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Abstract

With the view of examining the oxidation behavior of Zircaloy-4 under limited steam supply occurring in severe accidents of LWRs, Zircaloy-4 cladding specimens were examined at the isothermal oxidation temperatures of 1000 and 1300 °C under a steam atmosphere, flowing at a reduced and constant rate in the range of $3 \sim 170$ mg/cm^2· min.

The effect of steam starvation, which was restricted to very low levels of steam supply rate, was observed at the two examined temperatures. And the critical supply rate of steam starvation was evaluated to be 13 and 20 mg/cm^2·min for the oxidation at 1000 and 1300 °C, respectively.

Variation of the oxidation duration between 2 and 60 min at 1000 °C allowed to compare the reaction kinetics for three different rates of steam supply. The short-term results confirmed the reduced reaction rates for the lower steam supplies. At the longer times, however, a clear trend towards linear kinetics was observed for the lower supplies. This can be interpreted as the result of earlier breakaway transition under limited steam supply.

In the test at 1300 °C, an acceleration of the oxidation rate was measured for the specified steam supply rate between 20 and 60 mg/cm^2· min. This related strongly with high hydrogen concentration in the atmosphere.

Hydrogen blanketing - the retarding effect of hydrogen on Zircaloy oxidation - was not identified in the examined temperature range.

Zusammenfassung

Oxidation von Zircaloy-4 unter begrenztem Dampfangebot bei 1000 und 1300 °C

Im Hinblick auf das Oxidationsverhalten von Zircaloy-4 unter begrenztem Dampfangebot während schwerer Unfälle von Leichtwasserreaktoren wurde die Oxidation von Zircaloy-4 Hüllrohrproben in Dampfatmosphäre bei konstanten Temperaturen von 1000 und 1300 °C untersucht. Die Flußdichte des strömenden Dampfes wurde dabei konstant gehalten und auf den Bereich 3-170 $mg/cm^2 \cdot min$ reduziert.

Bei beiden untersuchten Temperaturen wurde Dampfmangel beobachtet, der auf sehr niedrige Bereiche des Dampfangebots begrenzt war. Die kritischen Dampf-Flußdichten wurden zu 13 bzw. 20 $mg/cm^2 \cdot min$ für die Oxidation bei 1000 bzw. 1300 °C bestimmt.

Die Variation der Reaktionsdauer zwischen 2 und 60 min bei 1000 °C erlaubte den Vergleich der Oxidationskinetik für drei verschiedene Dampfangebote. Die Kurzzeit-Ergebnisse bestätigten den verminderten Reaktionsumsatz für die geringeren Dampf-Flußdichten. Über die längeren Reaktionszeiten wurde für diese jedoch die klare Tendenz zu linearer Kinetik beobachtet. Das kann als Folge des frühzeitigeren Übergangs zu Breakaway-Oxidation bei vermindertem Dampfangebot gedeutet werden.

In den Tests bei 1300 °C wurde eine Beschleunigung der Oxidation für vorgegebene Dampf-Flußdichten zwischen 20 und 60 $mg/cm^2 \cdot min$ gemessen. Dies stand in enger Beziehung zu hoher Wasserstoffkonzentration in der Atmosphäre.

Das sog. "hydrogen blanketing", die verzögernde Wirkung von Wasserstoff auf die Oxidation von Zircaloy, wurde im untersuchten Temperaturbereich nicht nachgewiesen.

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1. Introduction

Concerning severe fuel damage (SFD) accident in light-water-cooled nuclear power reactors, it is one of the highly important items to evaluate the oxidation behavior of Zircaloy cladding, since the reaction rate of its oxidation has a major influence on core heatup and related damage.

The Zircaloy-steam reaction has already been widely investigated for the loss-of-coolant accident (LOCA) analysis (1) ∿ (6), and the picture is now fairly clear. However, in most of these investigations, oxidation experiments were performed under the condition of so-called unlimited steam supply. On the other hand, the calculation with MARCH2 code for severe accidents (7) showed that sufficient steam was not supplied to oxidize all Zircaloy in the reactor core. And it is also expected that Zircaloy in the upper portion of the core would be oxidized under limited steam supply if the reaction in the lower portion would be very intense and a flow channel blockage would occur. It can be, therefore, expected that some part of the Zircaloy in the core would be oxidized under the steam-starved and hydrogen enriched atmospheric condition. Consequently, it is probably not appropriate to apply the reaction kinetics of Zircaloy-steam oxidation obtained from the previous data set directly to the SFD analysis.

It has already been known that Zircaloy would be less oxidized under the condition of limited steam supply. For instance, the author et al. (8) reported that less oxidation of Zircaloy was measured in stagnant steam for oxidation temperatures between 900 and 1200 °C. However, in this series of the test, the atmospheric condition inside the reaction chamber varied largely during each test because of the hydrogen generation with Zircaloy-steam reaction. Chung and Thomas (9) showed that the Zircaloy oxidation rates at 1200 to 1700 °C were slower in hydrogen-steam mixtures than in pure steam or helium-steam environments. And they concluded that the retardation of oxidation rates could be caused by the hydrogen-blanketing.

Referring to their experiments, however, the experimental apparatus was not adequate to allow well controlled atmospheric conditions. In the tests by Chung and Thomas (9), the 90 mm long Zircaloy-4 cladding specimen was positioned vertically in a bell jar and heated in a hydrogen-steam mixture supplied through an inlet. Consequently, hydrogen enrichment in the upper space of bell jar is possibly expected to occur during each test, especially in cases of low supply rates of hydrogen-steam mixture.

Many more investigations under well controlled atmospheric conditions, therefore, desired to perform in order to make clear the oxidation behavior of Zircaloy under conditions expected in SFD accidents. The present work describes the results of Zircaloy-4 oxidation experiments conducted at 1000 and 1300 °C in an atmosphere, provided by steam flowing at a reduced and constant rate in the range of 3 ∿ 170 $mg/cm^2 \cdot min$.

2. Experimental

2.1 Specimen and Apparatus

The chemical composition of Zircaloy-4 used in this experiment is listed in Table 1. A schematic illustration of the specimen and the apparatus for Zircaloy-steam oxidation is shown in Fig. 1. Tubular specimens of 30 mm in length were prepared by cutting PWR size Zircaloy-4 cladding tubes of 10.75 mm in outer diameter and 9.30 mm in inner diameter. Prior to oxidation, the specimens were pickled in a mixture of nitric and hydrofluoric acids for one minute and then rinsed in distilled water. The apparatus consists of a quartz-made reaction tube of 20 mm in inner diameter, an electric resistance furnace and a steam generator.

2.2 Experimental Procedures

Before each oxidation test, the atmospheric pressure loop of the apparatus was purged with argon gas and then with steam. The specimen was inserted into the mid-part of the reaction tube within the furnace, which had been previously stabilized at a specified test temperature, and oxidized in steam of reduced and constant flow rate in the range of 3 ∿ 170 $mg/cm^2 \cdot min$, realized by a small steam generator and calibrated through the evaporation rate during steady-state operation for several hours. The longitudinal temperature difference in the length of 60 mm of the mid-part of the furnace was maintained within ± 1 °C during each test. The uniformity of temperature distribution along the mid-part of the furnace was, therefore, considered to be sufficient for the oxidation experiment of small-sized specimen. The temperature was measured with a Pt-Pt/18%Rh thermocouple spotwelded on the inner surface of the specimen at its mid-point. The specimen was isothermally oxidized at 1000 or 1300 °C. Temperature overshooting due to the exothermic reaction between Zircaloy and steam was avoided, if necessary, by shifting the location of the specimen. After maintaining the isothermal oxidation for a predetermined duration ranging from 2 to 60 minutes, the specimen was quickly pulled out of the furnace and cooled.

2.3 Evaluation

The weight of the specimen was measured with a direct reading balance before and after each test, thereby the weight gain due to oxidation was calculated. All of the specimens were examined metallographically to know the extent of the reaction and the morphology of oxide film. In addition to these measurements, selected specimens were analyzed by hot extraction analysis to determine the content of absorbed hydrogen and oxygen.

3. Results and Discussion

3.1 Oxidation at 1000 °C

Experimental conditions and measured weight gain of the specimens oxidized at 1000 °C for 15 min are listed in Table 2. In these experiments, the steam supply rate is defined as the weight of steam which passes the unit cross-sectional area of the reaction tube in one minute, i.e. $mg/cm^2 \cdot min$.

Figure 2 shows the correlation between the weight gain of Zircaloy specimens oxidized at 1000 °C for 15 min and the steam supply rate. Leistikow and Schanz (10) have given an empirical expression for the weight gain of Zircaloy in unlimited steam flow in the form,

$$\tau = 0.724 \sqrt{t} \exp(-10481/T) \qquad \langle 1 \rangle$$

where τ : Oxygen uptake (g/cm^2),

t : Oxidation time (s),

T : Oxidation temperature (K).

