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THE OXIDATION AND CORROSION OF ZIRCONIUM AND ITS ALLOYS

XV. Further studies of zirconium-niobium alloys.

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1962

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THE OXIDATION AND CORROSION OF ZIRCONIUM AND ITS ALLOYS.

XV, FURTHER STUDIES OF ZIRCONIUM-NIOBIUM ALLOYS

by

B. Cox
P. G. Chadd
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ABSTRACT

The oxidation resistance of binary and ternary zirconium alloys containing 0.5 to 5 wt.% niobium and ternary additions of Sn, Cu, W, Mo, Sb, V, Ge, Pd, Pt, Fe and Mn has been studied in steam and in air. The lowest oxidation rate was achieved with a Zr-1%Nb-1%Cu alloy.

A study of the effect of heat treatment on these alloys has shown that either a 24 hour anneal at 580°C, or cold-working of the material will result in good oxidation resistance.

Some alloys containing high percentages of niobium (20-60 wt.%) have been examined. All these alloys were susceptible to non-uniform oxidation at long times, leading (in some instances) to cracking of the specimen. Such alloys are not considered reliable for use as structural materials involving long exposures to high temperature water or steam.

The rate of hydrogen absorption by alloys containing small additions of niobium is very much less than that found for zircaloy-2.

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1. Introduction

Zircaloy-2 has been used widely as fuel cladding in reactor systems where high temperature water is employed as coolant, and more recently it has been manufactured into pressure tubes to contain the coolant during its passage through the reactor core. It will not necessarily be the most suitable alloy for use under the more arduous conditions of exposure envisaged in future power reactors, and there is a need for the development of alloys with superior strength and a lower rate of hydriding during aqueous corrosion. This report describes an investigation of the corrosion and hydriding of a family of zirconium-niobium alloys.

The oxidation resistance of the zircaloys (-2, -3 and -4) is conferred by the addition of small quantities of elements with a low solubility in zirconium (Sn, Fe, Cr, Ni). Many other alloys based on the addition of similar quantities of other insoluble elements have been tested. An alternative approach to the problem of improving the oxidation resistance of zirconium is based upon the addition of alloying elements which have a relatively high solubility in zirconium. Of the possible systems which might be studied, only niobium has a low enough neutron capture cross-section to permit its addition in quantities greater than about two weight per cent.

A preliminary study of the Zr-Nb binary system⁽¹⁾ showed that there were two regions of composition in which an alloy with oxidation resistance and hydrogen absorption properties^(2,3) superior to those of zircaloy-2 might be found. The first of these regions involved additions of 0.5 - 5.0 wt.% niobium and the second region involved 50-60 wt.% niobium. A closer study of both regions, and of the effects of ternary additions to alloys containing 1 wt.% Nb and ~60 wt.% Nb has now been carried out.

All the high-niobium alloys showed evidence of non-uniform oxidation, particularly at edges, and for that reason, despite low oxidation and hydrogen uptake rates in some instances, they cannot be considered reliable for extended service exposures. Among the low niobium alloys and Zr-Nb-Sn alloys there were several which offered promise of oxidation rates as low as zircaloy-2 and hydrogen absorption rates considerably lower. However, the Zr-1%Nb-1%Cu alloy was apparently better than any of the above, and a closer study of this ternary system offers the best promise of producing an alloy combining a low oxidation

rate with low hydrogen absorption properties.

2. Experimental

Alloys were fabricated from sponge zirconium by double arc-melting as buttons $\frac{1}{2}$ " dia. The compositions of the alloys are given in Table I. Ternary additions were made from metal of "specpure" quality. The analysis of the original sponge is given in Table II, and the O, H and N analyses of the alloys in Table III. It was assumed that the concentration of minor alloying impurities would not differ significantly from that of the sponge used. No specific tests were performed for contamination with tungsten.

Specimens of the experimental alloys were machined to $\frac{1}{2}$ " dia x 0.030" thick discs, abraded to 4/0 emery, and attack-polished to give a high surface finish. Specimens of the commercial Zr-2 $\frac{1}{2}$ % Nb billet were cut from sheet, abraded and pickled. A support hole (0.040" dia) was drilled in each specimen, and the specimens were degreased and dried before the initial weighing. Weighings were performed to an accuracy of $\pm 5\mu\text{g}$; oxidation rates were based on the geometrical surface area.

Specimens were oxidised in steam at atmospheric pressure at 50°C temperature intervals between 300 and 500°C. The furnaces used were of the design reported previously⁽¹⁾.

Hydrogen analyses were carried out at Woolwich Outstation (AERE) by a "warm extraction" method⁽⁴⁾.

Experimental alloys were normally tested in the cast condition. A commercially produced billet of Zr-2 $\frac{1}{2}$ % Nb was also tested for comparison with the experimental alloys. As received this alloy was in the 30% cold-worked condition. Samples of the alloys were heat-treated in evacuated silica ampoules. Rapid quenching rates were attained, when required, by breaking the ampoule after plunging it into water. The furnace cooling rate was about 1°C per minute.

3. Results

Zr-2 $\frac{1}{2}$ % Nb and Zr-2% Nb - $\frac{1}{2}$ % Sn alloys

In figures 1 and 2 the oxidation in steam of the commercially-produced zirconium-2 $\frac{1}{2}$ % niobium alloy and an experimental Zr-2% Nb- $\frac{1}{2}$ % Sn alloy are compared, both alloys being in the cold-worked condition. It can be seen

that at 300°C the alloy containing tin is apparently superior; whereas with increasing temperature the tin-free alloy shows appreciably lower oxidation rates than the alloy containing tin.

Figs. 3-5 show the effect of heat treatment on the oxidation in steam of the Zr-2 $\frac{1}{2}$ % Nb alloy. At 350°C specimens annealed just below the monotectoid temperature (~600°C) show the lowest oxidation rates, whilst at 400 and 500°C the specimens oxidised in the "as-received" condition (~30% cold-worked) had the best oxidation resistance. At all temperatures, specimens quenched from the β -phase showed the lowest oxidation resistance.

The oxidation behaviour of the Zr-2 $\frac{1}{2}$ % Nb alloy in air at 300-400°C is shown in fig. 6. The alloy oxidised more rapidly in air than in steam at the same pressure, the rate of oxidation in air at 300°C being 1.1 mgm/dm² day compared with a rate of 40.06 mgm/dm² day in steam. Apparently anomalous oxidation behaviour was observed in laboratory air at 500°C; the oxidation rate being much higher than in either moist or "dried" air. This may represent experimental scatter rather than a genuine difference due to the composition of the air. Results in moist air at 500°C are shown in Fig. 7.

Group I alloys

Figures 8-12 show the results obtained for alloys of Group I (Table I) oxidised in steam at temperatures of 300-500°C, in the cast condition.

At 300°C the results do not extend far enough in time for any distinction to be made between the majority of the alloys in this group. At 350°C it is found that the post-transition oxidation rates (of those alloys containing tin) increase steadily with niobium content; longer exposures are necessary before any discrimination can be made between the Zr-1% Nb and Zr-2% Nb alloys at this temperature. At 400°C and above, whilst (with the exception of the Zr-1 $\frac{1}{2}$ % Nb- $\frac{1}{2}$ % Sn alloy) the same generalisation can be made about the effect of increasing niobium content on alloys containing tin, the binary alloy containing 2% Nb is definitely superior to that containing only 1% Nb. At all temperatures the alloy containing 5% Nb shows the lowest oxidation resistance.

The effect of an anneal at 580°C (Fig. 13) is to make differences between the oxidation resistance at 500°C of most of the alloys considerably smaller. This results from a reduction in the rate of oxidation of alloys

containing relatively high niobium contents, and an increase in the rate of oxidation of some of the alloys with low niobium contents. The binary alloys containing 1 and 2% Nb appear to have been affected little by this heat treatment, however. Incomplete results on annealed specimens oxidised at 350°C suggest that at this temperature the spread of the oxidation rates of these alloys may be less than at 500°C.

In figs. 14 and 15 the oxidation behaviour of the alloys in moist air at 500°C is shown for "cast" and "580°C annealed" specimens. Contrary to expectations, in both conditions the oxidation resistance is apparently little different from that in steam at the same pressure. The Zr-2 $\frac{1}{2}$ % Nb, in the annealed condition is the only alloy showing considerably faster oxidation in air (fig. 7). The effect of heat treatment is again mainly to reduce the variation from alloy to alloy.

Group II alloys

Figures 16-20 show the results obtained with the Zr-1% Nb-1%M alloys (Group II) in atmospheric pressure steam at 300 to 500°C. With the exception of three alloys (1% - Mn, Mo and Sb), all alloys lie in a single band at 300°C; with increasing temperature the spread of the results increases, however. At all temperatures (above 300°C) the 1% Cu and 1% Fe alloys are the best; the copper alloy being generally the slightly better of the two at long times. The effect of annealing for 24 h. at 580°C (Fig. 21) on the oxidation behaviour at 500°C is similar to that observed with the Group I alloys; the range of behaviour is reduced by improved oxidation resistance of the worst alloys, although the 1% Fe alloy apparently shows worse oxidation resistance than in the cast condition and the 1% Cu alloy is now the best alloy. A longer anneal (7 days at 580°C) reduced the oxidation resistance of all this group of alloys (Fig. 22) when compared with a 24 h. anneal. However, most alloys were still better than in the cast condition, and the copper alloy remained very much better than any of the others. The oxidation behaviour of Group II alloys in moist air in the "cast" and "24 hr/580°C annealed" conditions is shown in figures 23 and 24. Most alloys in the "cast" condition oxidise faster in air than in steam; the 1% Cu and 1% Sb alloys, however, show apparently little difference, and the 1% Pd alloy appears to be more resistant in air than in steam. The anomaly shown by the 1% Pd alloy remains with annealed specimens,

although all other alloys oxidise more rapidly in air than in steam.

Group III and IV alloys

Figures 25 and 26 show the results obtained for alloys of Groups III and IV in the form of bands. Of the ternary additions made to alloys in Group III only vanadium additions regularly resulted in alloys giving low oxidation rates (i.e. at bottom of band). In an effort to reduce the concentration of niobium required for good oxidation resistance in the high Nb region, the effect of ternary additions of vanadium or tin on alloys containing 20-30 wt.% Nb was also examined, and shown to effect no improvement.

The rapidly accelerating portion of the oxidation curve, following transition, was generally associated with preferential attack at edges, and in some instances led to cracking of the specimens.

Hydriding

In figure 27 the results of a hydrogen analysis on specimens of the Zr-2 $\frac{1}{2}$ % Nb alloy oxidised in atmospheric pressure steam are recorded at temperatures of 400-500°C; some results in steam at 500 p.s.i. and in air saturated with water vapour are also included. A decrease in the rate of absorption of hydrogen with decreasing temperature is apparent. Although the results at 500°C agree at low weight gains with those reported for a Zr-2% Nb- $\frac{1}{2}$ % Sn alloy⁽⁵⁾; at higher weight gains the results for the Zr-2 $\frac{1}{2}$ % Nb alloy are lower. The results at 400°C agree well with data from KAPL⁽¹⁴⁾, whereas at 450 and 500°C a more rapid rate of uptake was found.

The effect of heat treatment on the hydrogen absorption behaviour at 500°C is shown in figure 28. A comparison of these results with the oxidation behaviour (fig. 5) reveals no obvious correlation between the effect which a given heat treatment has on oxidation and hydrogen absorption.

Figures 29 and 30 present hydrogen absorption data for Groups I and II alloys respectively. In group I alloys the spread of the results generally leaves the alloys with the lowest niobium content at the top of the band, and vice-versa; of the ternary additions made in Group II alloys, however, the elements apparently giving a reduction in the rate of hydrogen absorption (W, Mo, Sb and Pt) do not improve the oxidation resistance of the binary

alloy (see fig. 20). Hydrogen uptake, by alloys with higher niobium contents than the above, generally decreases still further with increasing niobium content⁽³⁾.

4. Discussion

There have been many other investigations of alloys within the range reported here, notably at Chalk River⁽⁶⁻⁸⁾, KAPL^(9,10), Vallecitos⁽¹¹⁾, Metallgesellschaft AG (Frankfurt)⁽¹²⁾, Siemens-Schuckertwerke⁽¹³⁾, Culcheth⁽¹⁴⁾ and in the USSR^(15,16). The discussion of our results is best presented in the form of a series of conclusions drawn from our own work, followed by a short comparison with the results of previous work. No detailed comparison of oxidation rates will be attempted.

- (i) Although at 400°C and above the addition of tin to Zr-Nb alloys, containing 2-3% niobium, diminishes the oxidation resistance, at 300°C the evidence is not conclusive, and at 300°C the alloys containing tin may be superior to the binary alloys.

