CORROSION RATE TRANSIENTS OBSERVED BY LINEAR POLARIZATION TECHNIQUES AT Zr-1%Nb ALLOY

J. BERAN, K. ČERNÝ
ZJS SKODA plc., Pelzen,
Czech Republic

Abstract

Momentary corrosion rate of Zr-1%Nb alloy during nonisothermal autoclave experiments at temperature up to 328°C in various solutions was determined by T/R_p values (T - absolute temperature, R_p- polarization resistance), multiplied by temperature independent conversion factor. This factor was found by comparison of conventinal corrosion loss evaluation with electrochemical measurements. Corrosion rate transients in boric acid solutions and in lithium hydroxide differed significantly. Great differencies were also found in stabilized corrosion rates at the end of experiments. Temperature irregularities caused considerable changes in corrosion rate.

Introduction

Application of linear polarization techniques for continuous and remote corrosion monitoring of Zircaloy-2 was previously reported by a number of authors /1/,/2/,/3/. Further, this method was extensively used as well in corrosion test program of Zr-1%Nb alloy. For this purpose it was necessary to clarify some theoretical problems, develop high-pressure,high-temperature, radiation resistant electrochemical probes and carry out many autoclave experiments in various solutions to determine the coversion factor polarization resistance versus corrosion rate.

The main result of the theoretical work consisted in the introduction of criterion T/R_p instead of usual $1/R_p$. This modification provides great advantage for corrosion measurements during nonisothermal experiments. Momentary T/R_p values are converted into momentary corrosion rate simply by multiplication with temperature independent conversion factor.

Development of electrochemical probes for severe operating conditions resulted in the insulatory sealing based on voluminal increase of solid phase due to suitable chemical reaction between a porous body and a penetrant. Probes of this type with the designation TIV have been reported previously /4/.

Autoclave experiments for the determination of conversion factor by comparison of mean values $(T/R_p)_s$ with subsequent conven-

tional evaluation of mean corrosion rate were carried out in stagnant solutions without refreshing. Originally, the solutions were not deaerated. Besides the experimental data necessary for determination of conversion factor, autoclave experiments resulted in many interesting T/R_p transients, which reflected the corrosion aggressivity of test solutions.

Experimental results

Every point in the conversion diagram Fig.1 represents one corrosion experiment (test period beeing several hundred hours) with particular solution and indicates the comparison between mean