For the purpose of comparison, the value of weight gain calculated with Eq. <1> is also shown in Fig. 2 as a dotted line. Noticable difference in the weight gain of specimens is not seen in the range of steam supply rate above the critical value of some 13 $mg/cm^2 \cdot min$. In this range of the flow rate, the weight gain settles on the roughly constant level of 5 mg/cm^2. There is about 15% difference between the experimental data and the calculated value. Table 3 shows the oxygen and hydrogen content in Zircaloy specimens oxidized at 1000 °C for 2 ∿ 60 min. The oxygen and hydrogen were analysed in the two parts of each specimen, i.e. the top-end and the bottom-end to the direction of steam flow as shown in Fig. 3. Specimens of nrs. 209 and 214 were oxidized for 15 min in the range of steam supply rate above the critical value. In both cases, the content of oxygen in the top-end portion of the oxidized specimen is slightly higher than that in the bottom-end. Therefore, the difference can be partly interpreted as an effect of steam consumption along the specimen length.

On the other hand, a sharp decrease of weight gain is observed in the range of the rate below the critical value with decreasing the steam supply rate. This can be taken for the effect of steam starvation.

As shown in Table 3, the hydrogen content in the specimens of nos. 209 and 214 was analyzed to be 20 ∿ 30 wt.ppm. The initial hydrogen content in the cladding tube used in this experiment is specified to be 6 wt.ppm. It can be, therefore, estimated that these two specimens didn't absorb perceivable amount of hydrogen during oxidation at 1000 °C for 15 min. In contrast to these specimens, the specimen of no. 204 oxidized for 15 min in the steam flow of 3.2 $mg/cm^2 \cdot min$ contains 100 ∿ 110 wt·ppm of hydrogen. Consequently it is estimated that about 100 wt.ppm of hydrogen was absorbed in this specimen during oxidation. This is another effect of steam starvation.

During oxidation by steam, hydrogen is continuously generated on the surface of Zircaloy cladding by the reaction $Zr + 2H_2O \rightarrow ZrO_2 + 2H_2$. Thus the amount of hydrogen generated is directly proportional to the weight gain of the oxidized Zircaloy specimen. Therefore, the atmospheric condition in the reaction tube during each test can be calculated from the rate of steam supply and the weight gain of the specimen under the assumption that the hydrogen is distributed over the whole cross section of reaction tube and only accumulated in the next differential volume of reaction tube during continued oxidation. Some examples of the atmospheric conditions such as steam consumption ratio and hydrogen-steam volume ratio (VH_2/VH_2O) thus determined for the specimens oxidized at 1000 °C for 15 min are listed in Table 4 together with experimental results. In the case of the specimen no. 204, it is estimated that 17.1% of steam introduced into the reaction tube during the test was consumed by the oxidation reaction. And, on the assumption mentioned above, hydrogen-steam volume ratio (VH_2/VH_2O) in the reaction tube would vary from 0 to a certain value along the specimen length as shown schematically in Fig. 4. The ratio is calculated to be 0.21 for the specimen no. 204 at the position of bottom-end. Therefore, it can be estimated that the specimen was oxidized in a steam-hydrogen mixture whose volume ratio VH_2/VH_2O was in the range of 0 ∿ 0.21. It has already been pointed out by the author (8), (11) and Furuta et al. (12) that Zircaloy could absorb much hydrogen during steam oxidation at high temperatures under the atmospheric condition in which the hydrogen volume fraction is considerably high. The rate of 0.21 at the bottom-end of the specimen is not considerably high from the standpoint obtained by the author and Furuta et al. Nevertheless, the specimen no. 204 absorbed about 100 wt.ppm of hydrogen. It should be noticed in this case that a stagnant condition of steam flow could have taken place in the vicinity of the specimen due to the very low steam supply rate of 3.2 mg/cm^2·min, thereby a high volume ratio of hydrogen could be reached in the atmosphere. The steam supply rate of 3.2 mg/cm^2·min corresponds to the flow velocity of 0.31 cm/s at 1000 °C. The ratios for the specimens nos. 209 and 214 are 0.21 and 0.06, respectively. No perceivable amounts of hydrogen were absorbed in these specimens. The amount of hydrogen generated during each oxidation test can be estimated from the total weight gain of the specimen. Therefore, from both this amount of generated hydrogen and absorbed hydrogen content, the hydrogen absorption ratio of the specimen is easily calculated. The ratios are 14 $\sim$ 16, 0.5 $\sim$ 0.9 and 0.5 $\sim$ 0.9% for the tests nos. 204, 209 and 214, respectively.

Figure 5 shows calculated hydrogen-steam volume ratios (VH_2/VH_2O) at the bottom-end of the specimens and steam consumption ratios for the tests at 1000 °C for 15 min as a function of steam supply rate. In the plots of VH_2/VH_2O, a V-shape curve is discernible in the range of supply rate between 3.2 and 13 mg/cm^2·min. The ratio is seen to approach its peak of 0.21 at the supply rate of 13 mg/cm^2·min which corresponds to the critical value for the steam starvation at 1000 °C as shown in Fig. 2 and then it decreases with increase of the supply rate. The variation of the steam consumption ratio with steam supply rate bears a close resemblance to that of VH_2/VH_2O. The maximum ratio is 17.1% at the supply rate of 13 mg/cm^2·min. It is easy to understand that these two ratios decrease with increase of steam supply rate in the range of supply rate above the critical value, in which normal oxidation of Zircaloy is observed. However, it is very difficult to give an appropriate explanation to the V-shape curves in the range of steam supply rate below the critical value. Steam starvation refers to a condition in which the absolute amount of steam available per unit area of specimen surface is not sufficient to sustain the parabolic oxidation rates obtained under steam-saturated conditions. Consequently, oxidation mechanism of Zircaloy in the steam-starved condition is possibly different from that in steam-saturated condition. It is generally accepted that the rate determining step of Zircaloy-steam reaction is the diffusion of oxygen anions via an oxygen deficient form of ZrO_2. This mechanism should be influenced by the absolute amount of oxygen atoms available per unit area of specimen surface.

Figure 6 shows the correlation between the weight gain and the duration of oxidation at 1000 °C for three different steam supply rates. The experimental conditions and measured weight gain of specimens are listed in Table 5. For the purpose of comparison, the correlation for unlimited steam supply rate which was obtained by Leistikow et al. (2) is included in the figure. For the lowest steam supply of 3.2 $mg/cm^2 \cdot min$, the initially very small weight gain increases sharply with increasing reaction duration. In the case of the intermediate steam supply rate of 12.7 $mg/cm^2 \cdot min$, the weight gain kinetics can be expressed as a parabolic function up to 15 min followed by a linear one, whereas parabolic behavior persists up to 60 min in the case of the higher steam supply rate of 40.7 $mg/cm^2 \cdot min$.

Typical examples of oxide film microstructures of the specimens oxidized at 1000 °C are shown in Fig. 7. Photomicrograph (A) represents the very thin oxide film formed on the specimen surface oxidized for 15 min under the lowest steam supply rate of 3.2 $mg/cm^2 . min$. In the cases of (C) and (E), oxidized for 15 min under intermediate and higher steam supply rate, oxide films of about 25 μm in thickness are seen. This thickness of the oxide film is roughly in agreement with the value of 30 μm calculated with the empirical equation <2> (10) for the growth of oxide film in unlimited steam supply,

$$\phi = 0.208 \sqrt{t} \exp(-10107/T) \qquad <2>$$

where ϕ : Growth of oxide (cm)

t : Oxidation time (s)

T : Oxidation temperature (K).

Breakaway of the oxide film is observed on all the specimens oxidized for 60 min. However, the morphology of the oxide films differ from one another. A porous and thick oxide film is seen in the case of (B) oxidized under the lowest steam supply. And prominent breakaway, which could cause the deviation of the kinetics from a parabolic rate law shown in Fig. 6, is obvious in the case of (D) for the intermediate steam supply rate of 12.7 $mg/cm^2 \cdot min$. On the other hand, the oxide film is relatively thin for the higher steam supply, (F). Absorbed hydrogen content of the specimens oxidized for 60 min were analyzed to be 2300, 1400 and 410 wt.ppm (Table 3) for the steam supply rate of 3.2, 12.7 and 40.7 $mg/cm^2 \cdot min$, respectively.

3.2 Oxidation at 1300 °C

The experimental conditions and measured weight gain of the specimens oxidized at 1300 °C for 15 min are listed in Table 6.

Figure 8 shows the weight gain of Zircaloy-4 specimens as a function of steam supply rate for the tests at 1300 °C during 15 min. Below the critical steam supply rate of some 20 $mg/cm^2 \cdot min$, a sharp decrease of weight gain is observed. In the range of the supply rate between 20 and 60 $mg/cm^2 \cdot min$, a peak is obvious with its maximum about 15% above the level expected for unlimited steam. Relatively high contents of hydrogen between 340 and 1300 wt.ppm were analyzed for the specimens oxidized in this range. At higher steam supply rates the weight gain decreases gradually to a nearly constant level.