Dalgaard^(6,8) claims that tin additions to a Zr-2.5% Nb matrix decrease the oxidation resistance at all temperatures; however, a scrutiny of the results presented⁽⁷⁾ shows that this conclusion is only justified for experiments at 360°C and 400°C. At 316°C his data show no difference between the binary alloy and an alloy containing 0.5% tin. Metallgesellschaft AG⁽¹²⁾ found no significant difference in oxidation resistance at 350°C between alloys containing 2 and 3% Nb with and without 0.5% Sn (after annealing for 1 hr. at 650°C). Alloys containing 0.5 and 1% Nb were improved by the addition of 0.5% Sn (when annealed at 650°C); after 10 days annealing at 575°C all alloys containing 0.5% Sn were found to have superior oxidation resistance to the corresponding binary alloy. Thus for service at 300°C it is probable that the addition of 0.5% Sn to a binary Zr-Nb alloy, containing up to 3% niobium, will effect a small improvement in oxidation resistance.

- (ii) It is possible to produce billets of Zr-Nb alloys showing oxidation resistance as good as average billets of zircaloy-2. The possible range of results for Zr-Nb alloy billets cannot be estimated on the basis of these results however.
- (iii) The best oxidation resistance, at 300-350°C, probably results from an anneal at a temperature just below the monotectoid; cold-worked

material however, shows very nearly as good resistance, and the position could easily be reversed if a large number of experiments were performed to determine the random variation to be expected in repeating the two treatments. Annealing the Zr-Nb-Sn and Zr-1% Nb-1%M alloys at 580°C for 24 h. in general reduced the range of behaviour of the alloys by improving the oxidation resistance of the worst alloys, and in a few instances decreasing the oxidation resistance of the best. Longer anneals than 24 h. reduced the oxidation resistance of all alloys.

Metallgesellschaft AG concluded that the best oxidation resistance resulted from a 10 day anneal at 575°C. We have compared anneals for 1 day and 7 days at 580°C and find that the 7 day treatment results in overaging and a loss of some of the improved resistance conferred by the 1 day anneal. Vallecitos⁽¹¹⁾ and KAPL⁽⁹⁾ have also found that low temperature anneals give the best oxidation resistance. None of the heat treatment procedures employed at AECL are directly comparable with the above; a quench from 950°C followed by tempering at 500°C for 24 h. being the closest approximation. Dalgaard explains the effect of heat treatment on the oxidation resistance of Zr-Nb alloys in terms of the amount of niobium in solid solution; low concentrations of niobium in the α -phase being equated to good resistance. The effect of the length of the anneal at 580°C, however, suggests the converse.

In addition to the work reported here only Rosler⁽¹³⁾ has compared "cold-worked" with annealed material. In both instances it is concluded that "cold-worked" material is superior to material annealed at 750°C or above.

- (iv) Zr-Nb alloys oxidise more rapidly in air than in steam at the same temperature. The ratio of the rates of oxidation in air and steam is higher for the Zr-2½% Nb alloy than for some of the other experimental alloys, and a Zr-1% Nb-1% Pd alloy apparently oxidised less rapidly in air than in steam.
- (v) Among the Zr-Nb-Sn alloys the oxidation resistance at 350°C decreased regularly with increasing niobium content, at higher temperatures this generalisation was not so clear, but the ½ and 1% Nb alloys (with ½% Sn) were invariably the best of the group.

The decrease in oxidation resistance with increasing niobium content observed here, has been generally observed elsewhere. The effect of annealing at temperatures of 600°C and below is to reduce this effect of niobium content considerably. Thus, following a 24 hr. anneal at 580°C we observed little difference between the alloys of Group I at 350°C. Similar behaviour has been reported by Metallgesellschaft AG⁽¹²⁾ for alloys containing up to 5% Nb, and Klepfer⁽¹¹⁾ found that alloys containing 1-3.5% Nb showed little variation in oxidation rate following an anneal for 8 hr. at 1100°F (593°C).

- (vi) In the ternary Zr-1% Nb-1% M alloys only Cu and Fe additions regularly produced a significant improvement in oxidation resistance.

A number of investigators have studied the effect of ternary additions other than tin. Metallgesellschaft AG⁽¹²⁾ found that molybdenum and palladium additions decreased the oxidation resistance of alloys containing 2.5% Nb; chromium additions were found to result in no significant improvement in the resistance of a Zr-2% Nb-0.5% Sn alloy. Rosler⁽¹³⁾ found that ternary additions of either Cr, Mo, V and Fe improved the resistance of a Zr-1% Nb alloy to 500°C steam at atmospheric pressure, no improvement was effected when the same additions were made to a Zr-2.5% Nb alloy. The first observation is in agreement with the results obtained on annealed alloys here, but since Rosler did not test his alloys at lower temperatures, the value of this conclusion for alloys which will operate at temperatures close to 300°C is small.

At 350°C only Fe and Cu additions were observed to give any improvement in the oxidation resistance of a Zr-1% Nb alloy; the improvement resulting from the addition of copper being greater than that for iron. Dalgaard has reached the same conclusion for additions of iron and copper to a Zr-2.5% Nb alloy.

- (vii) All the alloys with high niobium contents (>20%) ultimately showed non-uniform oxidation at edges of the specimens. In some instances the specimens cracked as a result of this non-uniform oxidation, and the possibility of such cracking occurring as a general phenomenon eliminates these alloys as possible structural materials.
- (viii) Hydrogen absorption by alloys of Groups I and II at temperatures below 450°C is not greater than about 10% of that released by the corrosion reaction; at 500°C higher rates of uptake were observed. The rate of uptake at the lower temperatures is a considerable

improvement over the behaviour of zircaloy-2, which gives overall hydrogen uptakes of 30-40% in the post-transition region at 350°C.

An increase in the rate of hydrogen absorption following transition in 500°C steam has been observed also by Rosler⁽¹³⁾ and Klepfer⁽¹¹⁾. Other investigators^(10,14) have not observed this behaviour. At temperatures below 450°C the results presented here agree well with those of other investigations. The divergent results for hydrogen absorption in high temperature steam may result from variations in the rate of hydrogen uptake with heat treatment. Boulton⁽¹⁴⁾, however, has tested material in the same metallurgical condition as that used here, and the difference in this case may reflect susceptibility of the hydrogen uptake rate to small variations in the level of other gases in the steam.

Acknowledgements

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TABLE I

Composition of niobium alloys

Group	Nb%						Ternary additions (M)																	
							Sn	V	Cr	Mn	Fe	Co	Ni	Cu	Mo	Ag	Sb	W	Pt	Pd	Al	Si	Be	Ge
I	($\frac{1}{2}$) 115D	(1) 116D	($1\frac{1}{2}$) 117D	(2) 10A	($2\frac{1}{2}$) 118D	(3) 119D	$\frac{1}{2}\%$																	
		(1) 120D		(2) 89B		(5) 12A																		
II	Zr-1%Nb-1%M							125D		130D	129D			121D	123D		124D	122D	127D	128D				126D
III	Zr-59%Nb-1%M							51B	52B	53B	54B	55B	56B	57B	58B	59B	60B	61B	62B		76B	77B	78B	79B
	Zr-57%Nb-5%M							63B	64B	65B	66B	67B	68B	69B	70B	71B	72B	73B	74B	75B				
IV	(20) 14D	(25) 97D	(30) 15D	(35) 98D	(40) 41D																			
		(25) 100D						5%																
			(30) 99D					1%																
		(25) 102D						5%																
			(30) 101D					1%																

Numbers in each square are the alloy reference numbers. The letter following each number refers to the batch of zirconium sponge from which the alloy was made. Numbers in brackets give the weight per cent of niobium in the alloy, the percentage shown on the same line is that of any ternary addition also present.

TABLE II

Analysis of Zirconium sponge.

	O	H	N	Fe	Al	C	Cr	Cu	Ni	Pb	Mn	K	Ti	B	Hf	Mg
A Not known	for analyses of individual alloys produced from this material see reference 1															
B Batches 178-182	800	40	60	145	300	-	-	12	8	-	30	-	< 10	-	1.7%	10
C ZL213	1650	25	100	-	117	-	-	-	-	35	-	-	< 5	< 0.5	270	-
D ZL9015	1000	20	55-85	230	< 50	120	30	15	10	40	3	< 30	< 100	< 1	-	< 10

TABLE III

Oxygen nitrogen and hydrogen contents of alloys

Alloy No.		Final digit									
		0	1	2	3	4	5	6	7	8	9
10, 41, 12, 14, 15, 89	O	1000	900	1600		1200	1300				1400
	H	30	17	30		45	45				81
	N	40	280	230		175	225				55
51-59	O		950	1100	1000	650-1000	1500	800	650	600	1300
	H		10	13	17	16	29	17	15	10	12
	N		255	260	525	490	175	350	300	240	265
60-69	O	800	600-1100	650	700	350-750	1000	600	1300	900	1800
	H	10	7	12	12	19	29	23-58	33	12	41
	N	210	280	160	210	210	250	-	220	240	515
70-79	O	1200	1250	700	1000	800	1000	600	600	No	800
	H	50	10	17-56	12	15	22	27	22	fig-	26
	N	120	260	270	240	170	95	60	85	ures	175
97-102	O	1600	2100	1200					1500	1300	1100
	H	53	46	39					43	39	55
	N	70	90	45					65	50	45
130, 115-119	O	1400					400	600	1100	1200	800
	H	33					32	30	18	27	40
	N	475					125	115	570	260	295
120-129	O	500-1700	900	900	1100	1300	1000	400-900	600	700	1100
	H	30	22	15	19	22	25	28	22	20	25
	N	130	75	65	65	170	60	60	50	85	350



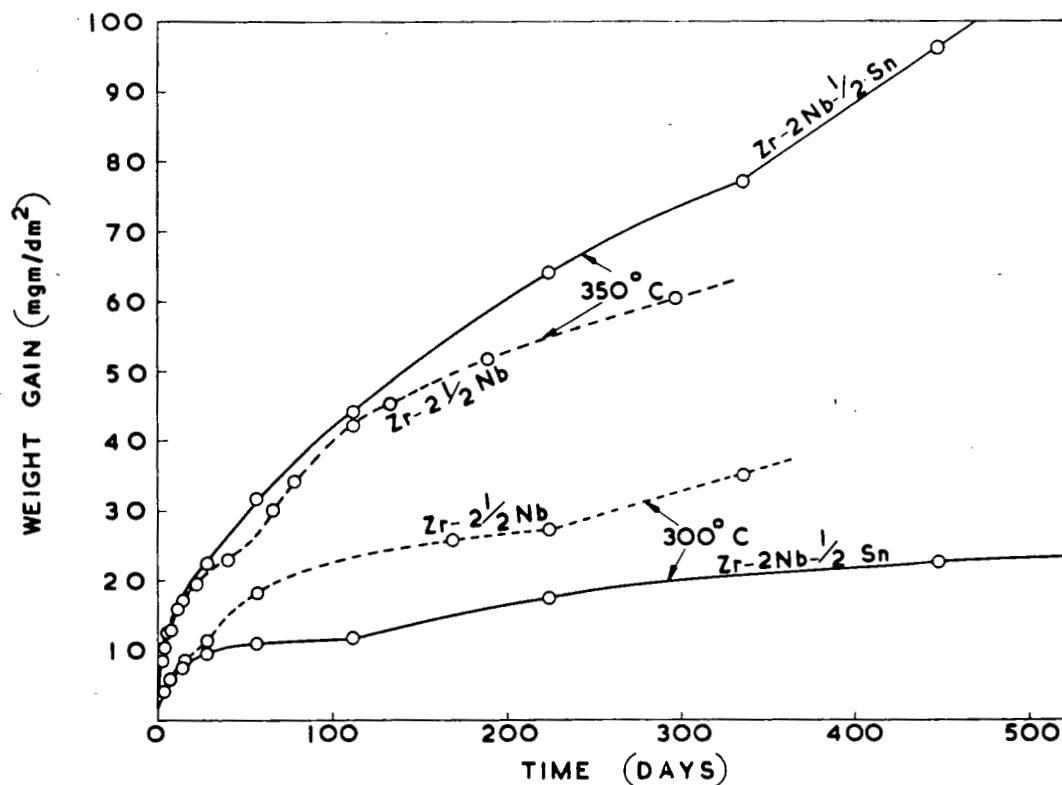


FIG.1. COMPARISON OF Zr-2 1/2 Nb AND Zr-2Nb 1/2 Sn ALLOYS AT 300 AND 350°C IN STEAM AT 1 ATM.

