water concentration has no effect for Zr-2, while it seems very effective for Zr-Nb-Sn. Some other slight differences are present between the two alloys as the table 2 shows, but no direct comparison may be done in view of the very high difference on the values of the variance and of the relative smallness of the differences found.

On the contrary the two alloys corrode in a very different way, Zr-2 is the best, Zr-Nb-Sn is the worst. This fact may explain that the water concentration is beneficial for the second alloy, while it has no significant influence on the first.

The corrosion speed of the second alloy may be lowered by an increased healing of the defects on the oxide layer caused by a higher water concentration. In turn this last effect could not be detected when a protective oxide is already present.

From the examination of the original raw data, the water content seems to counteract partially the very strong effect of the chlorine content.

The tremendous influence of this last parameter and the difficulties associated with the control of its level led to the very high value of the variance for the analysis shown above. To get more information about the relative influence of the other variables a second analysis has been done on the data of the above experiment, rearranged as a 2^4 factorial plan, excluding the treatments with factor E (chlorine concentration) at the higher level.

The essential data of this second analysis are reported in table 3.

A comparison with table 2 shows that the water level becomes significant, but confirms that the preoxidation does not influence, in general, the corrosion process for Zr-2, while for Zr-Nb-Sn the influence of the preoxidation is important. This fact may be explained with the same arguments developed above for the influence of the water concentration.

It is not surprising that great differences in the significance of various treatments and in the conclusions drawn from the two above reported analyses are apparent. In fact, the two tables are truly different because of the absence of the effect of the chlorine concentration in the second analysis. The orthogonality of the comparisons

allows the scaling down of the experiment size on the same data, but some information is necessarily lost. As a consequence very great changes of the general picture may result.

The exclusion of the high-chlorine data has, in fact, lowered the variance and withdrawn the highest of the hydrogen pick-up data among the whole set of experimental results.

The net effect is that of examining a narrower range of hydrogen pick-up data, with the exclusion of those which represented, roughly, data normally found at very long corrosion times.

The gain in the sensitivity of the experiment and in the value of the variance is then paid for by less general conclusions on the scaled down analysis.

In any case it is remarkable that the interactions of the surface treatment with the other variables are all significant also for Zr-2 though in a very reasonable way. In fact the change due to this factor may be explained by a "change of origin" of the corrosion curve by an amount proportional to the preoxidation given to the samples before exposure to the terphenyl.

The value of the variance for this second analysis is much lower than before. This fact confirms the above reported strong effect of the chlorine concentration and of its variability.

A formal analysis of variance table has not been done because of these difficulties with a high value of the variance in the complete set, while its application to the four factor experiment is of minor interest.

A larger experiment on new alloys is in progress. The design of this experiment has been made on the conclusions of the present work.

Conclusions and future work

The present research has been intended as a screening test to ascertain the parameters which are important for the corrosion of the zirconium alloys in terphenyl.

It has been concluded that the chlorine, temperature, time, and the water concentration (to a slight extent) are all important in the corrosion process.

The influence of the chlorine concentration has been found to be extremely high. In any case the corrosion rate and the hydriding rate of the two alloys examined were not low enough to allow any immediate practical use of these alloys. For this reason no further measurements have been done to complete or to improve the present results.

A second statistically planned experiment has been designed to do a screening among different and potentially more corrosion-resistant zirconium alloys.

This design has been made taking into account the results and the conclusions reported here. The level of the parameters has been chosen so as to obtain a wider understanding of the corrosion phenomenon from a practical point of view. The critical variables (like Chlorine, temperature, time) are examined at three levels, so that it is hoped that response surfaces will be obtained at the end of the experimental program. This work will be reported elsewhere.