Some estimations of the atmospheric conditions such as steam consumption ratio and hydrogen-steam volume ratio for the three selected tests at 1300 °C for 15 min are listed in Table 7 together with experimental data. In case of the specimen no. 183, oxidized in the very low steam supply rate of 3.5 $mg/cm^2 \cdot min$, it is estimated that 19.6% of the steam introduced into the reaction tube during the test was consumed by the oxidation reaction. And the hydrogen-steam volume ratio is calculated to be 0.24 at the position of bottom-end. In the case of no. 211, both steam consumption ratio and hydrogen-steam volume ratio are relatively low because of the higher steam supply rate. In contrast to these cases, the ratios are very high in the case of no. 150. It is estimated in this case that about half of introduced steam was consumed by the oxidation of Zircaloy and the hydrogen-steam ratio was 1.03 at the bottom-end. There is obvious correlation between the hydrogen-steam volume ratio and the absorbed hydrogen content. Hydrogen content of the specimen no. 150 is extremely high, which is estimated to have been oxidized in the atmosphere with high fraction of hydrogen. This tendency is in good agreement with the finding by the author (8) (11) and Furuta et al. (12) as previously described. Hydrogen absorption ratios are 18 ∿ 21, 2.2 ∿ 8.4 and 0.4 ∿ 1.2% for the tests nos. 183, 150 and 211, respectively.

The photomicrographs of these three specimens oxidized at 1300 °C for 15 min are shown in Fig. 9. Photomicrograph (A) respresents the structure of the specimen no. 183 oxidized under the lowest steam supply rate of 3.5 $mg/cm^2 \cdot min$. The oxide film formed on the specimen surface is very thin and the microstructure is seen to consist mostly of needle-shaped previous-β (α') phase crystals. Photomicrographs (B) and (C) show the microstructure of the specimens nos. 150 and 211 oxidized under intermediate and higher steam supply rates of 29.0 and 159.0 $mg/cm^2 \cdot min$, respectively. Very thick double layer oxide films formed on the outer and inner surface of the specimens are seen in both cases. The thickness of these oxide layers lie in the region of 110 ∿ 120 μm, which is in good agreement with the value of 101 μm calculated with the empirical equation (2). Chemical analysis indicated that the specimens corresponding to (B) and (C) contained 340 ∿ 1300 and 50 ∿ 160 wt.ppm of hydrogen, respectively. However, there is no obvious difference between (B) and (C).

Figure 10 shows calculated hydrogen-steam volume ratio at the bottom-end location of the specimens and steam consumption ratios for the tests at 1300 °C for 15 min as a function of steam supply rate. In the plots of VH_2/VH_2O, the ratio is seen to have its peak of about 1.7 at the supply rate of 20 $mg/cm^2 \cdot min$ which corresponds to the critical value for the steam starvation at 1300 °C as shown in Fig. 8, and it decreases with decrease or increase of the supply rate. The variation of the steam consumption ratio with steam supply rate bears a close resemblance to that of VH_2/VH_2O. The maximum ratio of 63% is observed at the supply rate of 20 $mg/cm^2 \cdot min$.

The acceleration of oxidation was measured in the range of steam supply rate between 20 and 60 $mg/cm^2 \cdot min$ as shown in Fig. 8. For this range of the supply rate, the hydrogen-steam volume ratio lies in the region of 0.3 ∿ 1.7. It has already been known that the oxidation kinetics of Zircaloy by steam is possibly accelerated in the specified atmosphere with high fraction of hydrogen. Furuta and Kawasaki (12) investigated the oxidation behavior of Zircaloy-4 in steam-hydrogen mixtures at temperatures ranging from 950 to 1100 °C. And they identified fluctuations of the reaction rates for critical hydrogen-steam volume ratios of 0.2 to 0.4 as shown in Fig. 11. In their tests at 1100 °C for 900 s (15 min), for instance, about 20% larger weight gain was measured for the hydrogen-steam volume ratio of 0.3.*

The cause of such kinetics fluctuations is not yet obvious, which seems to be strongly related with the high hydrogen fractions in the atmospheres.

On the other hand, Chung and Thomas (9) performed oxidation experiments of Zircaloy-4 at temperatures ranging from 1200 to 1700 °C in hydrogen-steam mixtures and observed significantly smaller oxidation rates compared with those in steam-saturated conditions. They named this retarding effect of hydrogen on Zircaloy oxidation "hydrogen blanketing". However, as previously shown in Figs.

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[*] The hydrogen-steam volume ratio was prescribed at the inlet of the reaction tube and hydrogen generated by the reaction was not taken into account in the tests by Furuta et al. Therfore, the ratio in the present work cannot be directly compared with that of their tests.

8 and 10, hydrogen blanketing was not observed in the present work. Smaller oxidation rates observed in the range of lower steam supply rate could be regarded as the effect of steam starvation. And acceleration of the oxidation was measured in the atmospheres with high hydrogen fraction, in which "hydrogen blanketing" might be expected. It should be noticed that the actual hydrogen-steam ratios in the vicinity of the cladding specimen could be largely different from the prescribed ones in their experiments due to the inadequacy of the apparatus, i.e. bell jar type reaction chamber.

4. Conclusions

Oxidation tests of Zircaloy-4 were performed at 1000 and 1300 °C under limited steam supply with a view to examing the oxidation behavior of Zircaloy in severe fuel damage accident conditions of LWRs. The following conclusions were obtained:

(1) The effect of steam starvation was restricted to very low levels of steam supply rate. The critical supply rates for steam starvation were evaluated to be 13 and 20 $mg/cm^2 \cdot min$ for the oxidation at 1000 and 1300 °C, respectively.

(2) In the tests at 1000 °C for 2 ∿ 60 min, a clear trend towards linear kinetics was observed for the lower steam supplies at the longer duration of oxidation. This could be interpreted as the result of earlier breakaway transition under limited steam supply.

(3) In the tests at 1300 °C, an acceleration of the oxidation rate was measured for specified steam supply rates between 20 and 60 $mg/cm^2 \cdot min$. This related strongly with high hydrogen concentration in the atmosphere.

(4) Hydrogen blanketing was not identified in the examined temperature range.

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Table 1 Chemical composition of Zircaloy-4 cladding specimen used in experiment

Element	Content (wt.%)	Element	Content (ppm)
Sn	1.58	O	1100
Fe	0.22	H	6
Cr	0.10	N	< 100
Ni	-	C	-
Zr : Balance			

Table 2 Experimental conditions and measured weight gain of specimens oxidized at 1000 °C

Specimen Nr.	Temperature (°C)	Time (min)	Steam Supply Rate ($mg/cm^2 \cdot min$)	Weight Gain (mg/cm^2)
147	1000	15	27.3	5.15
149			29.0	5.05
151			9.7	2.76
152			5.8	1.00
155			80.4	5.08
156			4.3	1.04
158			8.0	1.74
160			6.8	1.16
162			21.0	5.04
164			23.4	4.93
166			31.1	4.99
168			30.5	5.05
170			53.8	5.09
172			57.6	5.04
174			51.0	5.00
176			81.2	5.26
178			24.4	5.14
180			16.3	4.88
182			3.5	1.11
184			7.2	1.43
186			4.0	1.23
188			14.7	4.92
190			23.1	5.20
192			12.1	4.25
194			47.6	5.00
196			71.6	5.42
204			3.2	1.20
209			12.7	4.81
214			40.7	5.02

Table 3 Oxygen and hydrogen content in Zircaloy specimens oxidized at 1000 °C for 2 ∿ 60 min

Specimen Nr.	Time (min)	Steam Supply Rate (mg/cm^2· min)	Oxygen content (wt%)		Hydrogen content (wt%)	
			Top	Bottom	Top	Bottom
202	2	3.2	0.31±0.04	0.36±0.06	0.005±0.001	0.004±0.001
204	15		0.93±0.44	0.66±0.28	0.011±0.001	0.010±0.001
205	60		6.90±1.06	2.41±0.50	0.23±0.02	0.23±0.01
207	2	12.7	1.03±0.12	0.83±0.07	0.001	0.001
209	15		1.92±0.37	1.80±0.23	0.003±0.001	0.002±0.001
210	60		6.89±1.39	5.28±0.90	0.14±0.02	0.14±0.01
212	2	40.7	0.94±0.15	1.01±0.06	0.001	0.002±0.001
214	15		2.20±0.44	2.10±0.49	0.002±0.001	0.003±0.002
215	60		4.22±0.90	3.66±1.83	0.040±0.019	0.042±0.004

Table 4 Some experimental results and calculated atmospheric conditions for the spcimens oxidized at 1000 °C for 15 min

