

Investigation on the Oxidation Mechanism of Titanium

P. KOFSTAD, K. HAUFFE* and H. KJÖLLESDAL

Central Institute for Industrial Research, Blindern, Oslo, Norway

Oxidation of titanium has been studied in the temperature region 300—1 000°C. Four different rate laws have been found in the indicated temperature intervals: logarithmic (< 300°C), cubic (300—600°C), parabolic (600—850°C), and parabolic + linear (> 850°C) rate laws. The indicated temperature regions are only approximate as the rate laws observed are also dependent upon the duration of the oxidation and the amount of oxygen present in the metal before the start of the oxidation. Thus the initial rate laws observed at any temperature eventually changes into the rate law corresponding to the higher temperature interval. For example at 300°C the oxidation follows a logarithmic rate law for the initial 300 min whereupon it gradually changes into a cubic rate law.

The following oxidation mechanisms are proposed: The logarithmic rate law is interpreted as an oxide film formation perhaps governed by a Mott-type mechanism, the cubic rate law is associated with a diffusion of oxygen into the titanium metal, the parabolic rate law is interpreted in terms of the usual Wagner high-temperature mechanism and with the assumption that a diffusion of oxygen ions through the TiO₂ scale is the rate determining step (< 1 000°C), and the linear rate law results from cracks in the oxide scale due to stresses in the oxide and a phase boundary reaction being the rate-determining reaction.

The reaction of oxygen with titanium at different temperatures has been studied by numerous investigators¹⁻²³. A comparison of the different reports and publications, however, shows large disagreements and discrepancies which include both rate laws and rates of oxidation.

The published data indicate that the processes involved in the reaction are rather complex, and no simple interpretation can be given to the diverse phenomena observed at different temperatures and oxygen pressures. This state of affairs is partly due to the high oxygen solubility in titanium and the possibility of formation of different oxides (TiO, Ti₂O₃, Ti₃O₅, and TiO₂) in the oxide scale. A probable reason for the disagreements between different

* Present address: Farbwerke Hoechst, Frankfurt am Main, Germany.

published data is the presence of gaseous impurities (O_2 , H_2 , N_2) and C in titanium and different pretreatments of titanium used by different investigators. It is well known that titanium dissolves large amounts of oxygen without forming an oxide scale at high temperatures ($> 800^\circ C$) and low pressures ($p_{O_2} < 10^{-3}$ mm Hg), and dissolved oxygen introduced during pretreatment such as annealing between rolling runs, etc., may change the characteristics of the oxidation reactions.

The mechanism of oxidation of titanium was investigated by studying the rate laws of oxidation and rate of oxidation as a function of temperature and oxygen pressure. As the knowledge of the structure and degree of order of the oxide scale is of primary importance in consideration of oxidation mechanisms, the oxide scale was studied by means of X-ray diffraction, electron microscopy, and metallographic techniques. Furthermore, because of the high solubility of oxygen in titanium and as the kinetics of oxygen penetration into the metal may be of importance for the rate laws observed, the oxygen penetration into titanium during the oxidation was studied by metallographic and microhardness techniques.

EXPERIMENTAL METHODS

Both high-purity van Arkel titanium and commercial Kroll titanium were used in the studies. Spectrographic analysis gave the following results:

Type of Ti	Impurities present		
	0.1 %	0.01 %	traces, 0.001 %
Van Arkel Ti		Fe, Mn, Al, Sn, Mg, Cr	Cu
Kroll Ti	Mg, Fe	Si	Ca, Cu, Fe, Sn, Mn

No analysis was made of gaseous impurities (O_2 , N_2 , H_2) and C. However, hardness measurements on the titanium gave fair indication as to the impurity level. The hardness, HV_{10} , was measured to 90–100 for the van Arkel titanium and 120–130 for the Kroll titanium annealed in high vacuum at $800^\circ C$ for 30 min. These results indicate that only small amounts of impurities were present in the titanium.

The titanium was melted in a laboratory type argon arc furnace. The melting was performed with an auxiliary wolfram electrode. A watercooled copper crucible permitted melting of 5 different samples each weighing about 20 g. All samples were remelted.

After melting, the buttons were coldrolled to the desired thickness in a small rolling mill. For specimens of small thickness, it was necessary to anneal in high vacuum at $800^\circ C$ between rolling runs. The metal sheets were cut in specimens about 3×1 cm². The thickness of the specimens varied between 0.05 and 0.003 cm, depending upon the testing temperature. The specimens were furthermore degreased in chloroform and acetone, polished with emerycloth and alumina and finally rinsed in distilled water.