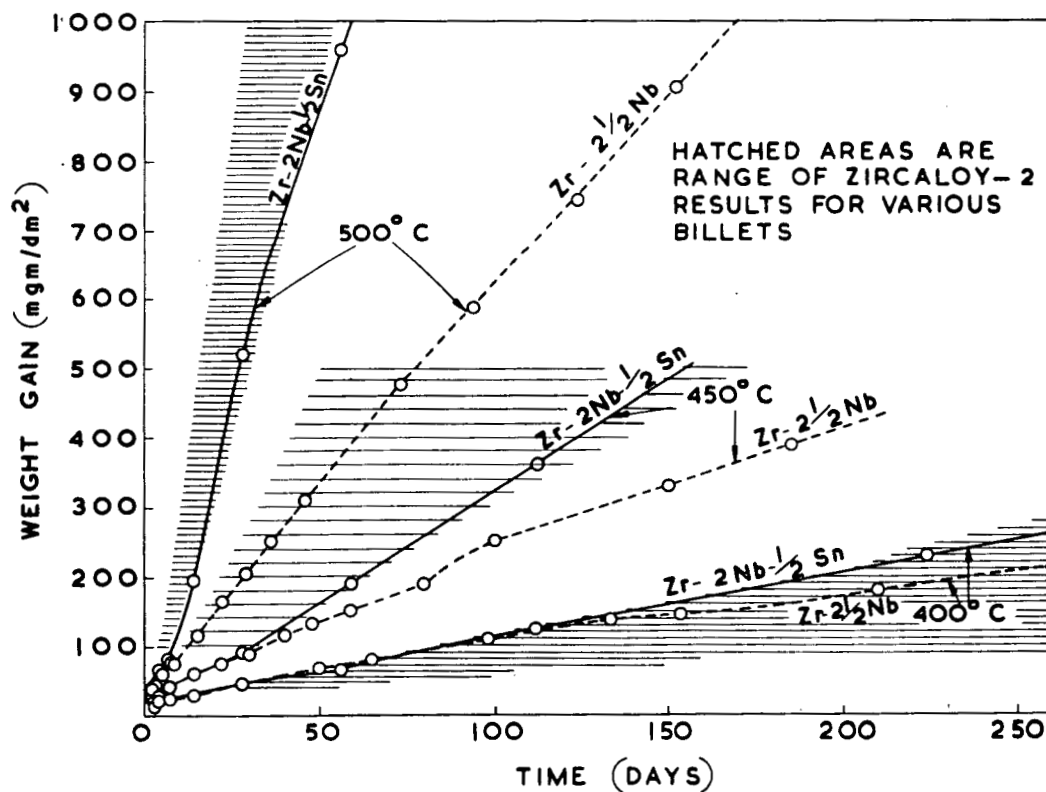


FIG.2. COMPARISON OF Zr-2 1/2 Nb AND Zr-2Nb 1/2 Sn ALLOYS AT 400-500°C IN STEAM AT 1 ATM.

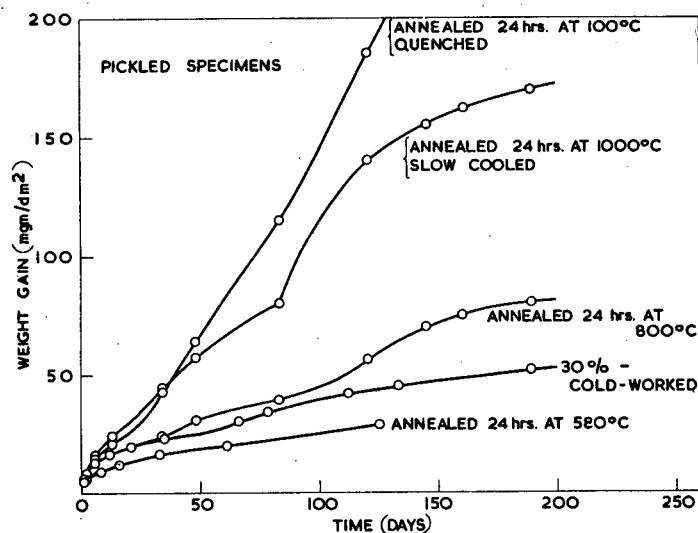


FIG. 3 EFFECT OF HEAT TREATMENT ON THE OXIDATION OF $Zr-2\frac{1}{2}Nb$ AT 350°C IN STEAM AT 1 ATM.

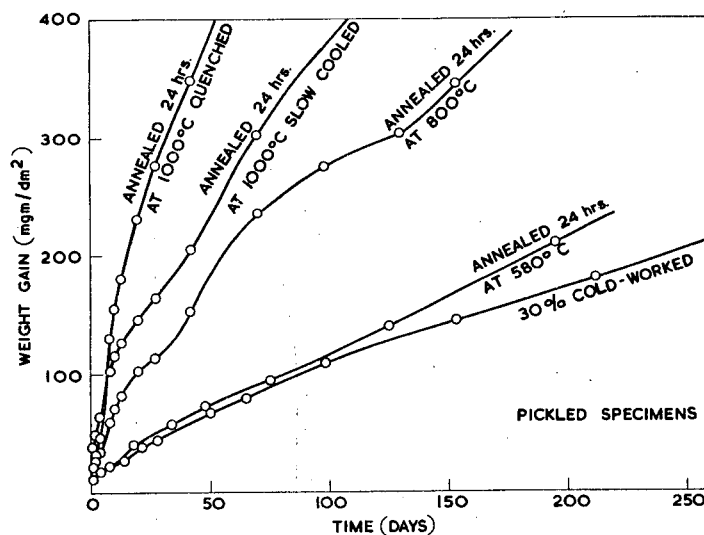


FIG. 4. EFFECT OF HEAT TREATMENT ON THE OXIDATION OF $Zr-2\frac{1}{2}Nb$ AT 400°C IN STEAM AT 1 ATM.

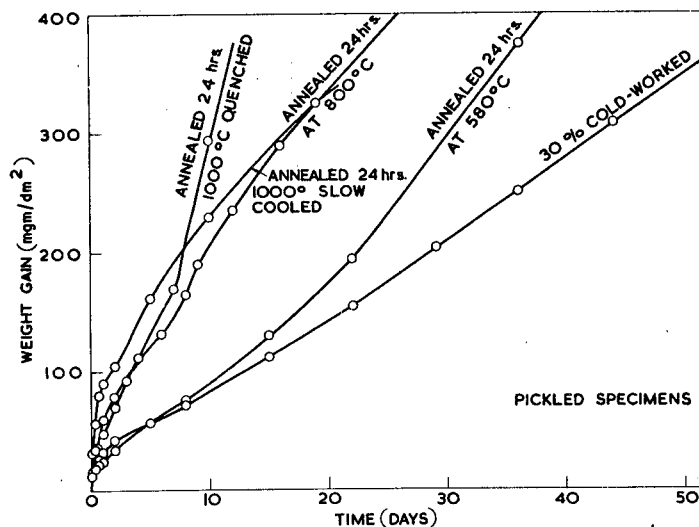


FIG. 5. EFFECT OF HEAT TREATMENT ON THE OXIDATION OF $Zr-2\frac{1}{2}Nb$ AT 500 C IN STEAM AT 1 ATM.

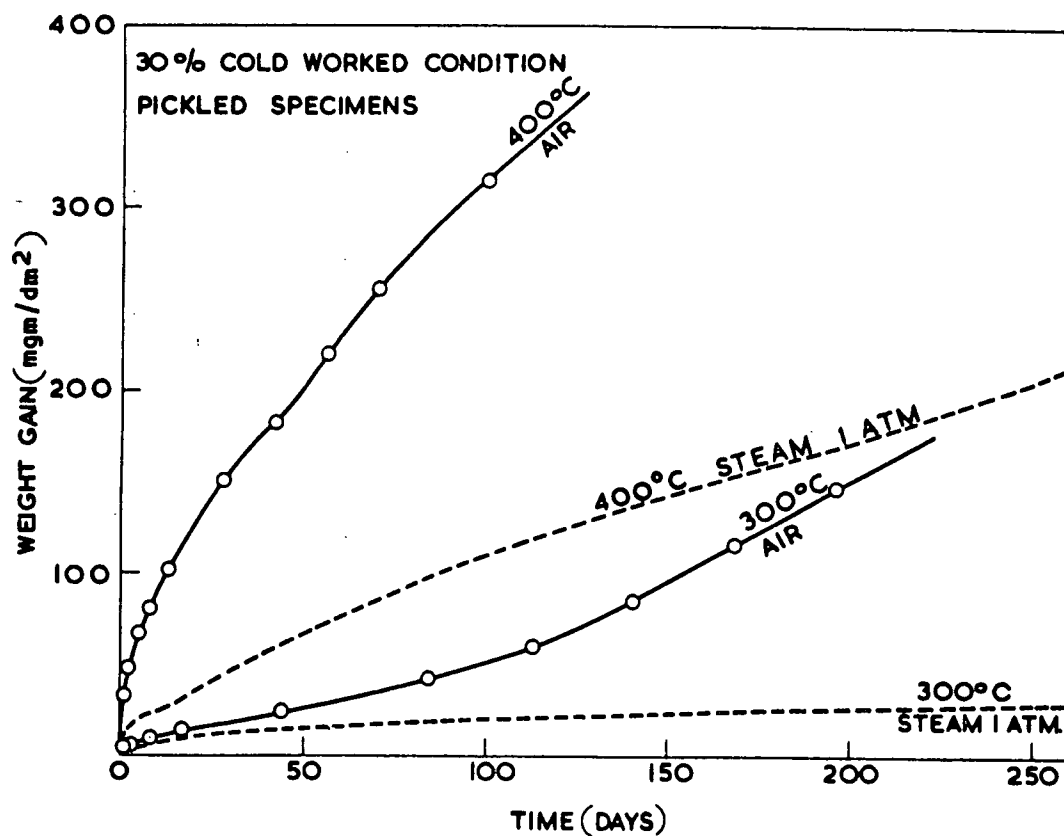


FIG. 6. OXIDATION OF $Zr-2\frac{1}{2}Nb$ ALLOY IN LABORATORY AIR AT 300-400°C

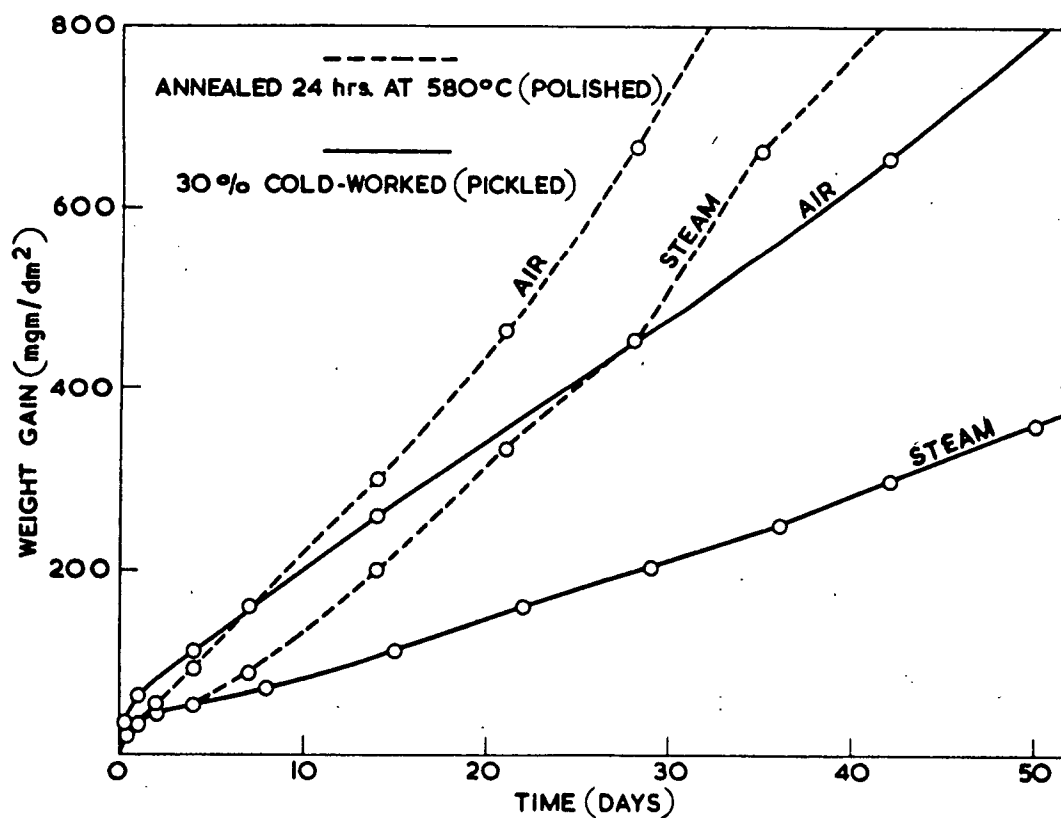


FIG. 7. OXIDATION OF $Zr-2\frac{1}{2}Nb$ ALLOY IN MOIST AIR AT 500°C 1 ATM.