Specimen Nr.	Steam Supply Rate $(mg/cm^2 \cdot min)$	Weight Gain (mg/cm^2)	Steam Consumption Ratio (%)	Hydrogen-Steam Volume Ratio* (VH_2/VH_2O)	Hydrogen Content (wt.ppm)	Hydrogen Absorption Ratio (%)
204	3.2	1.20	17.1	0.21	100 ∿ 110	14 ∿ 16
209	12.7	4.81	17.3	0.21	20 ∿ 30	0.5 ∿ 0.9
214	40.7	5.02	5.6	0.06	20 ∿ 30	0.5 ∿ 0.9

* : Ratio at the bottom-end location of specimen to the direction of steam flow

Table 5 Experimental conditions and measured weight gain of specimen oxidized at 1000 °C for 2 ∿ 60 min

Specimen Nr.	Temperature (°C)	Time (min)	Steam Supply Rate (mg/cm^2· min)	Weight Gain (mg/cm^2)
202	1000	2	3.2	0.42
203		5		0.56
204		15		1.20
205		60		10.47
207		2	12.7	1.96
208		5		2.86
209		15		4.81
210		60		14.69
212		2	40.7	1.99
213		5		3.00
214		15		5.02
215		60		10.15

Table 6 Experimental conditions and measured weight gain of specimen oxidized at 1300 °C

Specimen Nr.	Temperature (°C)	Time (min)	Steam Supply Rate (mg/cm^2 · min)	Weight Gain (mg/cm^2)
148	1300	15	27.3	32.34
150			29.0	32.17
153			5.8	2.89
157			4.3	2.52
159			18.4	23.23
161			6.8	2.47
163			21.0	29.08
165			23.4	32.53
167			31.1	32.57
169			30.5	31.60
171			53.8	28.69
173			57.6	27.67
175			51.0	30.12
177			81.2	26.36
179			24.4	31.53
183			3.5	1.50
185			7.2	3.97
187			4.0	1.67
189			14.7	17.88
191			23.1	30.83
193			12.1	11.29
195			47.6	30.05
197			71.6	26.85
199			77.9	27.50
200			132.2	25.10
201			174.6	24.95
206			106.1	26.38
211			159.2	25.20
216			40.7	30.94

Table 7 Some experimental results and calculated atmospheric conditions for the specimens oxidized at 1300 °C for 15 min

Specimen Nr.	Steam Supply Rate ($mg/cm^2 \cdot min$)	Weight Gain (mg/cm^2)	Steam Consumption Ratio (%)	Hydrogen-Steam Volume Ratio* (VH_2/VH_2O)	Hydrogen Content (wt.ppm)	Hydrogen Absorption Ratio (%)
183	3.5	1.50	19.6	0.24	160 ∿ 180	18 ∿ 21
150	29.0	32.17	50.6	1.03	340 ∿ 1300	2.2 ∿ 8.4
211	159.0	25.20	7.2	0.08	50 ∿ 160	0.4 ∿ 1.2

* : Ratio at the bottom-end location of specimen to the direction of steam flow

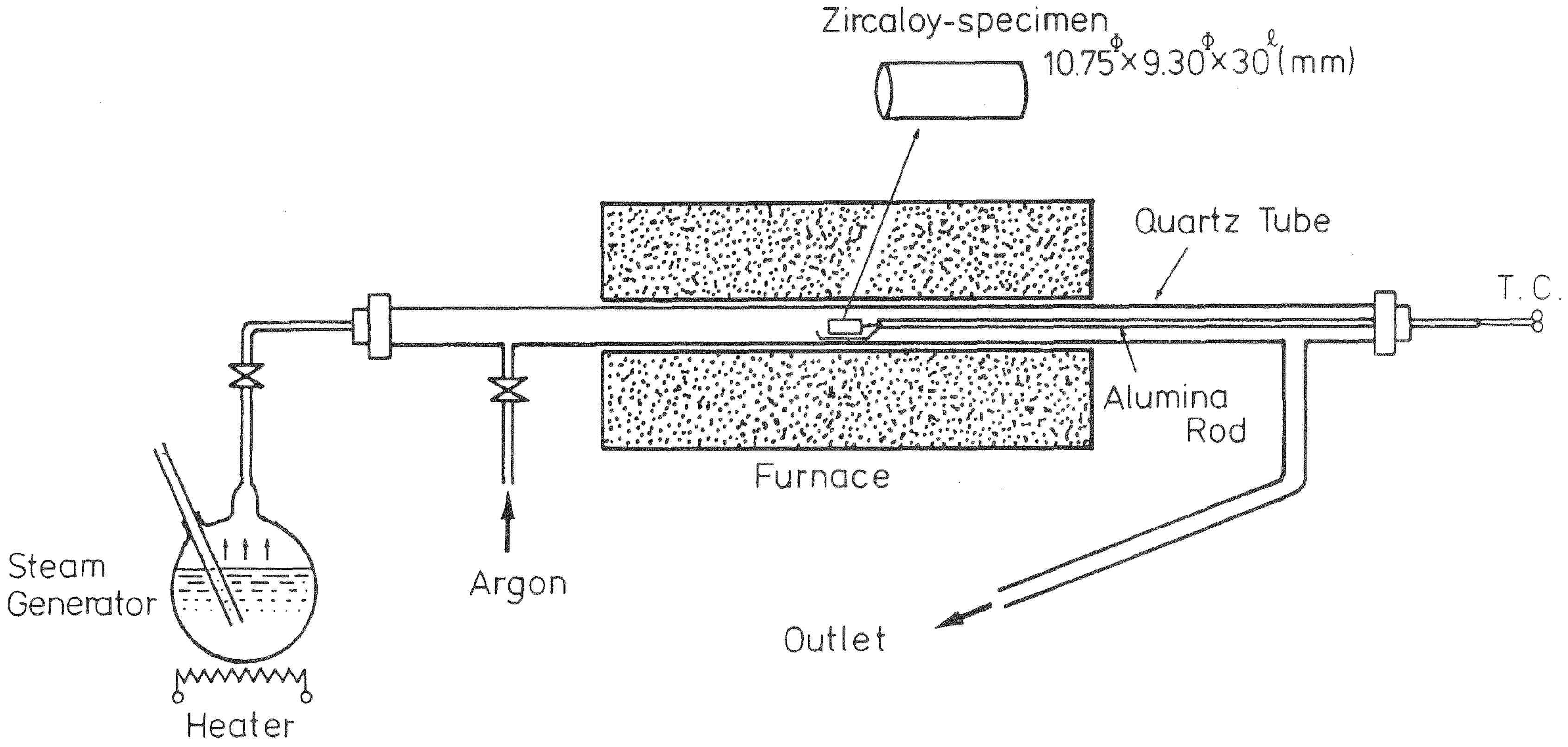

Fig.1 Schematic illustration of specimen and apparatus for Zircaloy oxidation in limited steam flow