The reaction of oxygen with titanium was measured both by a gravimetric and a volumetric method. The gravimetric method was employed at high temperatures (700 – $1000^\circ C$), and the experimental setup consisted essentially of a quartz helix hung vertically in a tube. The test specimen was suspended in a platinum wire, and the weight gain was followed by measuring with a cathetometer the vertical displacement of a pointer on the spring. By this method the weight gain was measured with an accuracy of $\pm 5 \times 10^{-5}$ g.

The measuring unit was incorporated in a vacuum system which was made of Pyrex with the exception of the reaction tube, which was made of transparent silica. The system was connected *via* a liquid air trap to a set of oil diffusion and rotary oil pumps.

Before the start of each run, the system was evacuated. After allowing time for temperature stabilization in the furnace surrounding the reaction tube, the run was started by closing the highvacuum line and admitting oxygen to the system. During oxidation at low pressures (< 1 mm Hg) oxygen was continuously pumped through the system and the pressure was regulated with a fine control needle valve.

In the temperature region 300–700°C the weight gain of titanium reacting with oxygen ranged from a few μg per cm^2 at 300°C to a few hundred μg per cm^2 at 700°C after about 5 h of oxidation. The gravimetric apparatus was not sensitive enough for this purpose, and the oxidation rate was therefore studied by measuring the volume of oxygen absorbed by the titanium specimen.

Essentially the apparatus consisted of a reaction chamber (with as small a volume as possible) connected to a large reference volume with a long uniformly graduated capillary. The absorption of oxygen was followed by observing the movement of a small, mobile drop of diethylphthalate indicator from the reference volume to the reaction chamber. In order to increase the mobility and thereby the sensitivity of the indicator drop, the capillary was treated with a water-repellent silicone compound.

With the exception of the reaction tube, which consisted of transparent silica, the apparatus was made entirely of Pyrex. The whole system was connected to an oil diffusion and a rotary oil pump.

The temperature in the furnace was regulated by a transducer regulator in combination with a platinum resistance thermometer within $\pm 0.1^\circ\text{C}$. The rest of the apparatus was enclosed in a chamber, its temperature being kept at $25 \pm 0.1^\circ\text{C}$.

In order to have a constant temperature gradient from the furnace to the rest of the system, the part of the reaction chamber which was outside the furnace, was equipped with a water jacket, through which water was pumped from a constant temperature bath kept at $25 \pm 0.1^\circ\text{C}$. A transparent silica rod was placed within the reaction chamber to reduce the volume, and the test specimens were suspended with a short platinum wire connected from a hook at the top of the reaction tube.

Before the start of the run the reaction chamber was evacuated, the furnace was lowered in position and the temperature adjusted to within $\pm 0.1^\circ\text{C}$. The run began when the highvacuum line was closed off, and the oxygen was admitted to the reaction chamber. Before measuring the movement of the indicator, the pressures in the reaction chamber and the reference volume were equalized *via* a short-cut line for 10 sec. Thus for each run there was an unrecorded period of about 20 sec. Comparison with the gravimetric method at 700–800°C gave excellent agreement.

The X-ray diffraction investigations of the oxide scales were carried out by means of a General Electric XRD-3 recording X-ray diffractometer.

The preparation of metallographic specimens of the oxidized titanium specimens proved rather difficult as the brittle oxide layer became heavily crushed and displaced during grinding and polishing. A number of methods were tried, and the mounting procedure which was finally adopted, was the following: After silver-coating by evaporation of silver *in vacuo* the specimens were heavily electroplated with copper and finally mounted in Wood's metal.

Although this procedure at last was found to be the most satisfactory for this very special type of specimens, it did in no way give the perfect results. Due to the brittle nature of the oxide scale and the outer part of the metal, a trench was usually left between the oxide and the metal.

Only transverse sections of the oxidized specimens were examined. After grinding, polishing with a finegrained diamond paste and final polishing with levigated alumina, the oxide layer was examined. The metal core was best examined after etching for approximately 30 sec. A mixture of 1 part conc. HNO_3 + 1 part $(\text{HF})_n$ in 2 parts of glycerol was found superior to etchants without HNO_3 .

The microindentation hardness testing was performed with a Reichert microhardness tester (No. 1109) used in connection with a Reichert universal camera microscope (model MeF). The indenter was a Vickers pyramid.