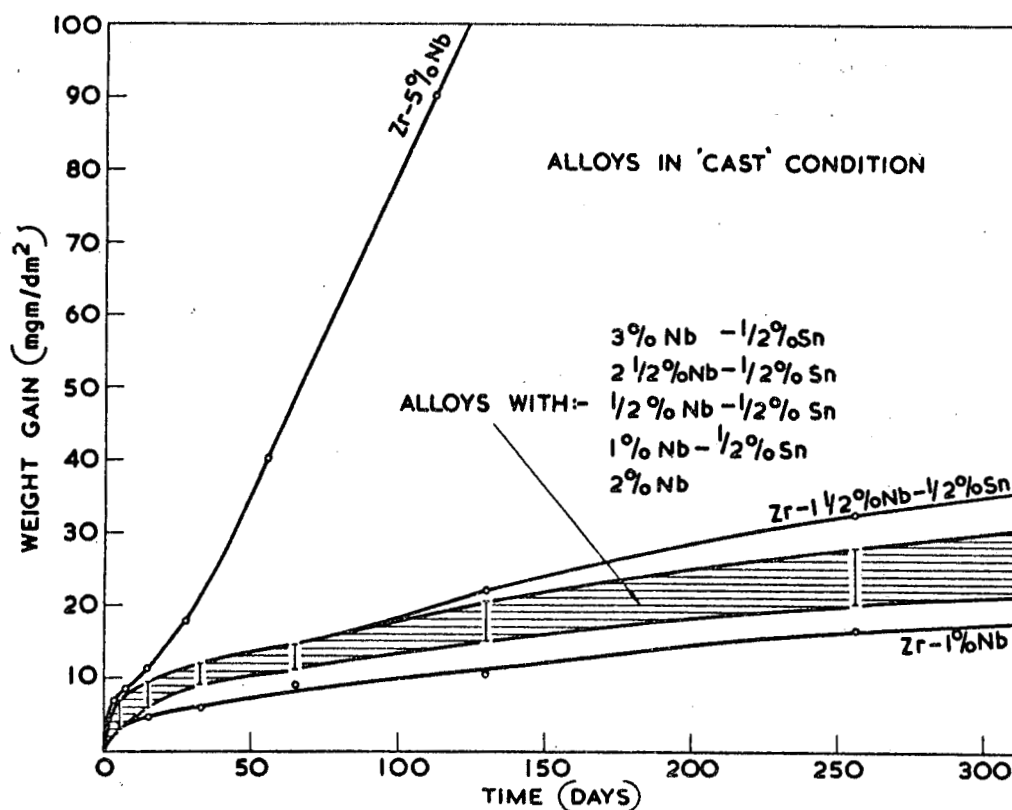


FIG. 8. OXIDATION OF Zr-Nb(-Sn) ALLOYS CONTAINING 1/2-5%Nb AT 300°C
IN STEAM AT 1 ATM.

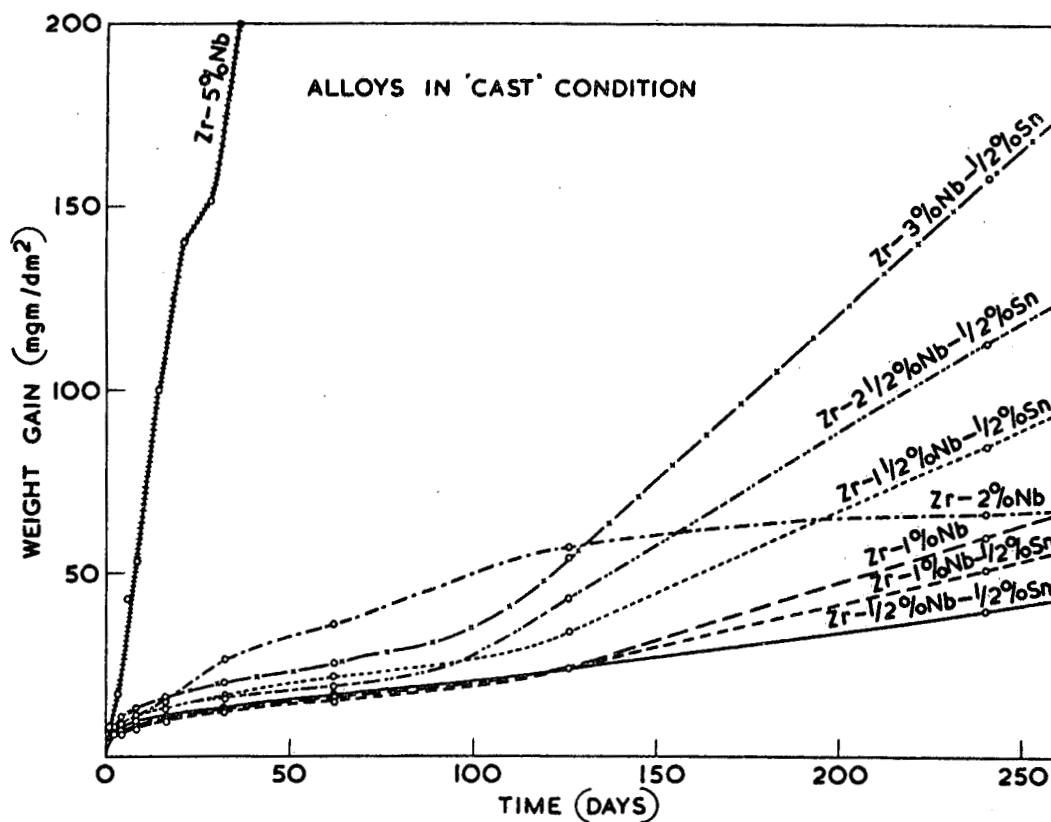


FIG. 9. OXIDATION OF Zr-Nb(-Sn) ALLOYS CONTAINING 1/2-5%Nb AT 350°C
IN STEAM AT 1 ATM

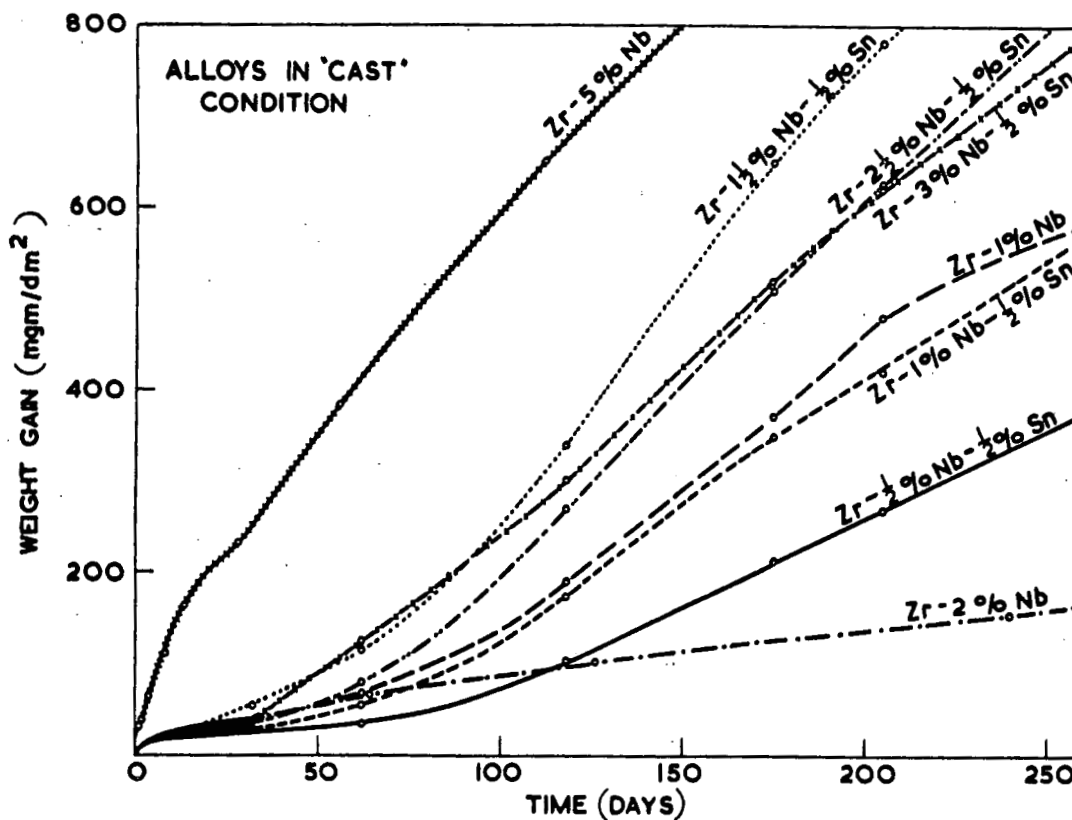


FIG. 10. OXIDATION OF Zr-Nb (-Sn) ALLOYS CONTAINING $\frac{1}{2}$ -5% Nb AT 400°C IN STEAM AT 1 ATM.

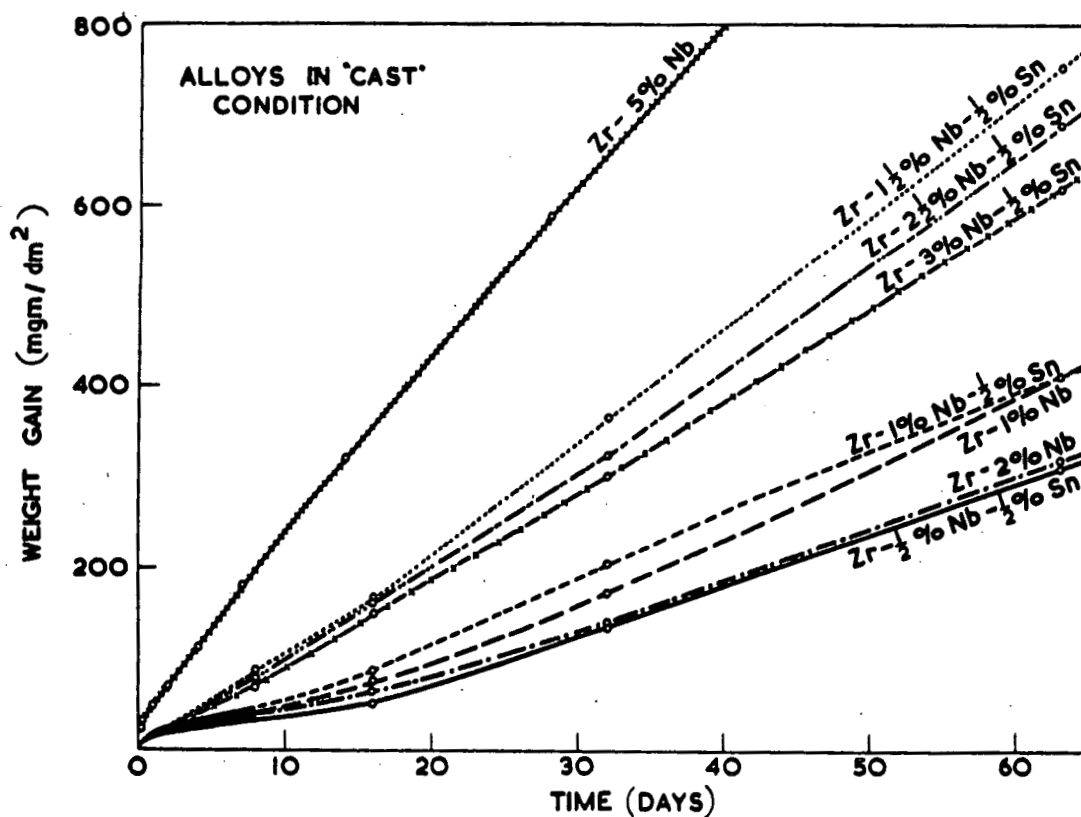


FIG. 11. OXIDATION OF Zr-Nb (-Sn) ALLOYS CONTAINING $\frac{1}{2}$ -5% Nb AT 450°C IN STEAM AT 1 ATM.