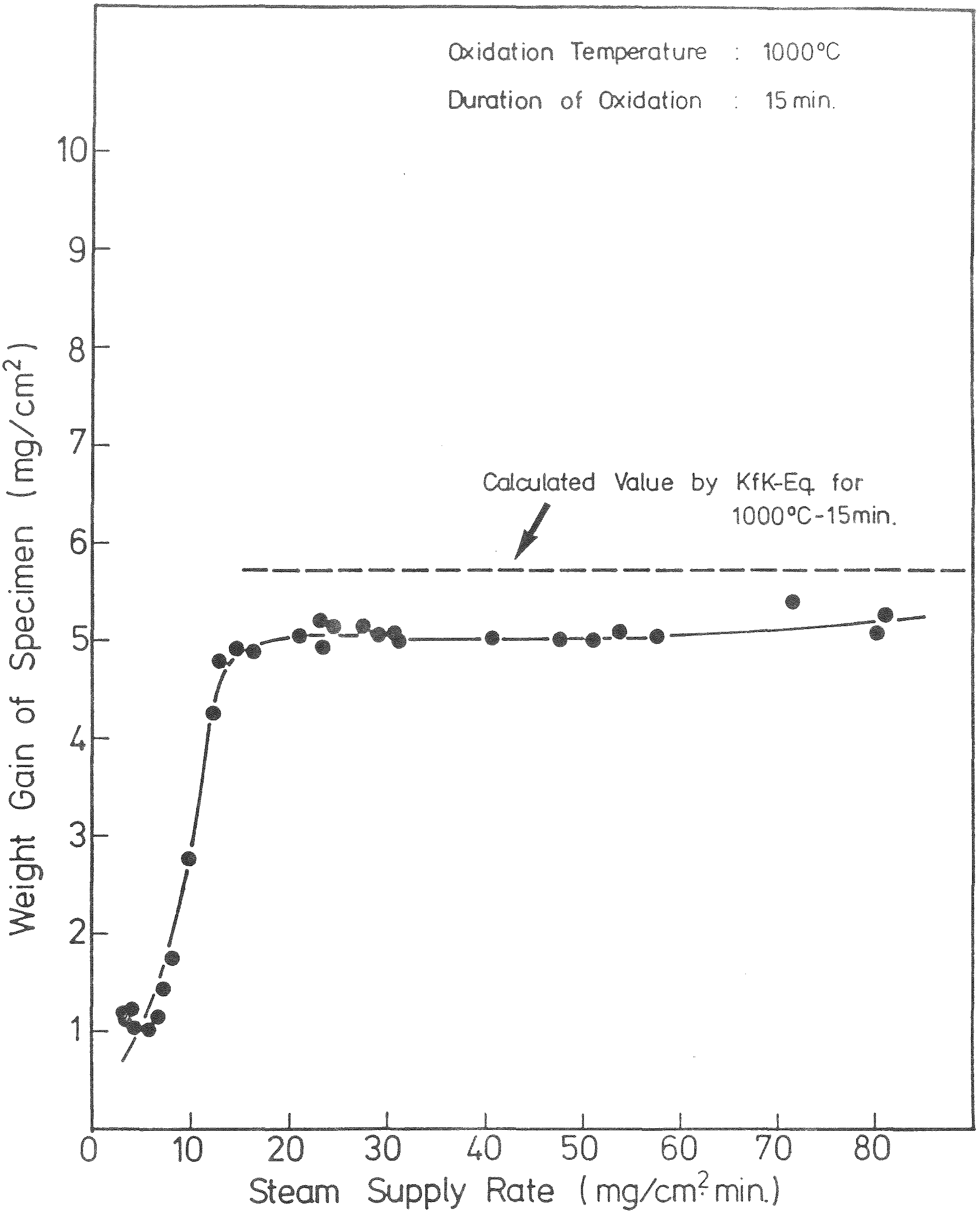

Fig.2 Correlation between weight gain of specimen and steam supply rate to the cross-sectional area of reaction tube

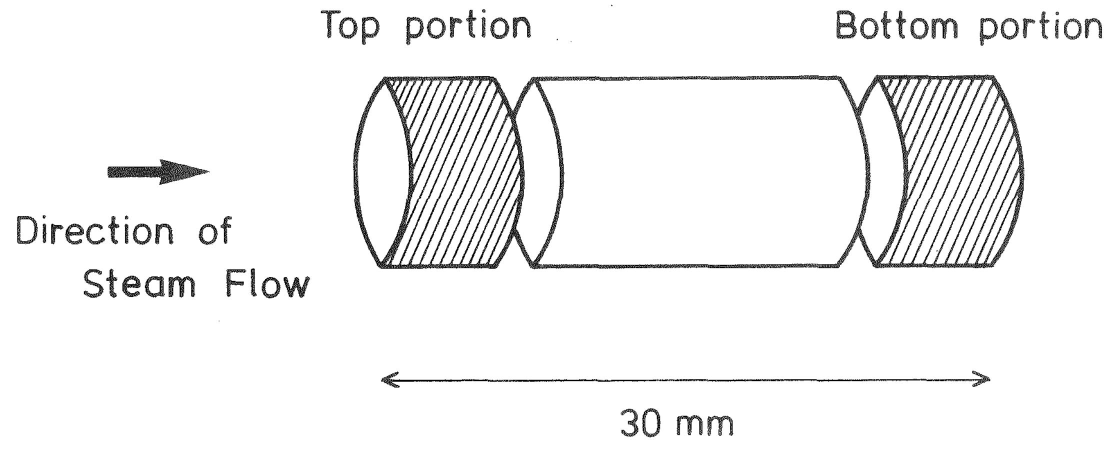

Fig.3 Sectioning of specimen into test pieces for hydrogen and oxygen analyses

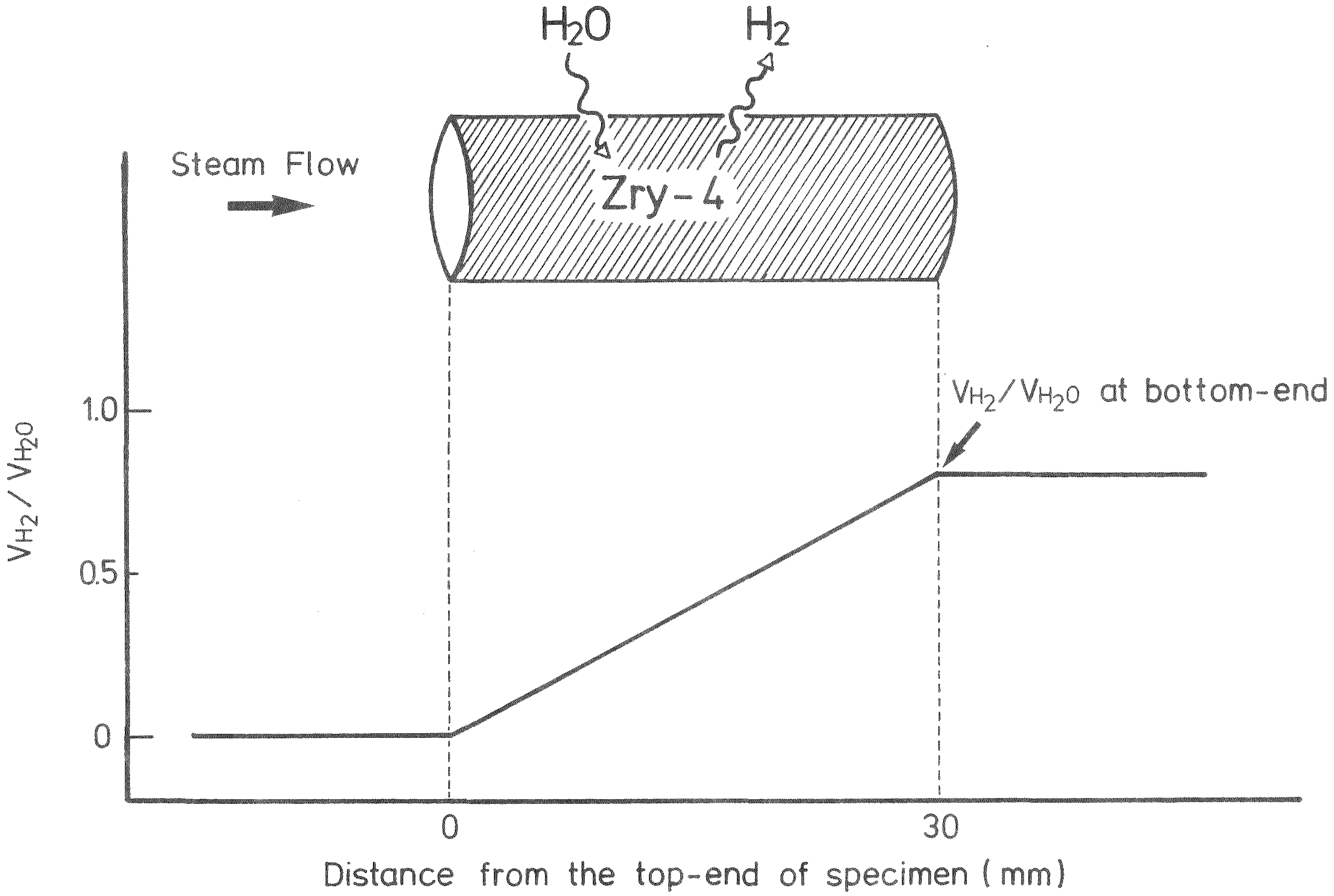

Fig.4 Schematic illustration of variation of V_{H_2}/V_{H_2O} as a function of distance from the top-end of specimen