Variations in microhardness at a single load over transverse sections of the specimens were recorded. A comparatively low load — 17 g — was chosen in order to allow a reason-

able number of indentations to be made. All microhardness indentations were made on specimens which had finally been electropolished and etched. The orientation of the various grains had a clearly visible effect on the shape of the indentation, and sometimes also on the calculated microhardness. Thus passing from one grain into another with a different orientation sometimes resulted in a jump in the hardness curve. Mostly, this effect was not pronounced. It is felt that the reported curves represent a fair average of the microhardness at the various depths below the specimen surface.

The shape of the base of the indentations mostly was not exactly square due to orientation differences of the grains. Near the edges the indentations were mostly very elongated in a direction perpendicular to the metal sheet surface. This is a consequence of the unavoidable rounding of the edges both during the mechanical- and the electropolishing. Normally the surface of the indentation is calculated by using the square of the mean length of the two diagonals of the base of the indentation. In the case of very elongated indentations this leads to an unreasonable large surface. Thus, instead of the square of the mean length, the product of the lengths of the diagonals has been used for d^2 in the formula

$$H_m = 1\,854.4 \frac{p}{d^2} \text{ kg/mm}^2$$

when calculating the reported microhardness values.

The hardness values close to the edges are very approximate only for said reason; in addition the brittle metal near the edges often crumbled even under the low load used.

A number of oxidized titanium specimens were studied by electron microscopy (RCA EMU 2D). All specimens were preshadowed and studied by a single stage carbon replica technique. This technique included 1) shadowing of the surface of the test specimen by vacuum evaporation of platinum under a certain angle, 2) direct vacuum evaporation of carbon on the preshadowed surface, 3) pressing the carbon side of the sample against molten polystyrene, 4) dissolving the specimen (TiO_2 layer and Ti) in a mixture of H_2SO_4 and $(\text{HF})_n$ at about 60°C , and after 5) dissolving the polystyrene, the specimens were ready for examination in the electron microscope.

EXPERIMENTAL RESULTS

During the course of the investigations a striking feature of the oxidation of titanium compared to other metals was the difficulty in obtaining satisfactory reproducibility and regularity in the results.

In the opinion of the authors this irregularity may be traced back to different pretreatment of the samples (rolling, high-vacuum preannealing etc.). Unless the pretreatment is performed under very controlled conditions, varying amounts of impurities may be introduced causing irregular oxidation behaviour. It seems of particular importance to achieve a high vacuum ($< 10^{-5}$ mm Hg) during annealing between rolling runs and before the start of the oxidation. As will be seen from the present results, titanium oxidizes equally fast at 10^{-3} mm Hg as at 1 atm. oxygen pressure. Thus, annealing at 10^{-3} mm Hg will cause a partial oxygen saturation of the outer layer of the titanium even without formation of an oxide scale, and this again brings about a different oxidation behaviour. On the basis of microhardness tests on transverse sections of the specimens it was found necessary to anneal the samples (0.30 mm thick) for 24 h at 850°C and $p_{\text{O}_2} < 10^{-4}$ mm Hg in order to obtain specimens homogeneous with respect to dissolved oxygen.

In a discussion of the experimental results it is convenient to distinguish between high temperature oxidation (600 — $1\,000^\circ\text{C}$) and low temperature oxidation (300 — 600°C).

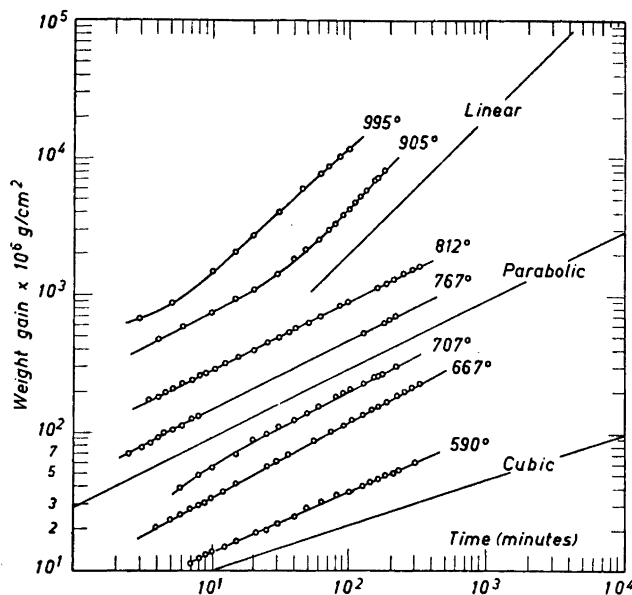


Fig. 1. Oxidation of melted and annealed (30 min at 800°C and $p_{O_2} < 10^{-4}$ mm Hg) van Arkel titanium (600–1 000°C).