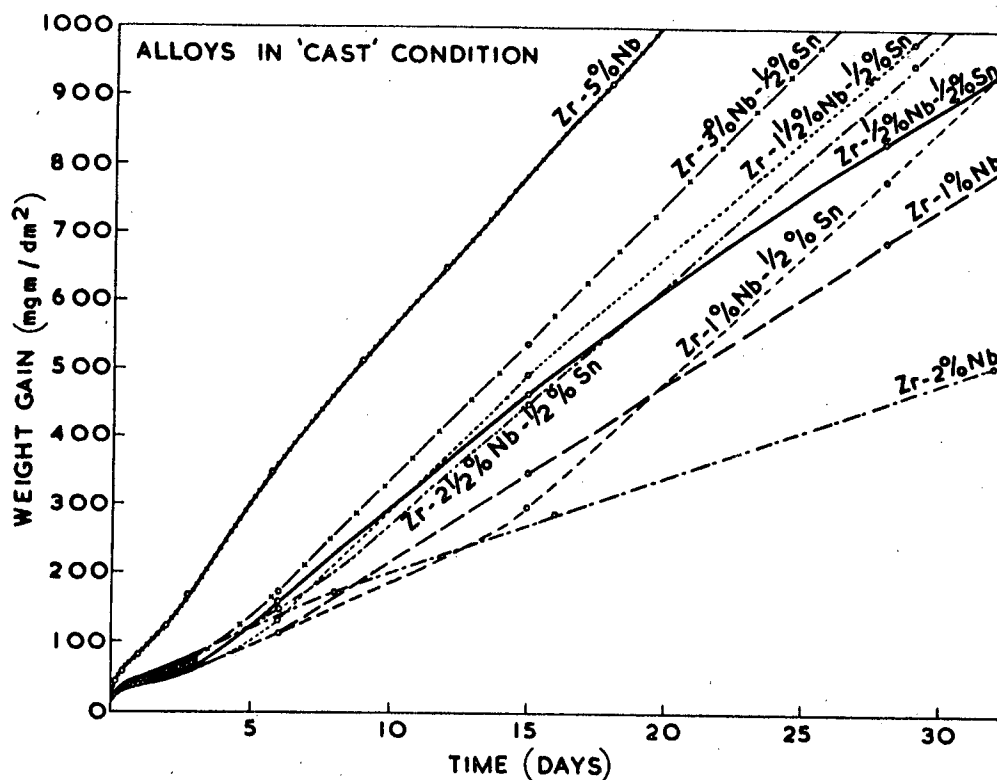


FIG.12. OXIDATION OF Zr-Nb (-Sn) ALLOYS CONTAINING 1/2-5% Nb AT 500°C IN STEAM AT 1 ATM.

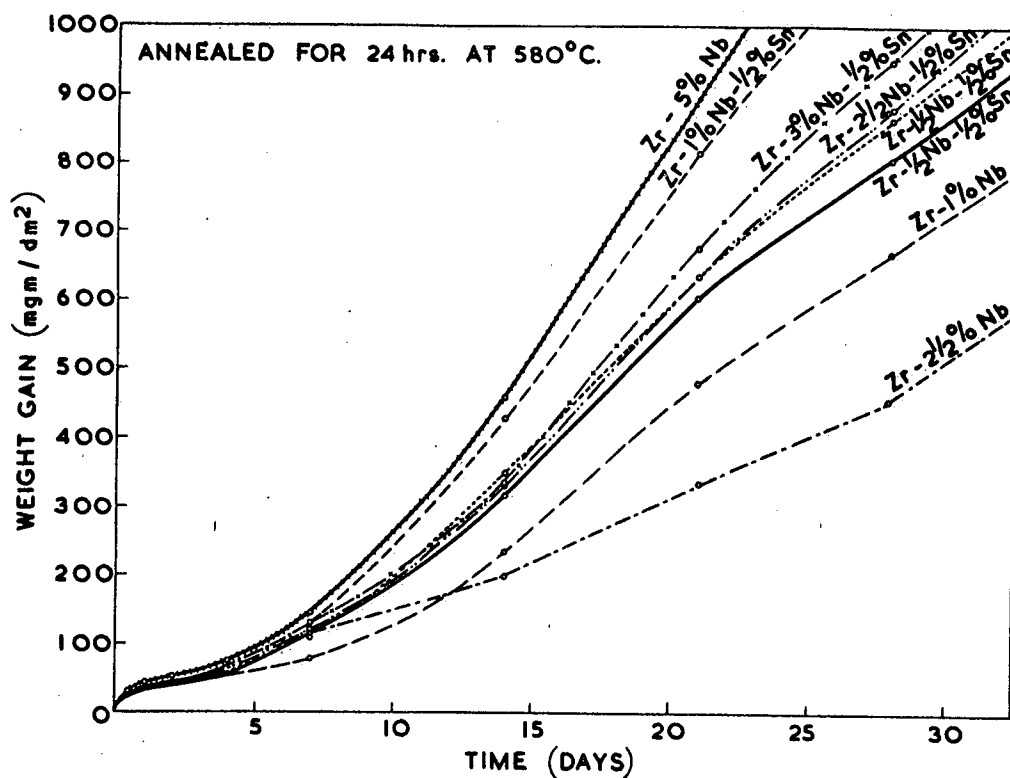


FIG.13. OXIDATION OF Zr-Nb (-Sn) ALLOYS CONTAINING 1/2-5% Nb AT 500°C IN STEAM AT 1 ATM.

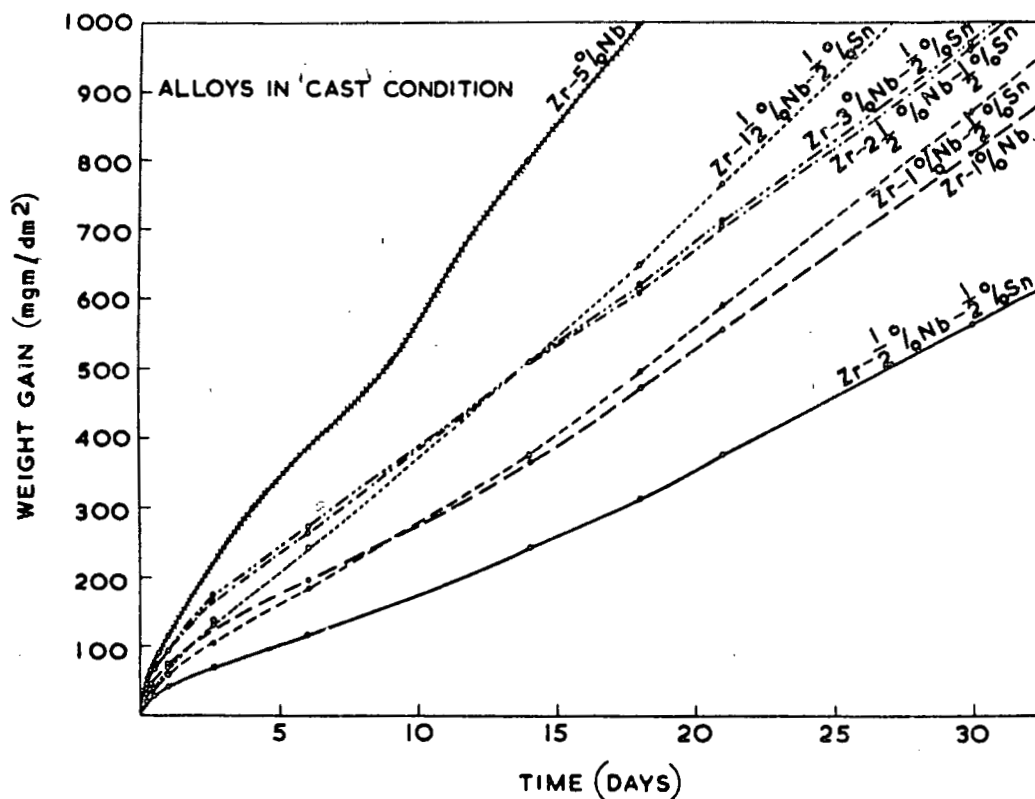


FIG. 14. OXIDATION OF Zr-Nb(Sn) ALLOYS CONTAINING $\frac{1}{2}$ -5% Nb
IN MOIST AIR AT 500°C

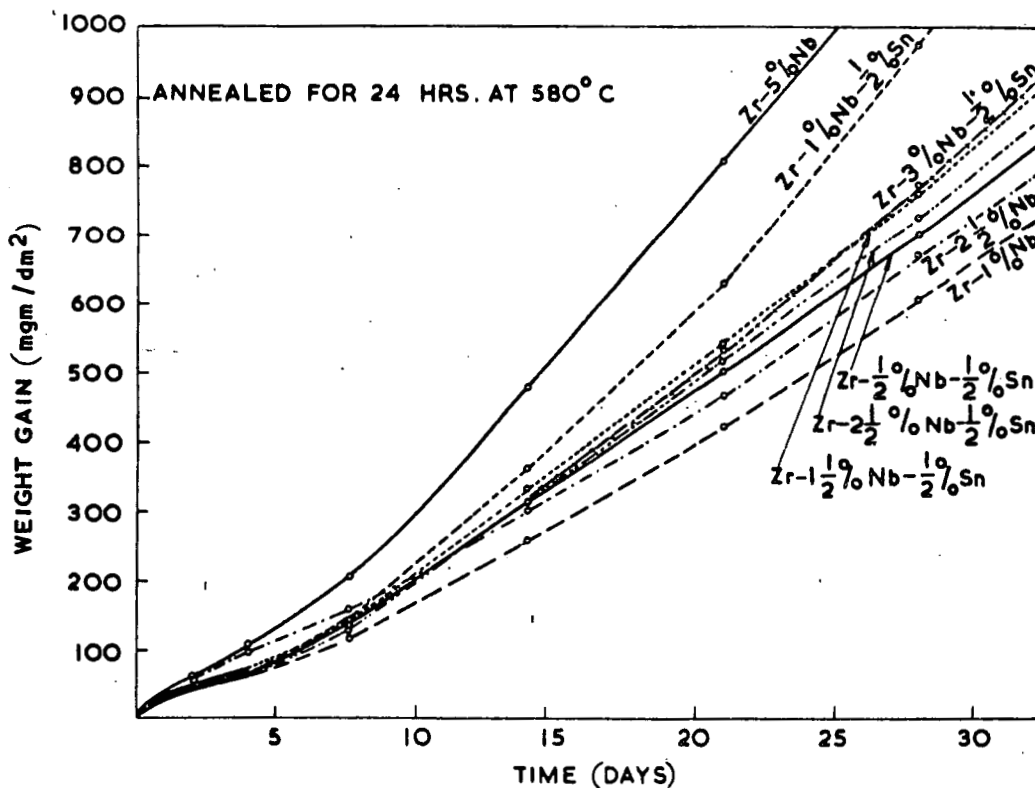


FIG. 15. OXIDATION OF Zr-Nb(Sn) ALLOYS CONTAINING $\frac{1}{2}$ -5% Nb
IN MOIST AIR AT 500°C

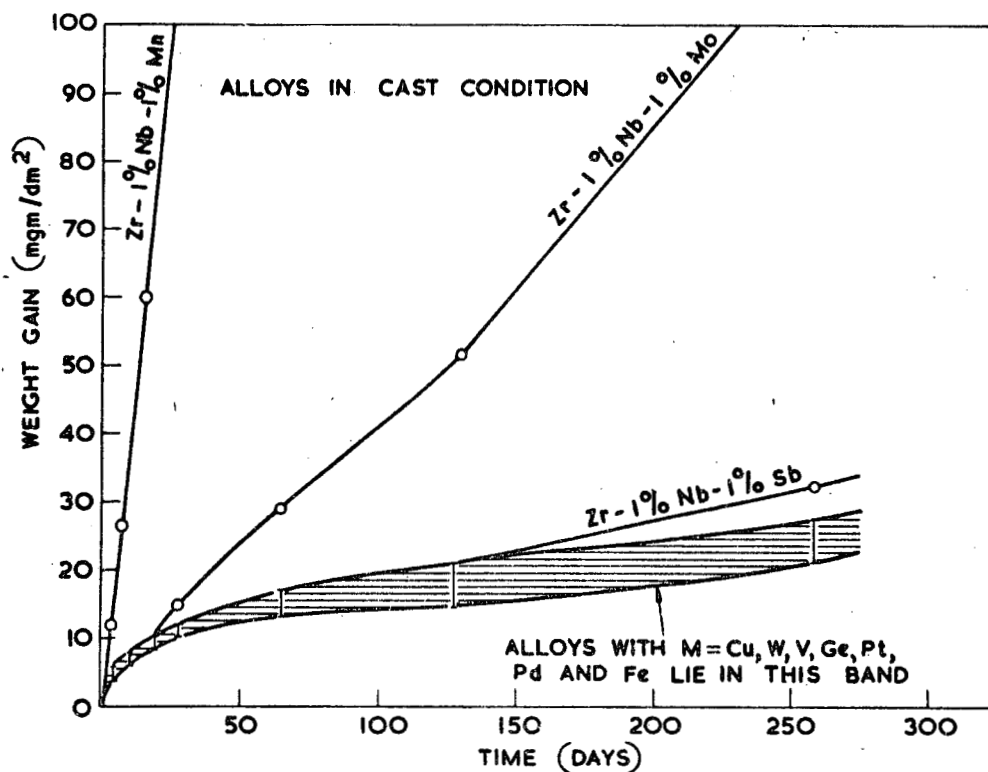


FIG. 16. OXIDATION OF Zr-1%Nb-1%M ALLOYS IN STEAM AT 300°C 1 ATM.