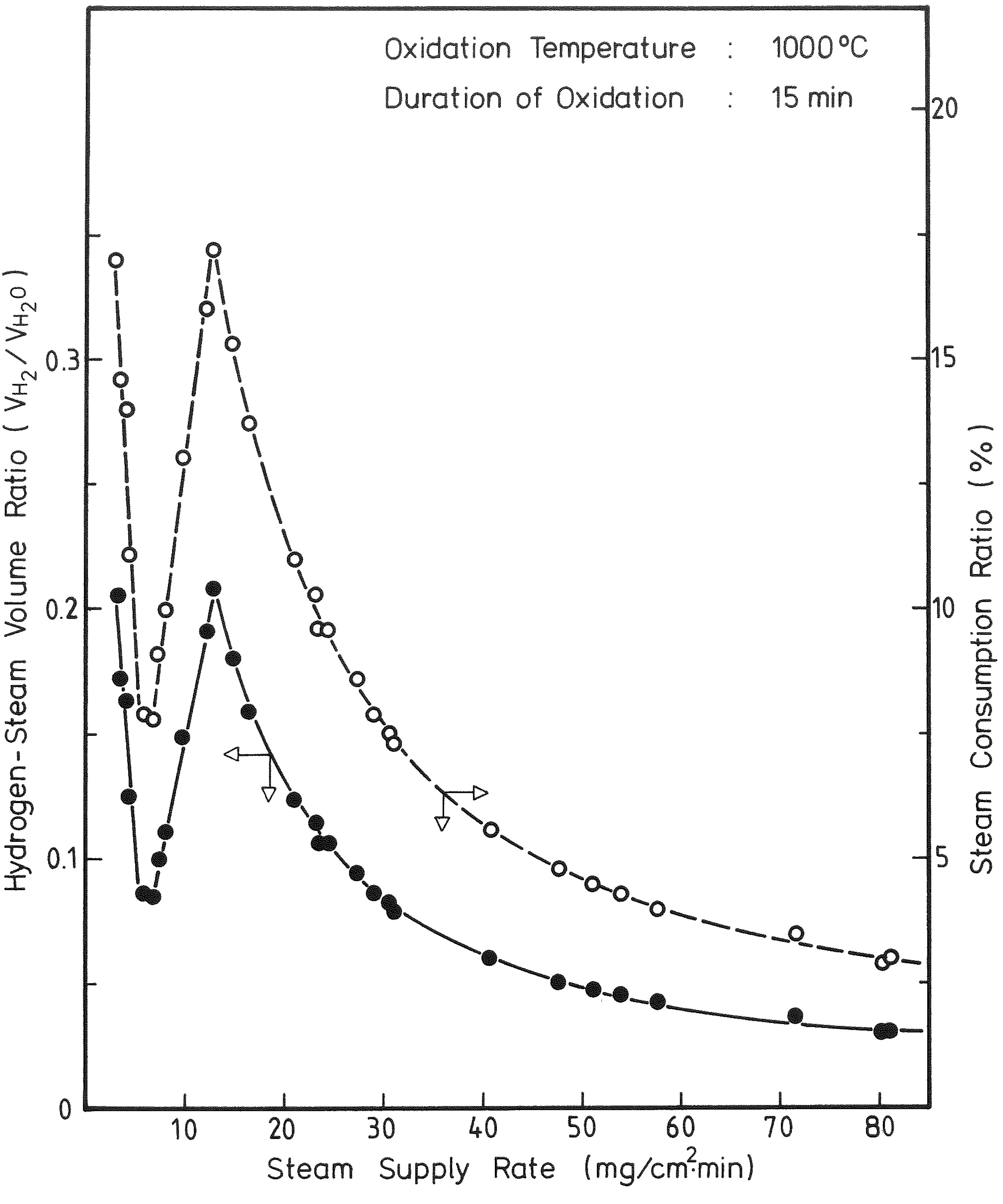

Fig. 5 Hydrogen-steam volume ratio and steam consumption ratio in the tests at 1000°C as a function of steam supply rate

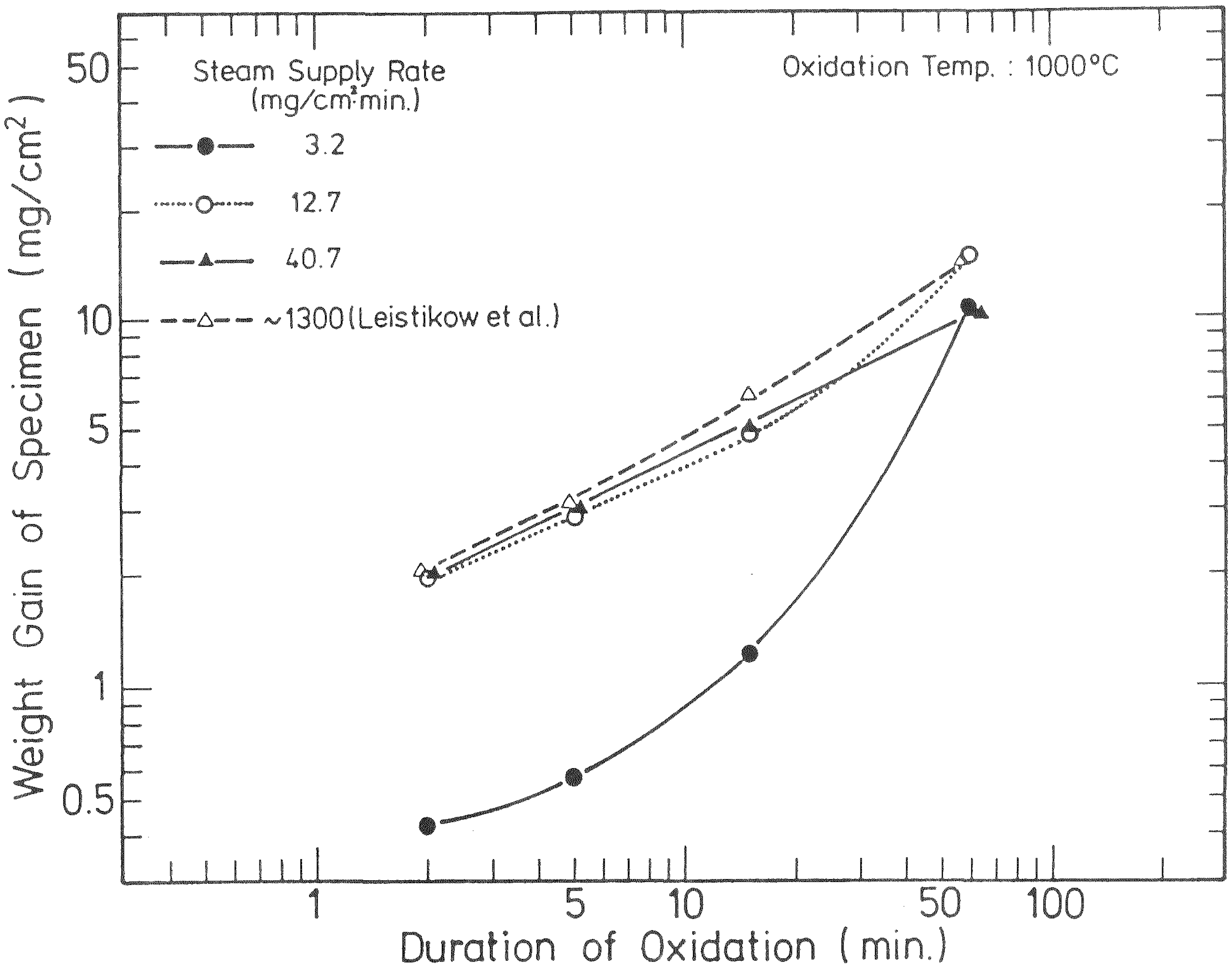

Fig. 6 Mass increase as function of duration of oxidation in steam at different supply rates (2~60min, 1000°C)