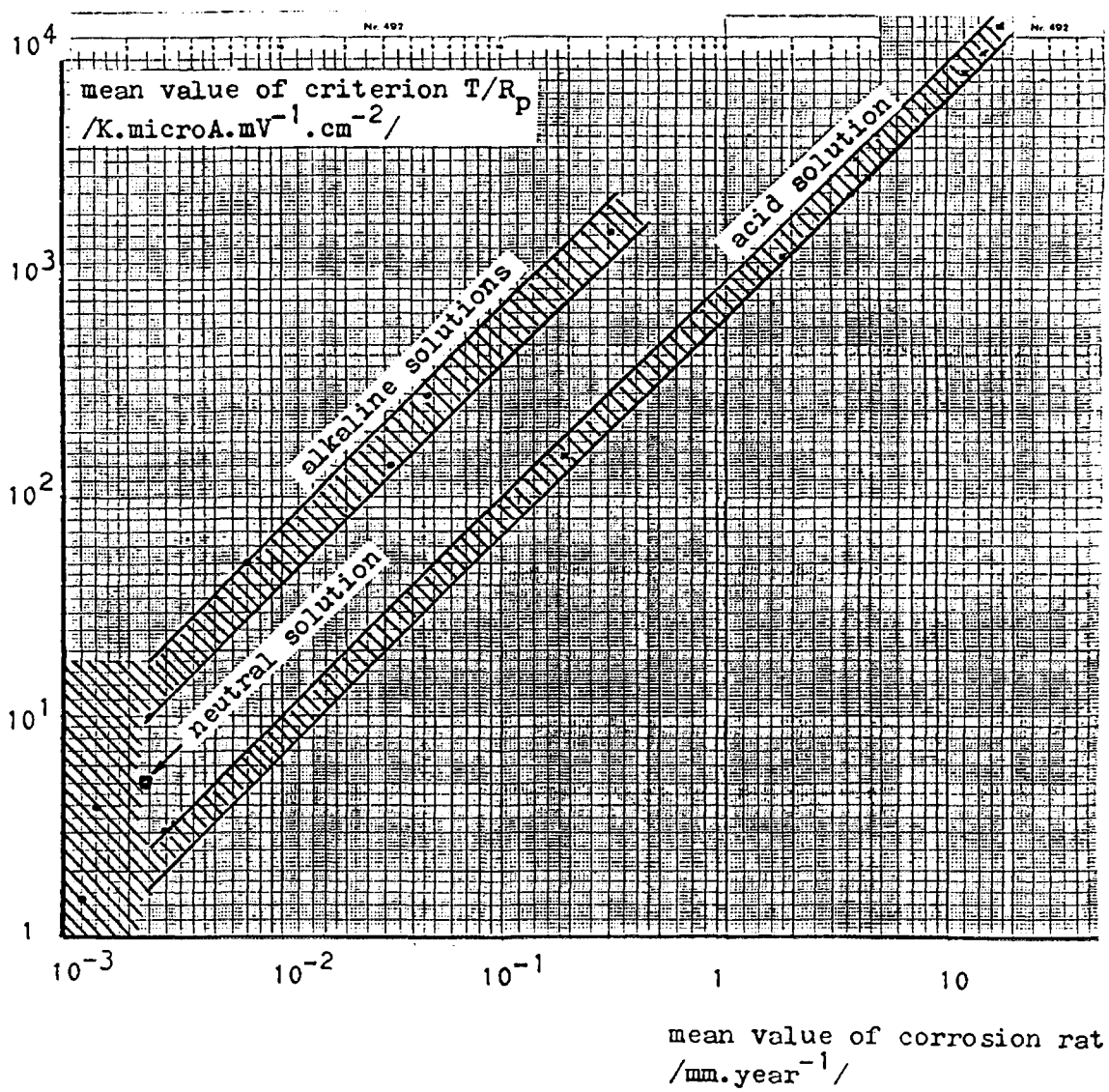


Fig.1

Conversion diagram for Zr-1%Nb and Zr-2.5%Nb alloys

T/R_p value and mean corrosion rate, which was evaluated by gravimetric method. Hatched area marks the individual scatter zones for alkaline and acid solutions. Theoretical treatment /5/ shows that identical conversion diagram is valid for momentary T/R_p values as well.

Autoclave experiments with typical corrosion rate transients are listed in Tab.1. Intentionally have been chosen solutions with extremely low, medium and extremely high corrosion rates. Temperature in all experiments was predominantly kept near 300°C, occasional temperature irregularities were caused by obligatory restrictions of power consumption. Test period amounted several hundred hours. Experiments with low corrosion rates required longer test periods owing to the necessity of subsequent conventinal gravimetric evaluation.

Fig.2 demonstrates temperature- and corrosion rate transients (at very low corrosion attack T/R_p transients) in boric acid partially neutralized by KOH + NH_3, pH_{20}=10.3. Initial peak of corrosion rate corresponds with temperature increase and reaches maximum value 0.02 mm.year^{-1}. Afterwards corrosion rate decreased during 20 hours to negligible values out of the conversion diagram. Nevertheless, it is permanently possible to measure even lowest T/R_p values. Coincidence of corrosion rate (T/R_p) fluctuations with temperature irregularities is observed in a similar way as in other experiments.