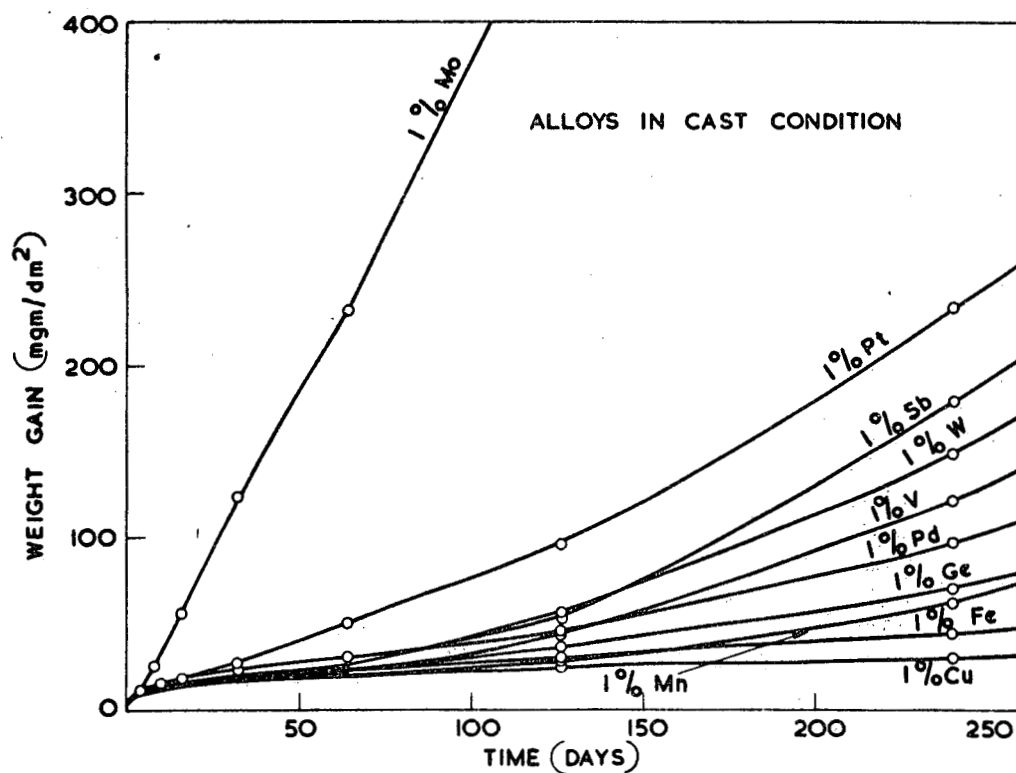


FIG. 17. OXIDATION OF Zr-1%Nb-1%M ALLOYS IN STEAM AT 350°C 1 ATM.

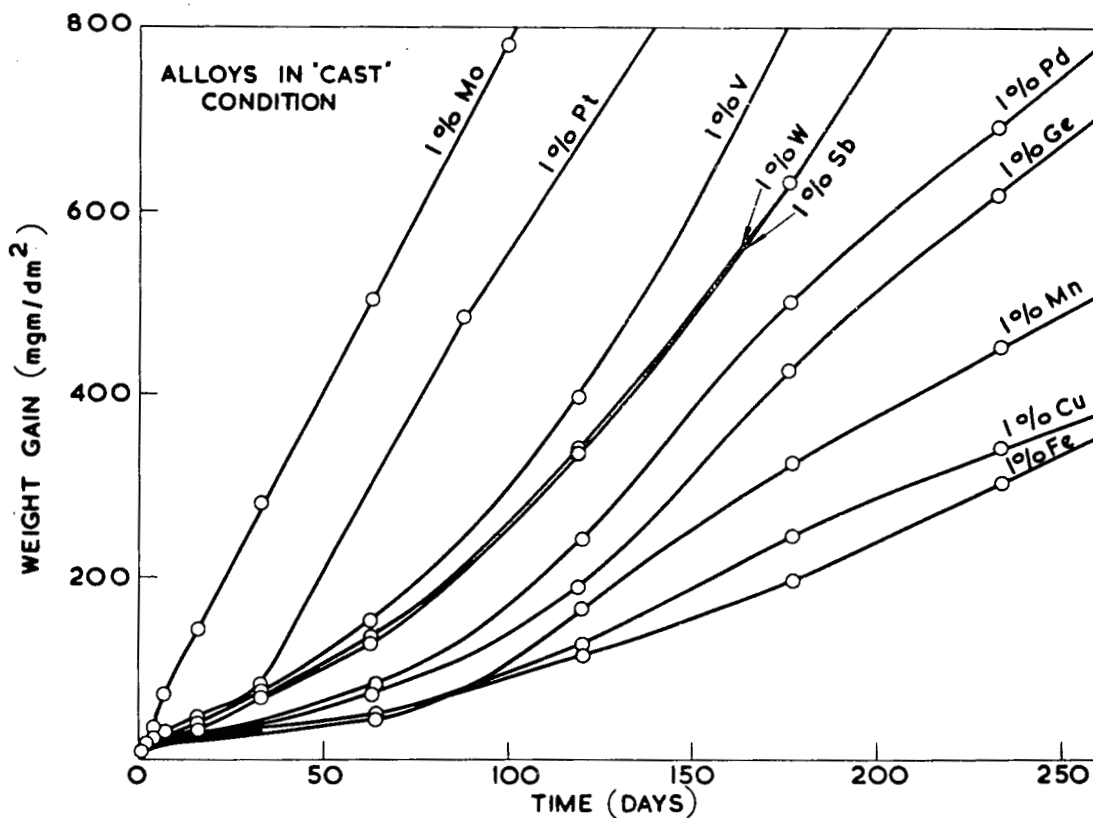


FIG. 18. OXIDATION OF Zr-1% Nb-1% M ALLOYS IN STEAM AT 400°C 1 ATM

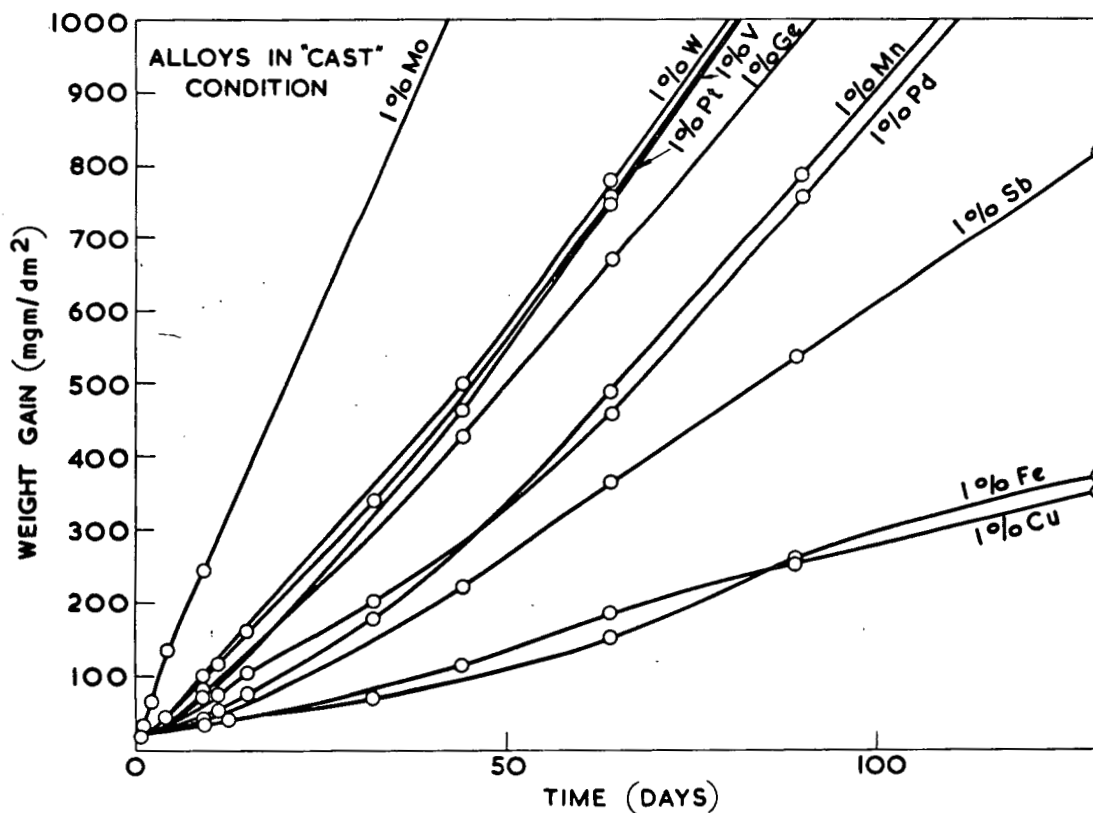


FIG. 19. OXIDATION OF Zr-1% Nb-1% M ALLOYS IN STEAM AT 450°C 1 ATM.

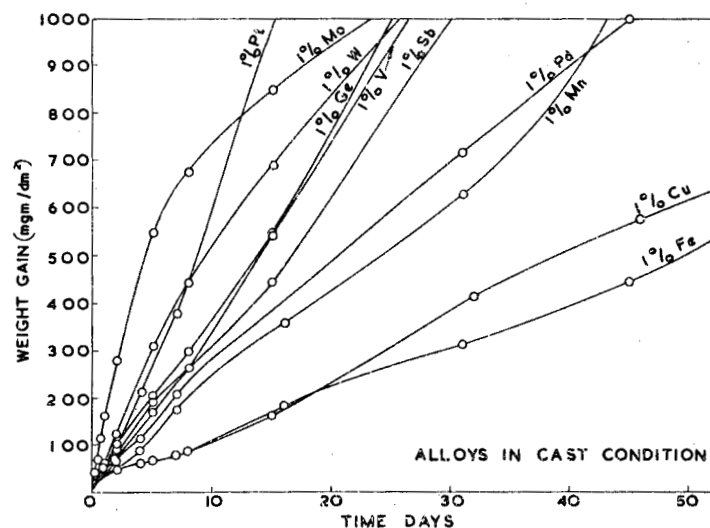


FIG. 20. OXIDATION OF Zr-1%Nb-1%M ALLOYS IN STEAM AT 500°C 1 ATM.

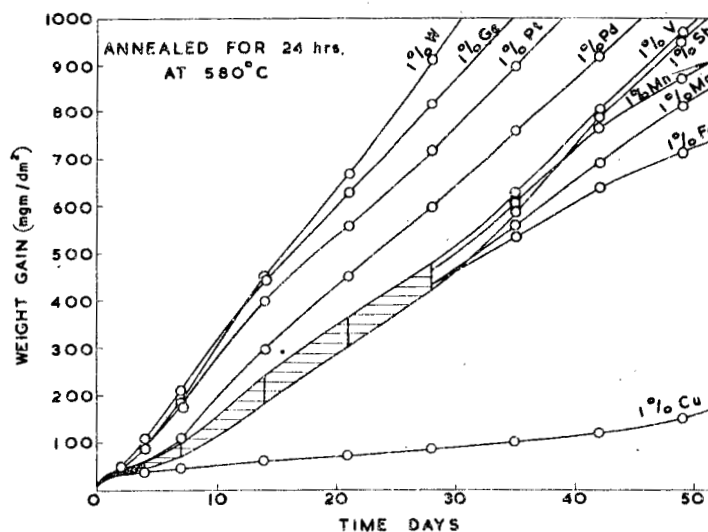


FIG. 21. OXIDATION OF Zr-1%Nb-1%M ALLOYS IN STEAM AT 500°C 1 ATM.

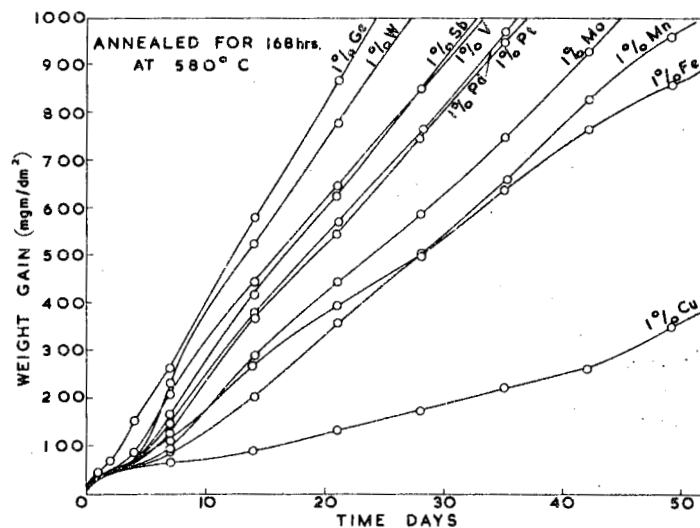


FIG. 22. OXIDATION OF Zr-1%Nb-1%M ALLOYS IN STEAM AT 500°C 1 ATM.