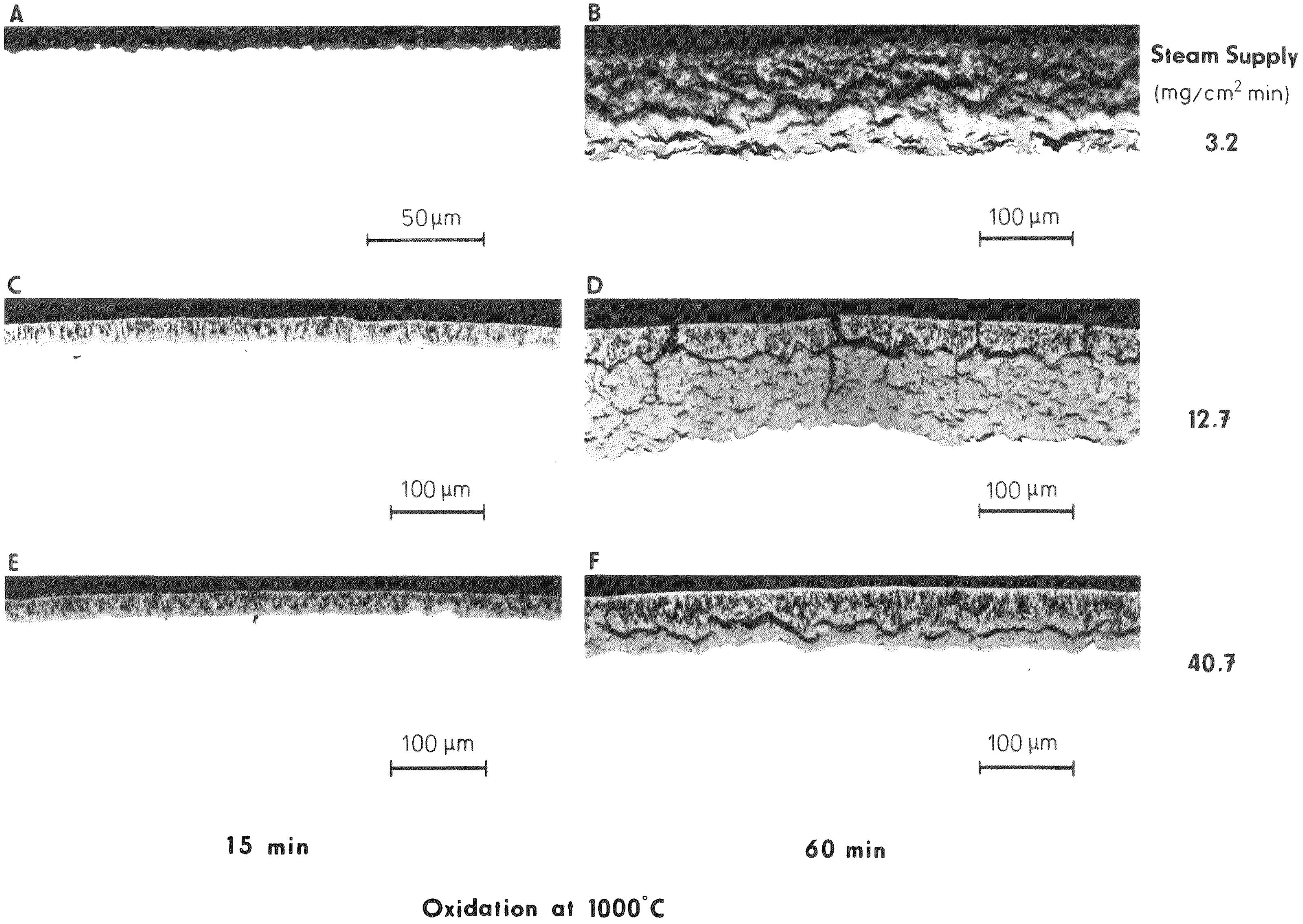

Fig.7 Photomicrographs of Zircaloy-4 oxidized at 1000°C for 15 or 60 min in steam at different supply rates

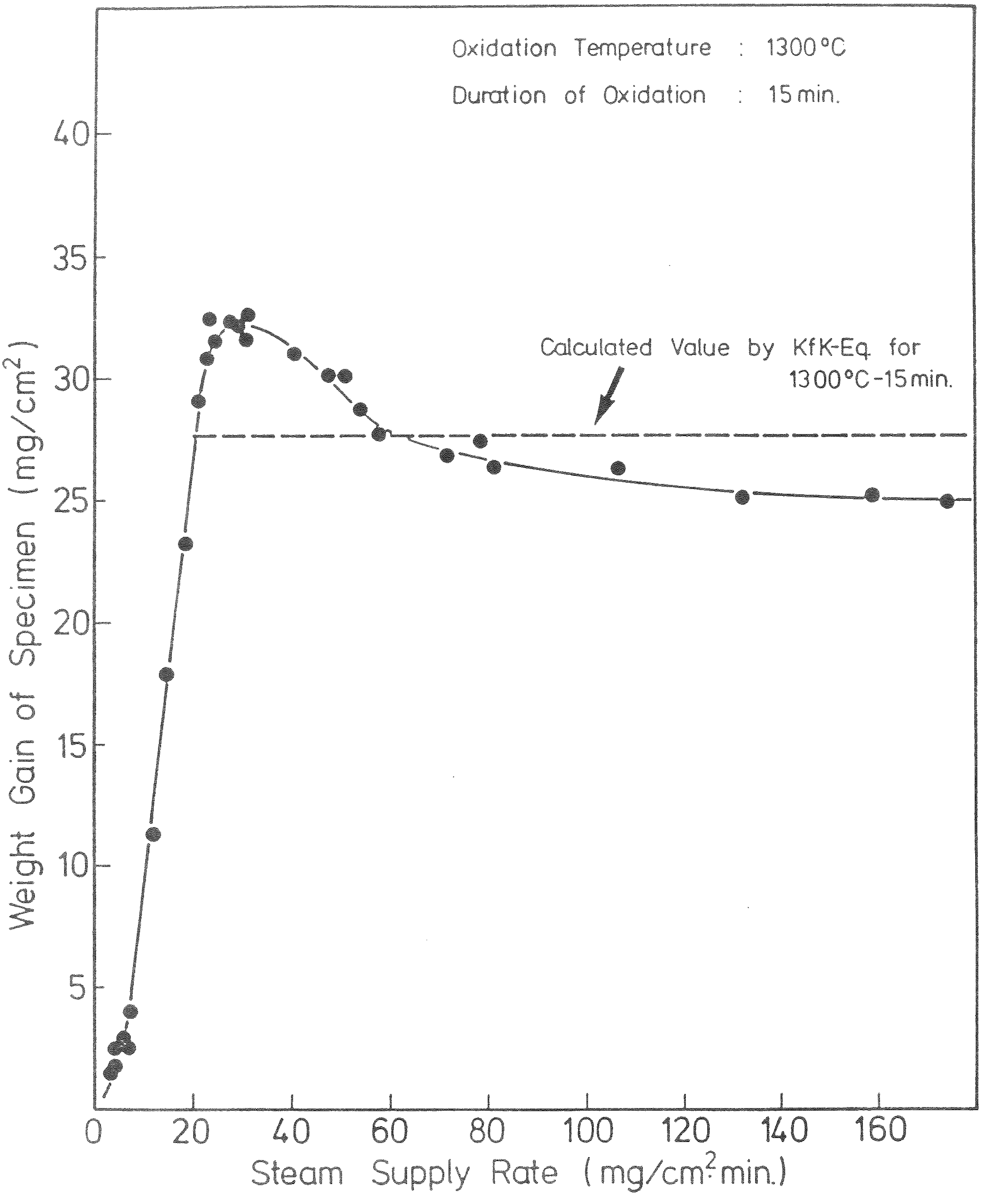

Fig. 8 Correlation between weight gain of specimen and steam supply rate to the cross-sectional area of reaction tube

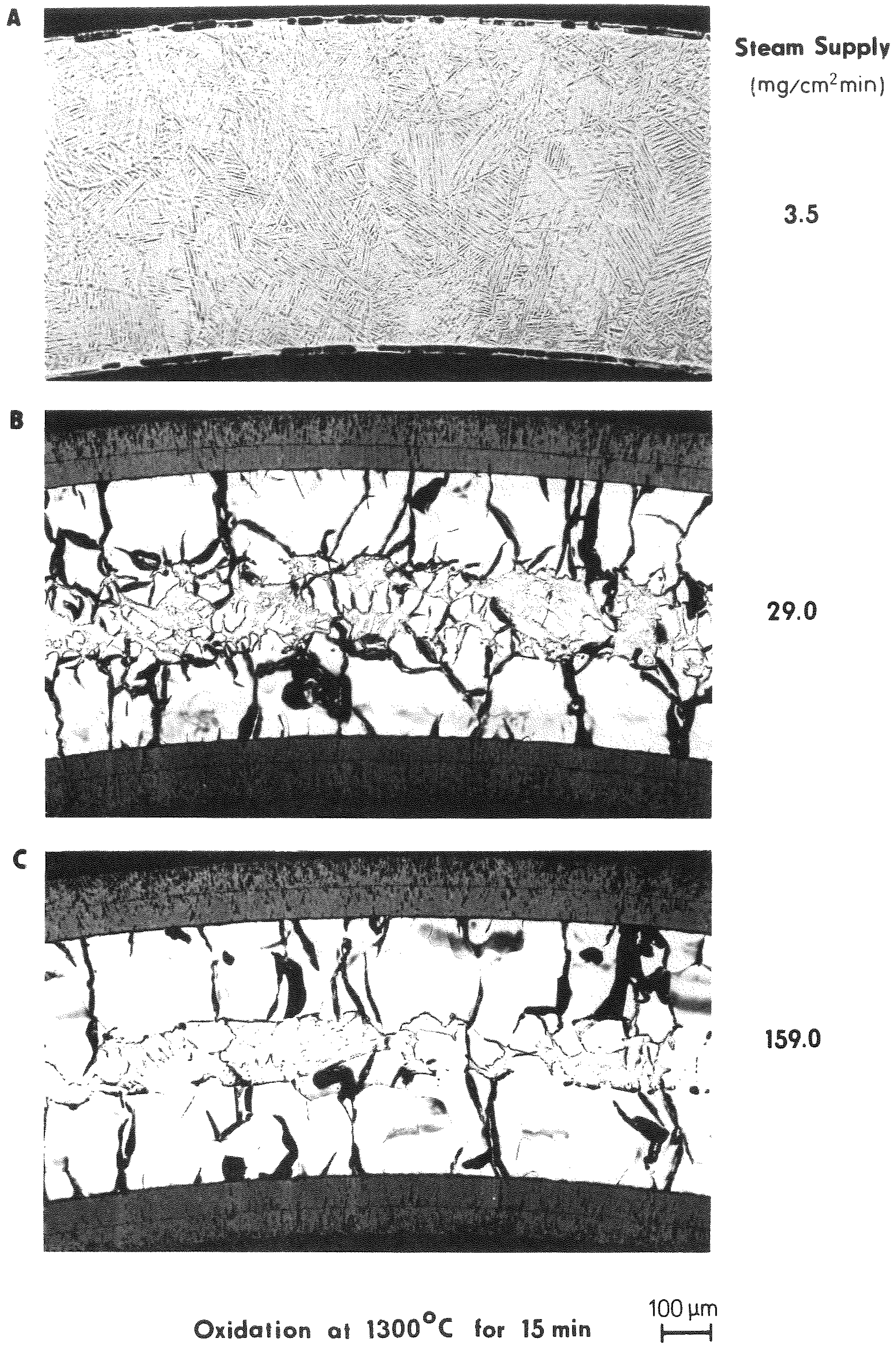

Fig.9 Photomicrographs of Zircaloy-4 oxidized at 1300 °C for 15min in steam at different supply rates