Fig.3 shows the transiets in analogous solution but without ammonia. Initial peak in corrosion rate is similar to that obser-

TABLE 1. LIST OF AUTOCLAVE EXPERIMENTS

Test solution	Characteristic temperature /°C/	Test period /hours/
boric acid 12 g/l + KOH + NH_3, pH_{20}=10.3	300-318	1285
boric acid 12 g/l + KOH without NH_3 pH=10.3	310-328	840
KOH + NH_3 40 mg/l pH=10.1	290	565
LiOH 3.5%	300	355

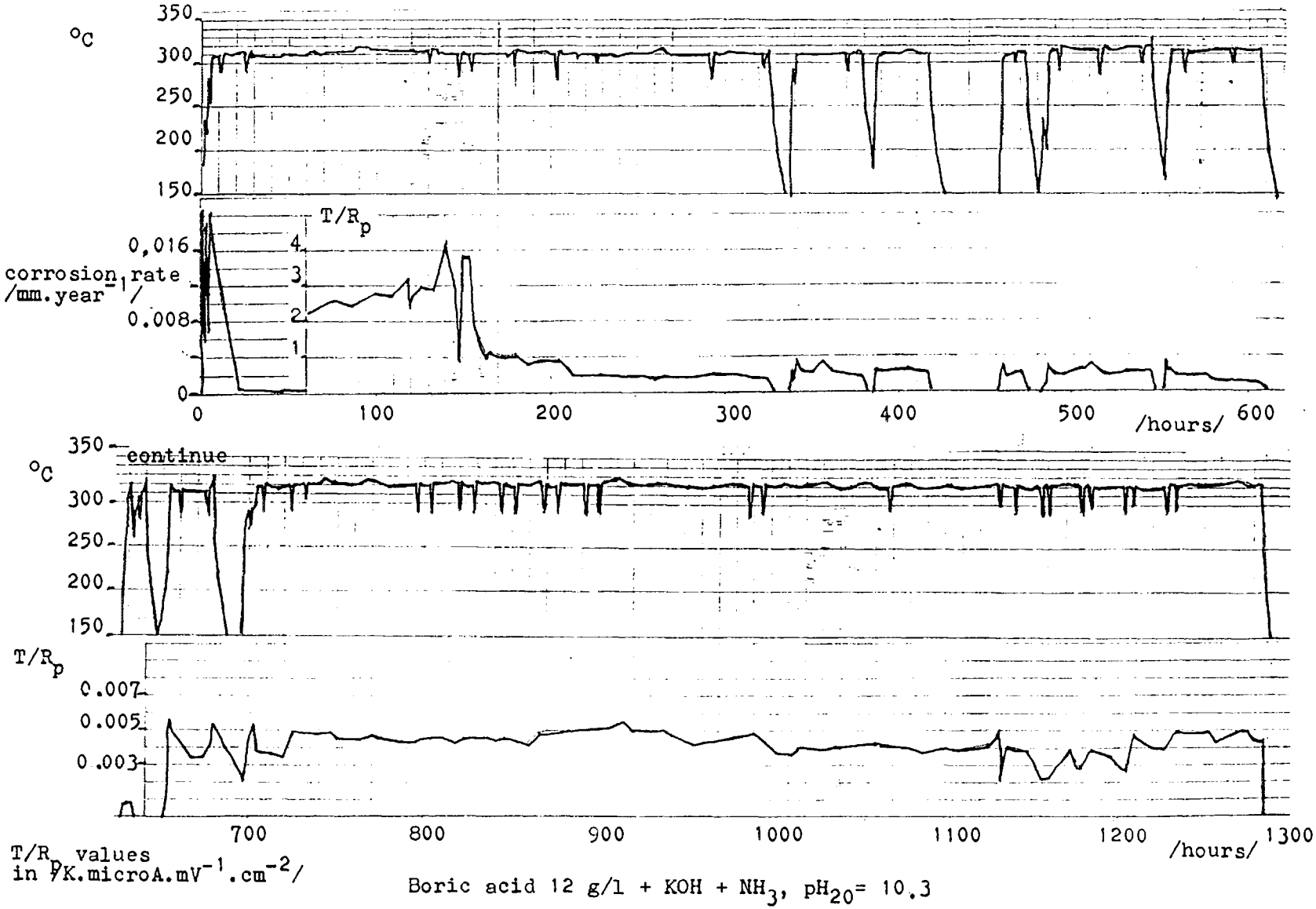
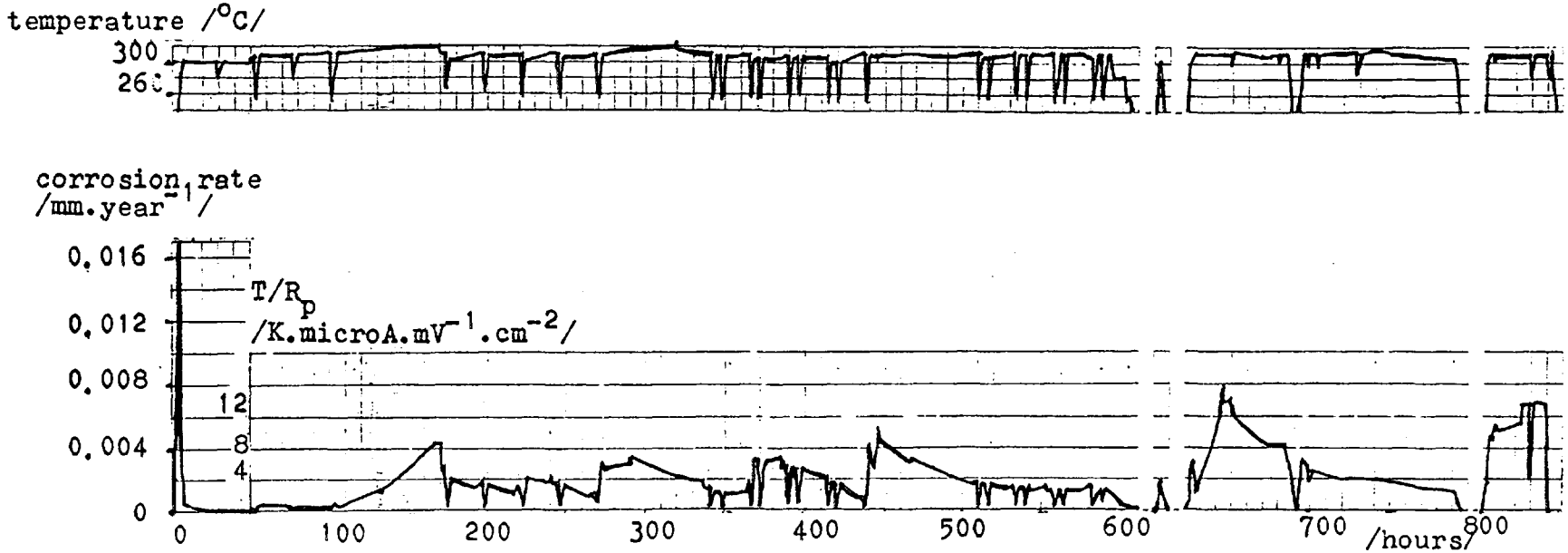