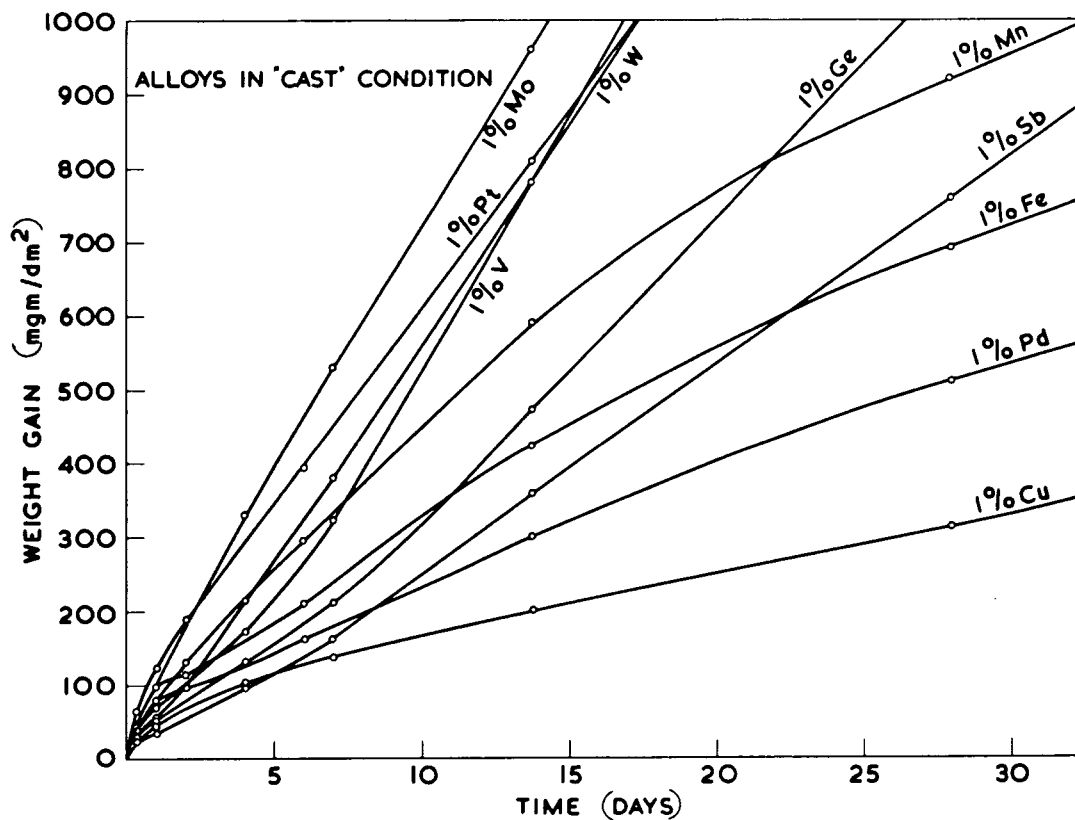


FIG. 23. OXIDATION OF Zr-1%Nb-1%M ALLOYS IN MOIST AIR AT 500°C

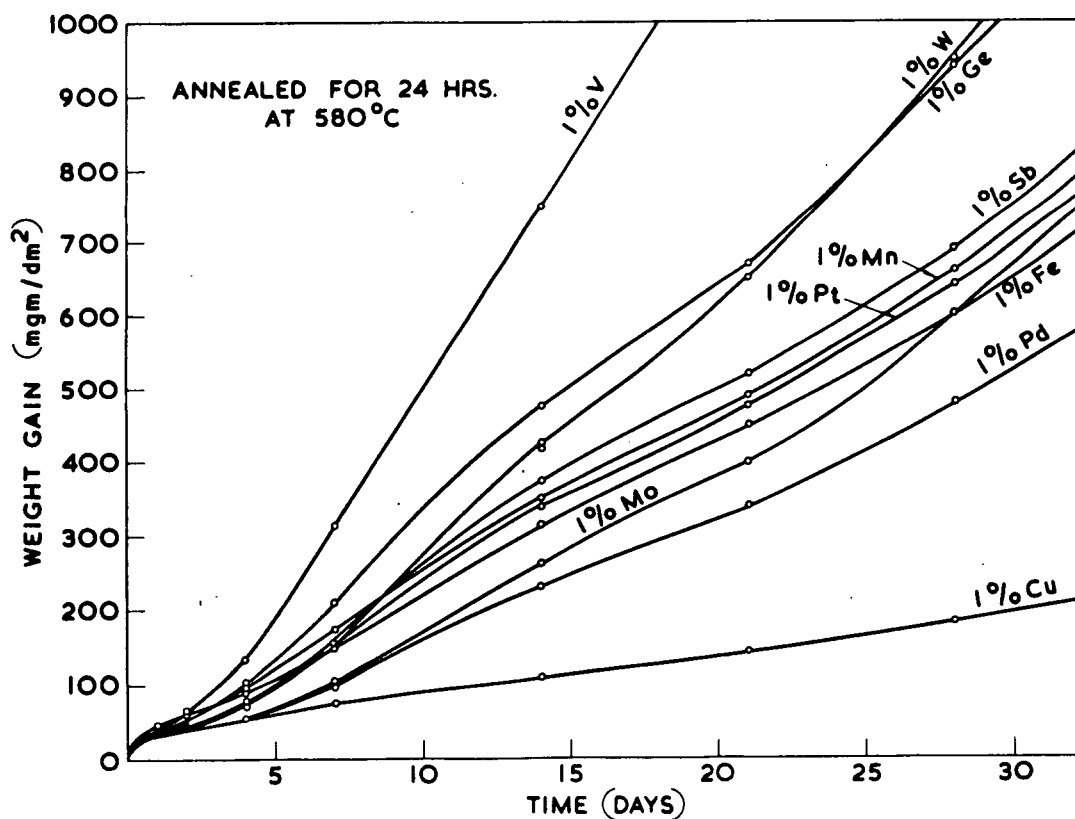


FIG. 24. OXIDATION OF Zr-1%Nb-1%M ALLOYS IN MOIST AIR AT 500°C

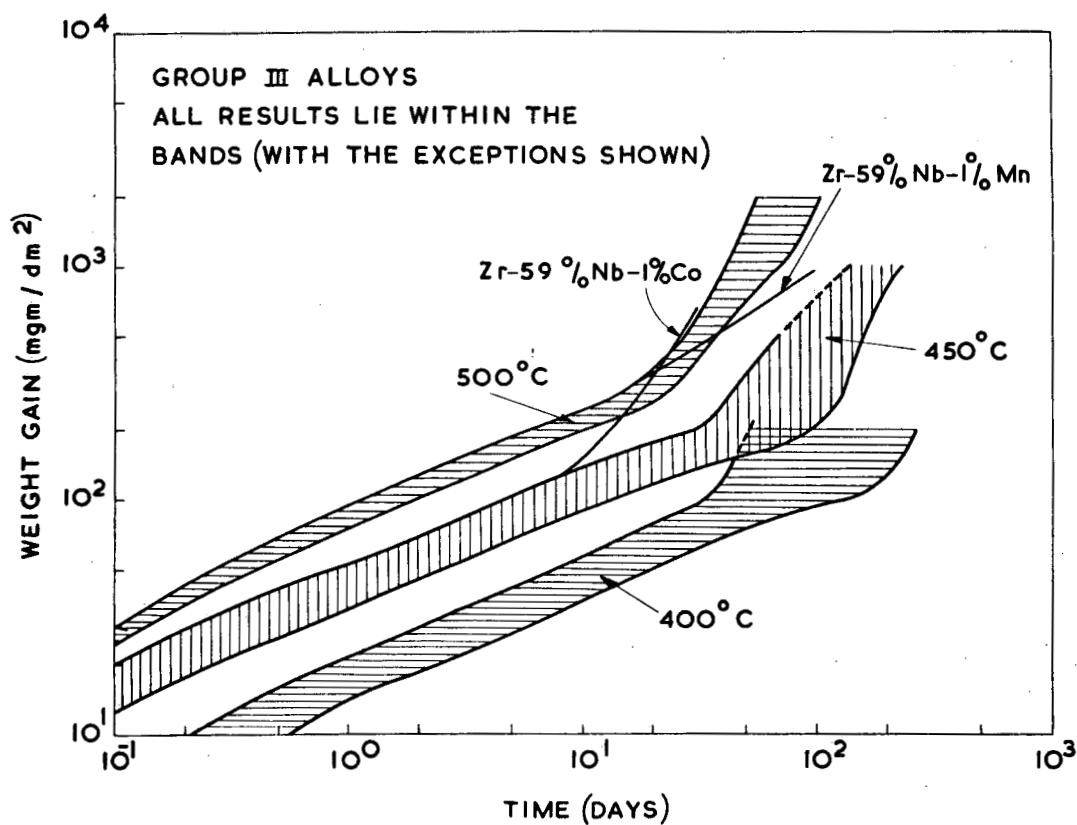


FIG.25. OXIDATION OF Zr-Nb TERNARY ALLOYS (CONTAINING 57-59% Nb)
IN STEAM AT 1 ATM.

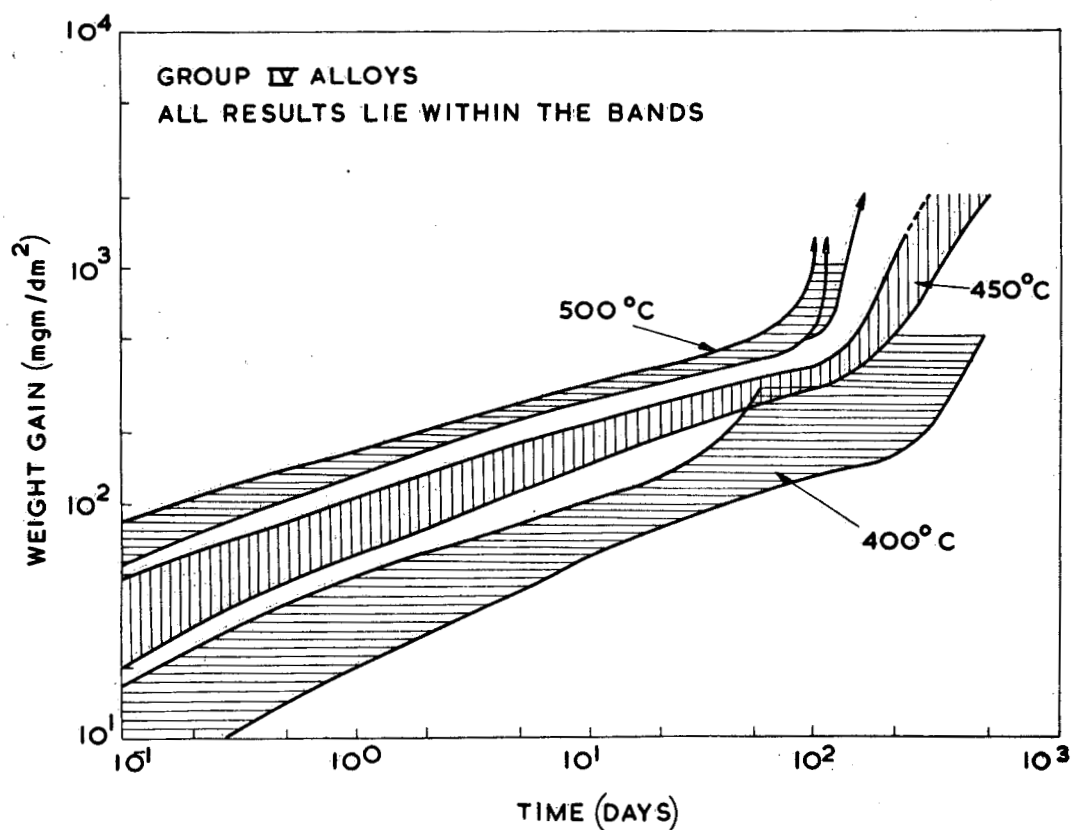


FIG.26. OXIDATION OF Zr-Nb BINARY AND TERNARY ALLOYS (CONTAINING 20-40% Nb)
IN STEAM AT 1 ATM.