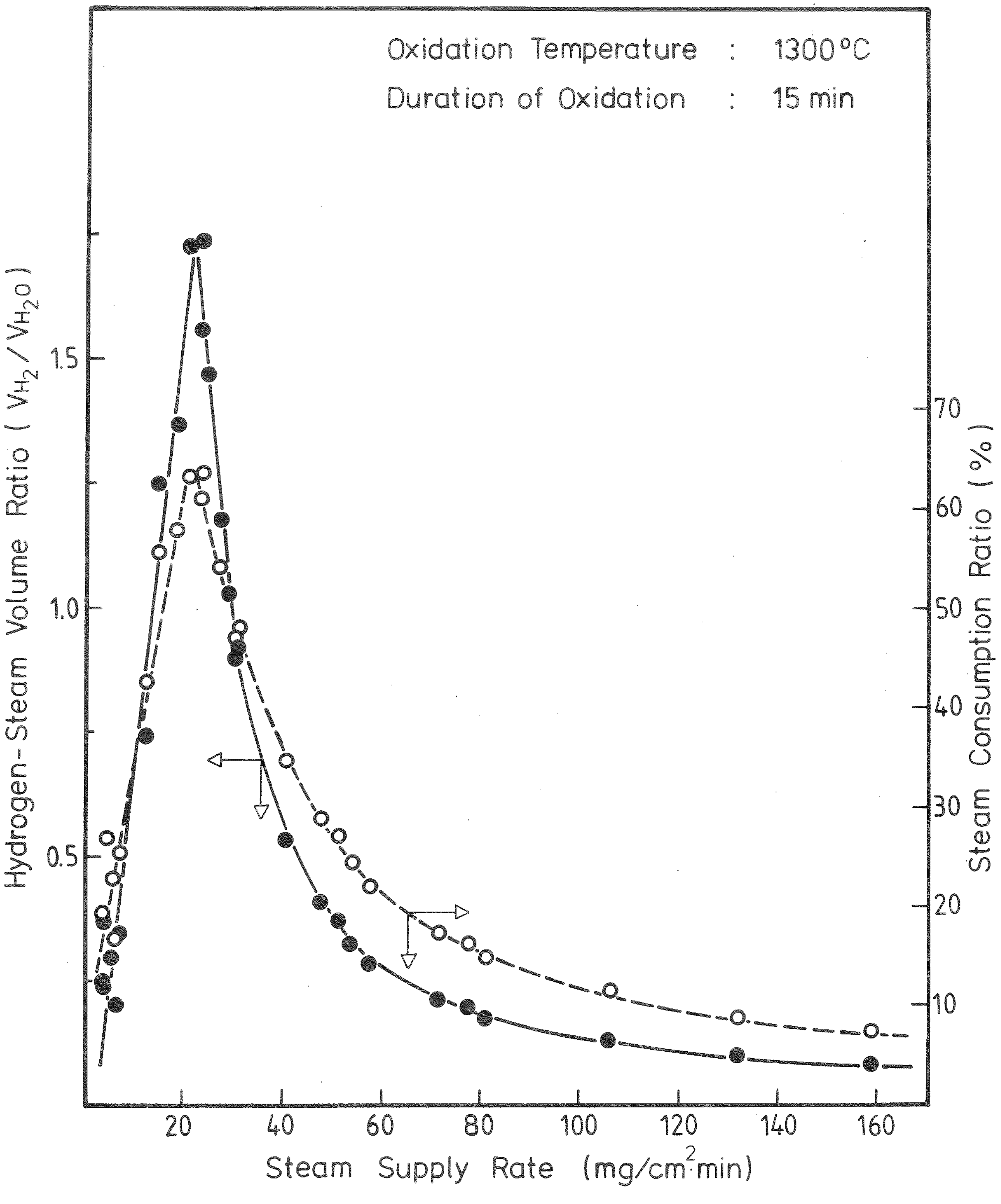

Fig.10 Hydrogen-steam volume ratio and steam consumption ratio in the tests at 1300 °C as a function of steam supply rate

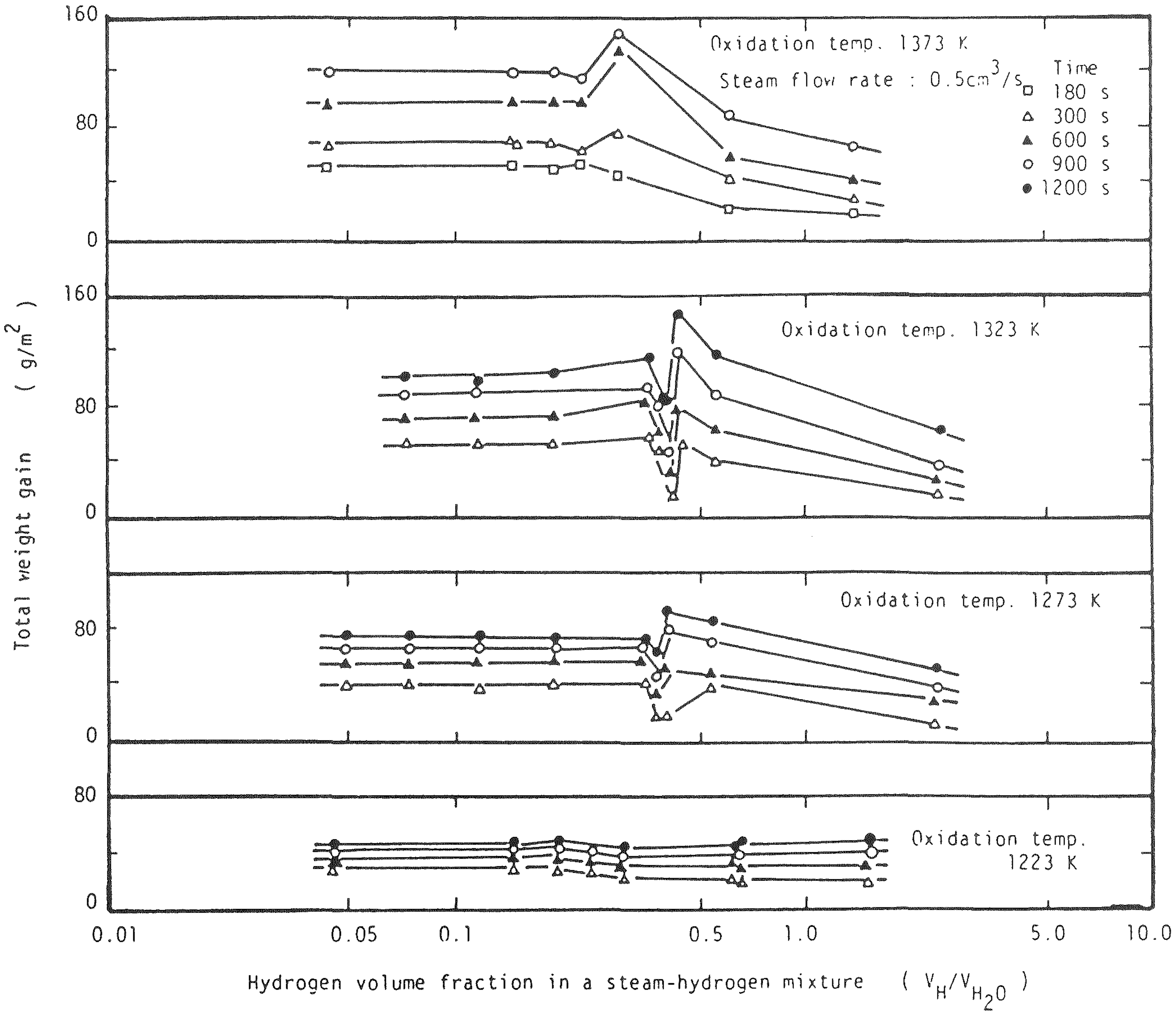

Fig.11 Variation of total weigt gain with hydrogen volume fraction in steam-hydrogen mixture (from Ref. 12)