°C
350
300
250
200
150
T/Rp
0,016
0.008
0
corrosion rate /mm.year⁻¹/
4
3
2
1
0
100
200
300
400
500
/hours/
600
continue
°C
350
300
250
200
150
T/Rp
0.007
0.005
0.003
700
800
900
1000
1100
1200
/hours/
1300
T/Rp values in /K.microA.mV⁻¹.cm⁻²/
Boric acid 12 g/l + KOH + NH3, pH20= 10.3

Fig.2



Boric acid 12 g/l + KOH, without ammonia, pH_{20}= 10,3

Fig.3

ved previously. Coincidence of corrosion rate (T/R_p) fluctuations with temperature irregularities is also expressed very distinctly. During the first 100 hours corrosion rate is extremely low. Subsequently, T/R_p values increases, remaining still out of the conversion diagram. Contrary to the experiment with ammonia, T/R_p values in this period are much higher.

Fig.4 presents corrosion rate transient in solution without boric acid, pH=10.1 being adjusted by KOH + NH_3. Initial peak of corrosion rate is higher and subsequent decrease followes very slowly. Corrosion rate after 100 hours still amounts about 0.02 $mm.year^{-1}$ and after 550 hours 0.004 $mm.year^{-1}$.

Corrosion rate transient during autoclave test in 3.5% LiOH shows Fig.5. Contrary to previous experiments, corrosion rate rapidly increases during initial heating to 0.2 $mm.year^{-1}$ and then