Table 2

Results of the statistical analysis of all the corrosion data

Treatment	Effect means for Zr-Nb-Sn	Effect means for Zr-2
(1)	197,1 **	229,0 **
A	-50,82 **	-1,148
C	194,0 **	219,9
AC	-49,66 **	7,502
D	35,49 **	70,64 **
AD	31,04 **	69,27 **
CD	34,51 **	61,93 **
ACD	32,94 **	77,91 **
E	189,9 **	228,2 **
AE	-46,95 **	-0,8462
CE	187,6 **	219,5 **
ACE	-45,95 **	7,838
DE	32,59 **	70,52 **
ADE	32,64 **	69,39 **
CDE	31,55 **	61,80 **
ACDE	34,69 **	78,05 **
F	-0,3283 *	-10,01
AF	4,524 *	12,55
CF	0,1805	-6,635
ACF	4,530	9,374
DF	2,183	8,179
ADF	0,6588	-5,952
CDF	2,166	11,77
ACDF	0,4525	-9,162
EF	0,8580	-9,998
AEF	3,723 *	12,65
CEF	0,9963 *	-6,785
ACEF	3,793 *	9,530
DEF	1,654	8,366
ADEF	1,378	-5,783
CDEF	1,672	11,59
ACDEF	1,115	-8,962
	VARIANCE	VARIANCE
	169.8	3622.8

Table 3

Results of the statistical analysis of the corrosion data.
Effect of chlorine excluded.

Treatment	Effect means for Zr-Nb-Sn	Zr-2
(1)	7,184 **	0,8508 **
A	-3,865 **	-0,3019 **
C	6,436 **	0,3823 **
AC	-3,704 **	-0,3359 **
D	2,898 **	0,1147 **
AD	-1,605 **	-0,1251 **
CD	2,953 **	0,1267 **
ACD	1,759 **	-0,1436 **
F	1,186 **	-0,01269
AF	0,8015 **	-0,1075 **
CF	0,8158 **	0,1497 **
ACF	0,7364 **	-0,1557 **
DF	0,5289 **	0,1131 **
ADF	0,7192 **	-0,1687 **
CDF	0,4936 **	0,1726 **
ACDF	0,6624 **	-0,2005 **
	VARIANCE	VARIANCE
	0,605	0,0194

Bibliography

1. W.K. Boyd et al., Corrosion studies in heat exchange media, BMI 1160.
2. V. Troutner, Corrosion in organic reactor coolants, Corrosion 16, 281.
3. F.H. Krenz, A. Sawatzky, Zirconium alloys in organics; a possibility. VII Nuclear Congress, Rome, June 1962.
4. W. G. Cochran and G.M. Cox,"Experimental Designs", J.Wiley & Sons, Inc., New York 1957.
5. C.A. Bennett and N.L. Franklin, "Statistical Analysis in Chemistry and the Chemical Industry", Wiley & Sons, Inc., New York 1963.
6. G.C. Imarisio, The compatibility of zirconium alloys with high temperature polyphenyls: Thermosiphon loops for controlled conditions corrosion measurements, Internal report (not available)
7. G.C. Imarisio, The compatibility of zirconium alloys with high temperature polyphenyls: Results of corrosion measurements on Zircaloy-2 and Zr-3 Nb-1 Sn, Internal report (not available)
8. M. Cocchi - R. Di Cola "MAEF 2 - Un programma per l'analisi degli effetti fattoriali in un esperimento del tipo 2^u ", Internal report (not available)

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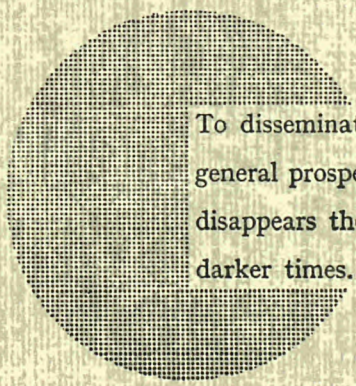

To disseminate knowledge is to disseminate prosperity — I mean general prosperity and not individual riches — and with prosperity disappears the greater part of the evil which is our heritage from darker times.

Alfred Nobel

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