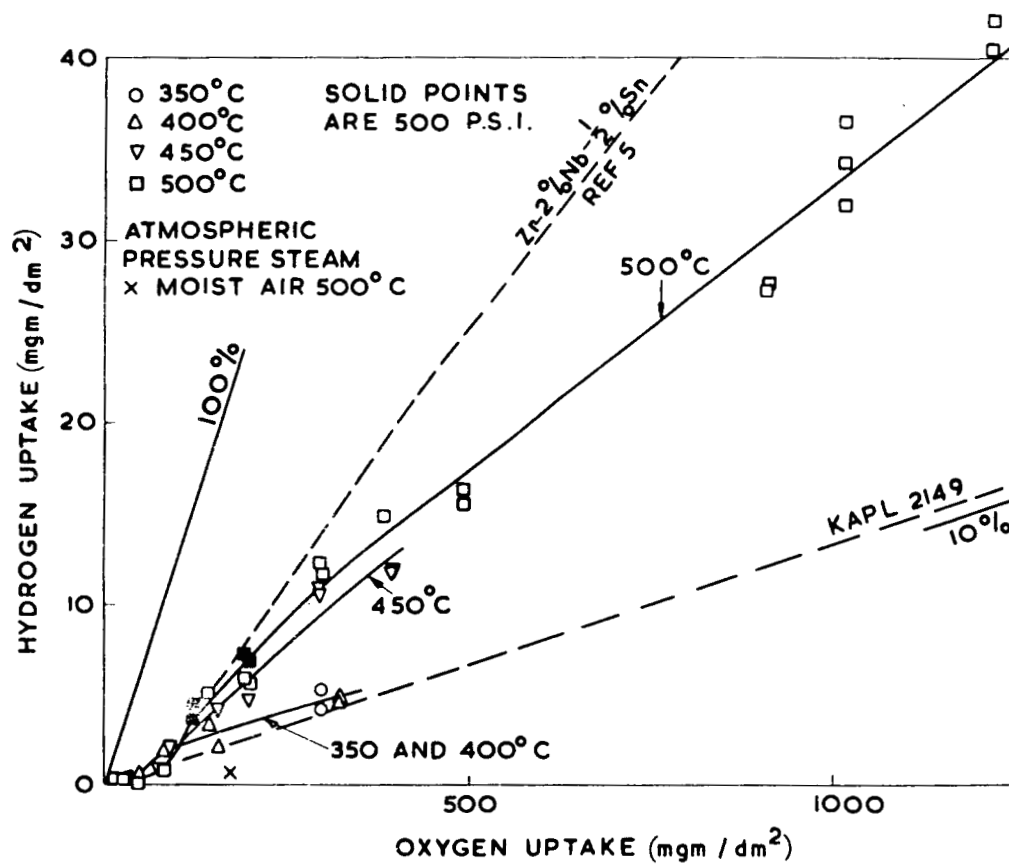


FIG. 27. HYDROGEN ABSORPTION BY $Zr-2\frac{1}{2}Nb$ ALLOY

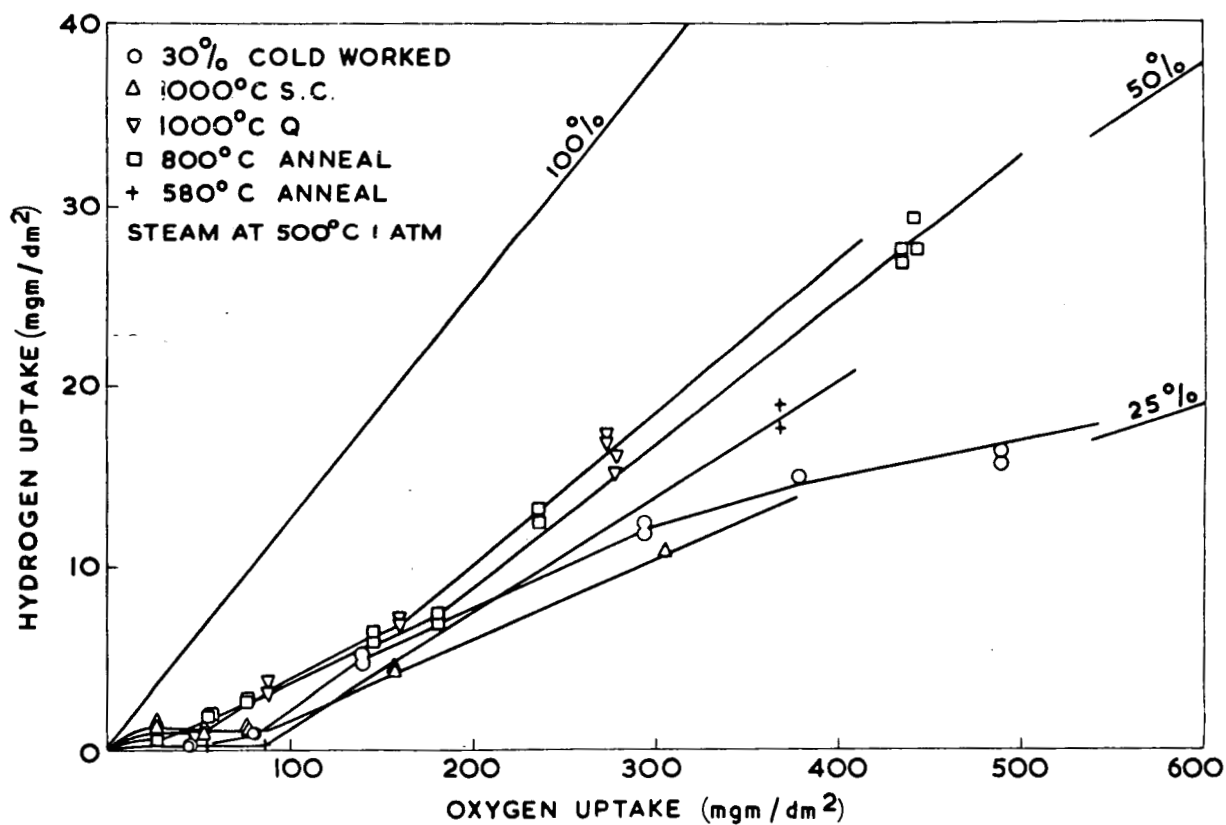
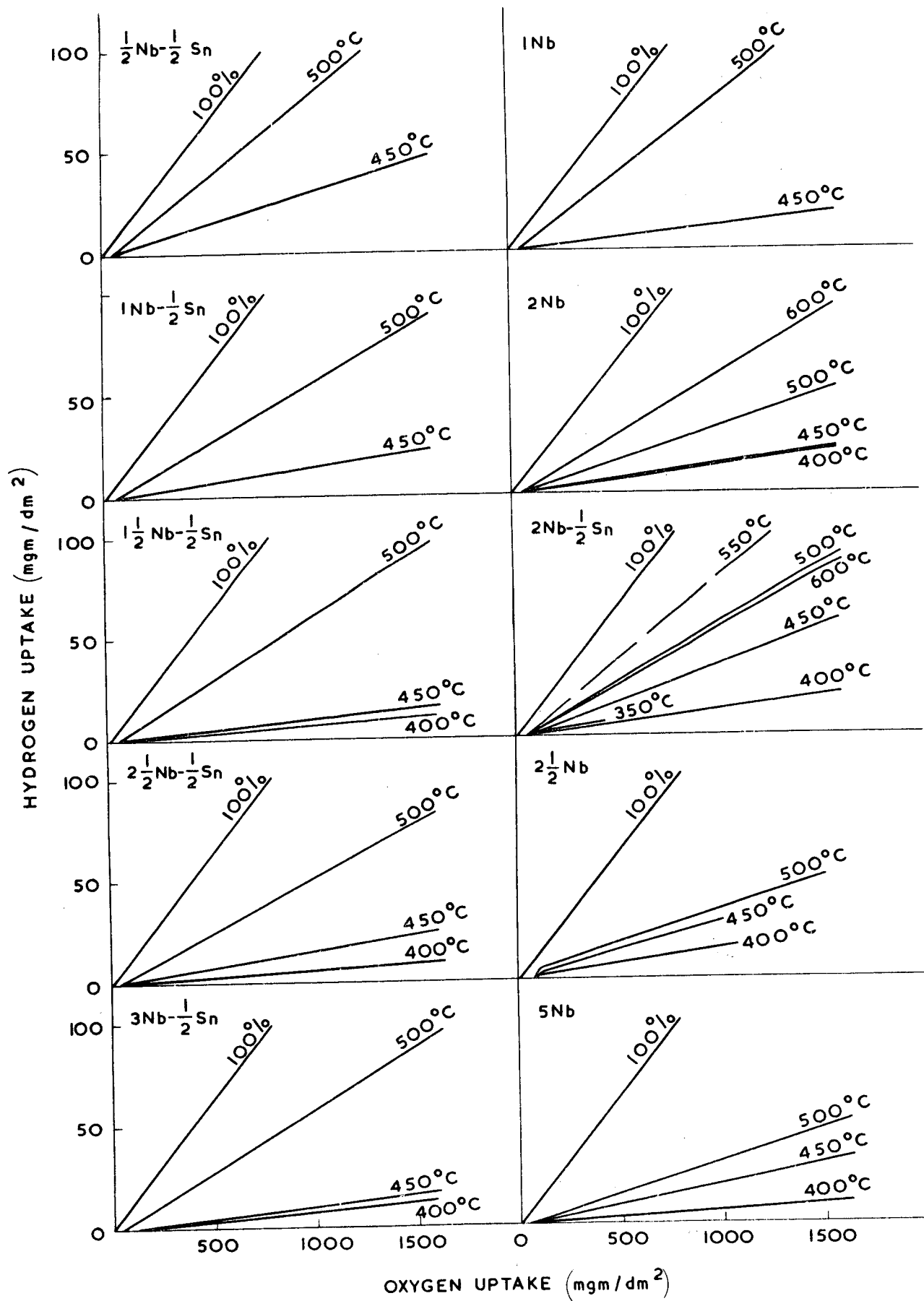
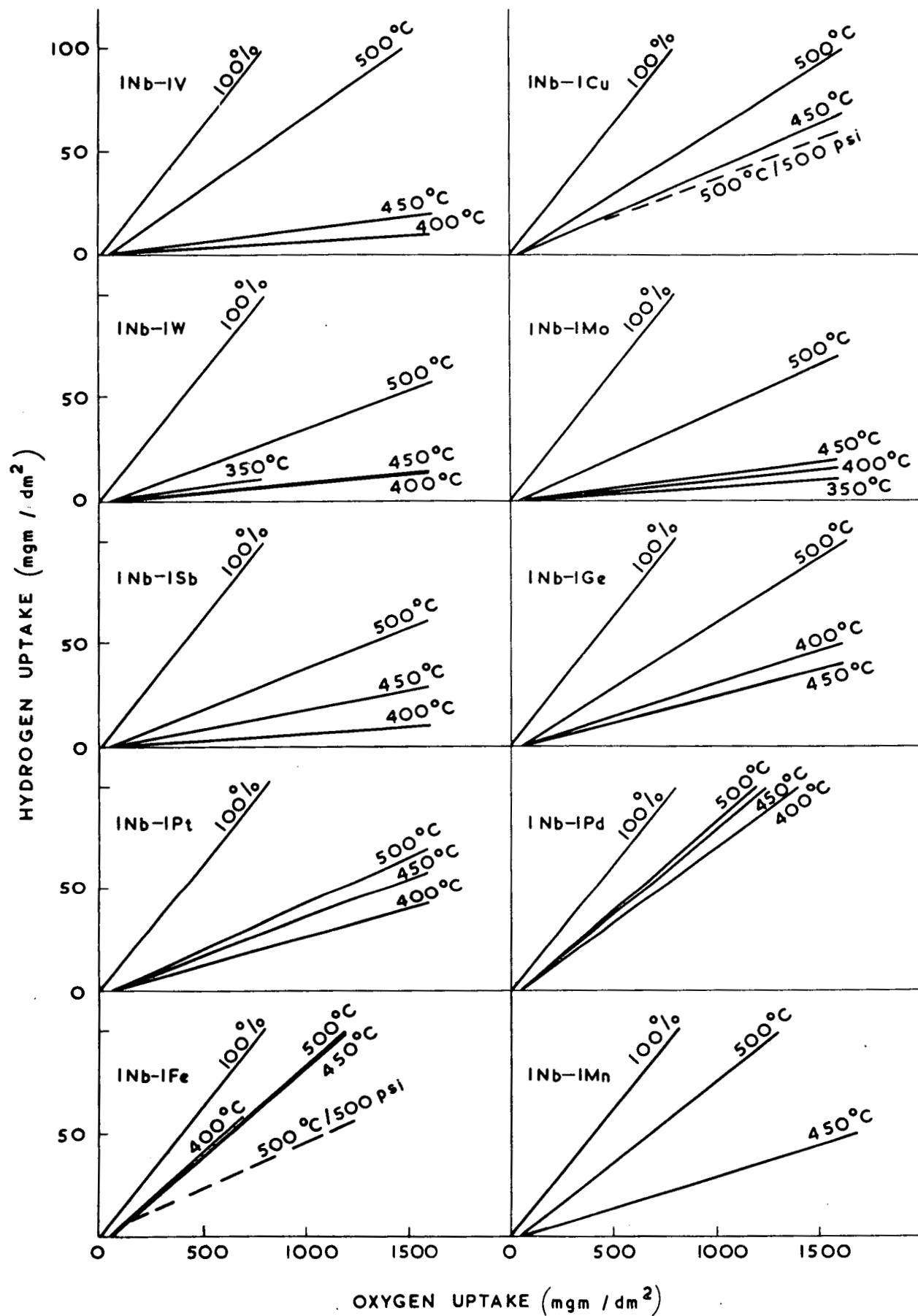


FIG. 28. EFFECT OF HEAT TREATMENT ON H UPTAKE BY $Zr-2\frac{1}{2}Nb$



A. E. R. E. R4134 FIG. 29. HYDROGEN ABSORPTION BY
LOW NOBIUM ALLOYS (STEAM 1 ATM)



A. E. R. E. R4134 FIG. 30 HYDROGEN ABSORPTION BY
Zr-INb-IX ALLOYS (STEAM 1 ATM)