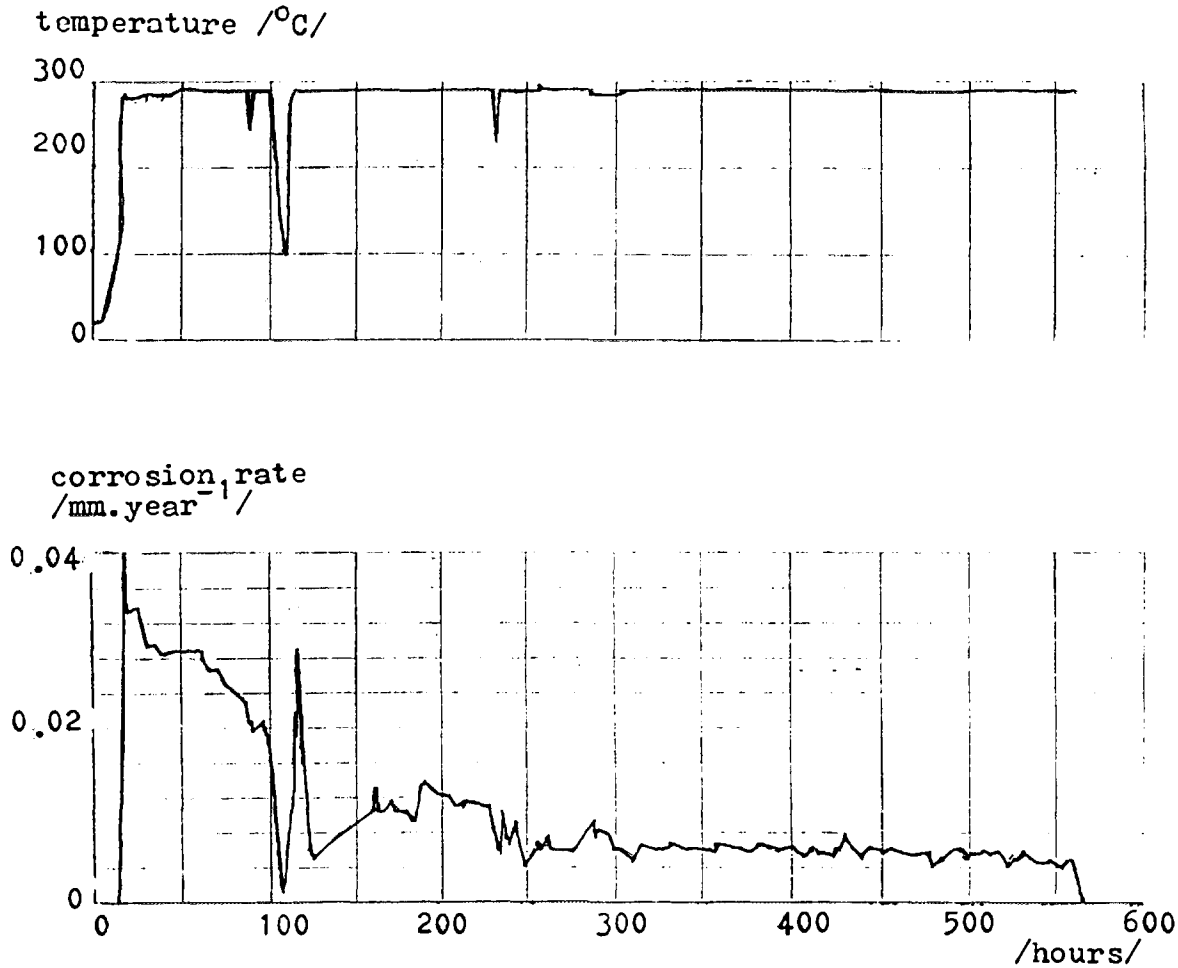


Fig.4

Ammonia 40 mg/l + KOH, pH_{20}= 10.1,
repeated autoclave corrosion test

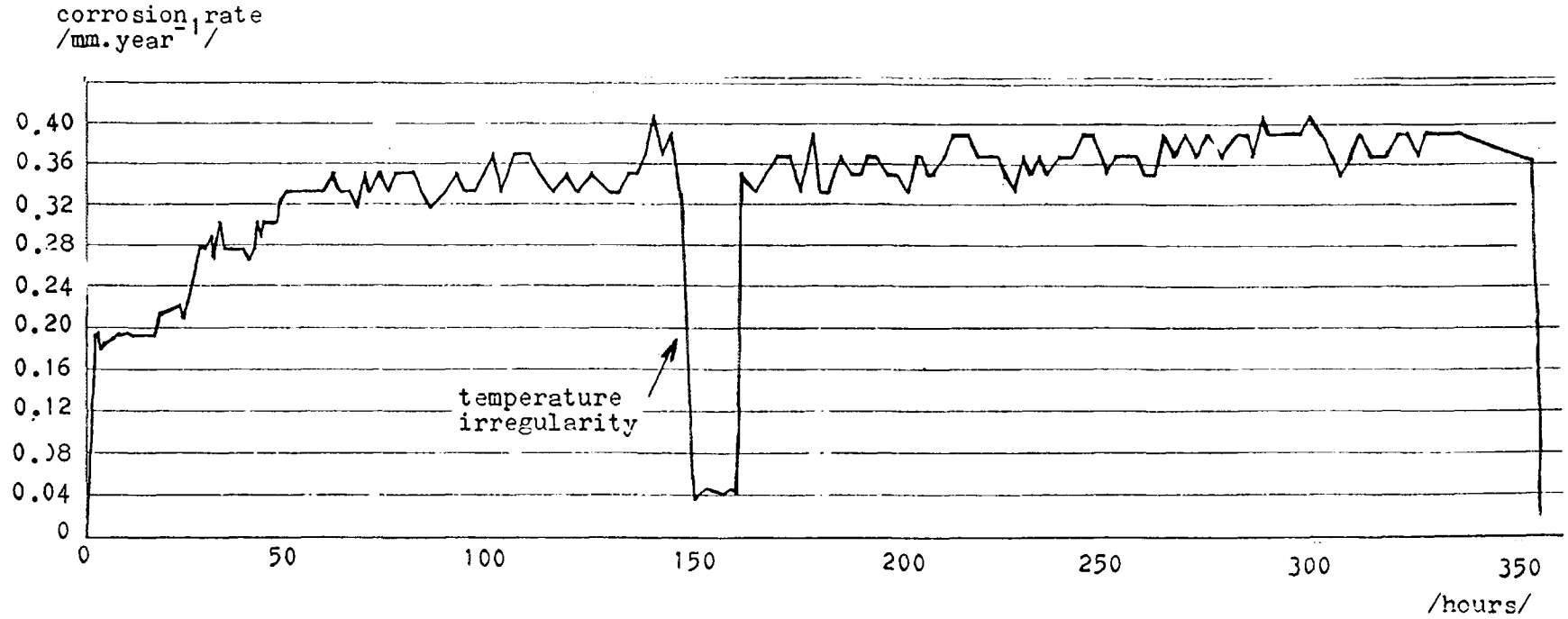


Fig.5

3.5 % LiOH solution , 300°C

follows gradual increase during 50 hours to 0.3 mm.year^{-1}. Typical initial peak of corrosion rate is absent. Slight steady increase of corrosion rate continues till the end of experiment and reaches about 0.4 mm.year^{-1}.

Conclusion

Corrosion rate transients of Zr-1%Nb alloy in various solutions obtained by T/R_p measurements reflected corrosion behaviour in aggreement with logical expectation. Interpretation of very low T/R_p values out of the conversion diagram in terms of corrosion attack requires additional investigation.

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