High temperature studies. A large number of experiments were carried out on van Arkel titanium, Kroll titanium, and RC-55 titanium. Generally, the length of oxidation lasted for 5 h, while in a few cases the oxidation reaction was followed for 1 week.

Considering the studies as a whole, a striking feature was the irregular oxidation behaviour in the temperature region 900–1 000°C. This irregularity was often associated with sudden increases in the oxidation rates, e.g. changes from (approximately) parabolic to (approximately) linear rate laws.

Another feature is the dependence of the oxidation on the type and purity of titanium. The experiments show that the Rem-Cru titanium type RC-55 (containing max. 0.2 % C) was oxidized faster than the relatively pure Kroll titanium ($HV_{10} = 120-130$) and the van Arkel titanium ($HV_{10} = 90-100$).

Melted van Arkel titanium. The van Arkel titanium was annealed for 30 min at 800°C at a pressure of 10^{-4} mm Hg. In addition, all specimens were annealed for 10 min in high vacuum at the oxidation temperature, as it took about 10 min to obtain a satisfactory temperature constancy in the furnace before the start of the oxidation run.

The results on melted van Arkel titanium between 600 and 1 000°C are shown in Fig. 1. The oxidation follows a parabolic rate law between approximately 600 and 850°C, while at higher temperatures there seems to be a gradual change from this to an approximately linear one with time. It is interesting to note that the shift from a parabolic rate law region to a generally linear rate law region occurs near to the temperature where titanium changes from

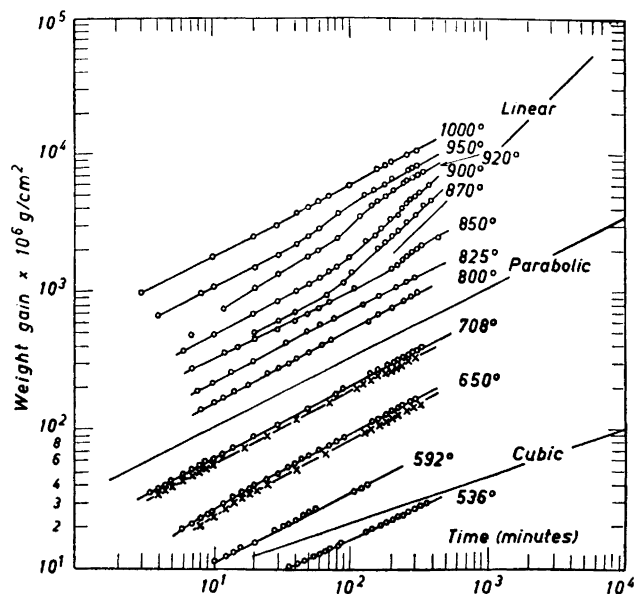


Fig. 2. Oxidation of Kroll titanium 536 and 592°C oxidized in dry air.

the α - to the β -modification. This effect is not unreasonable considering the importance of oxygen solubility in titanium metal during the oxidation reaction, and considering the higher rate of diffusion of oxygen in β - than in α -titanium.

The colour of the oxide scale after 5 h of oxidation in 1 atm. O_2 were as follows: At 1 000°C — light yellow, at 900°C — white, at 800°C — light grey, at 700°C — dark grey, and at 600°C — metallic grey.

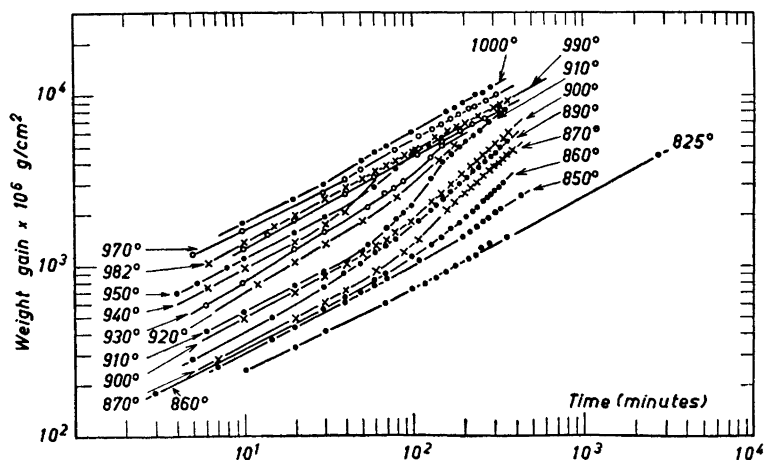


Fig. 3. A detailed study of oxidation of Kroll titanium (800–1 000°C).

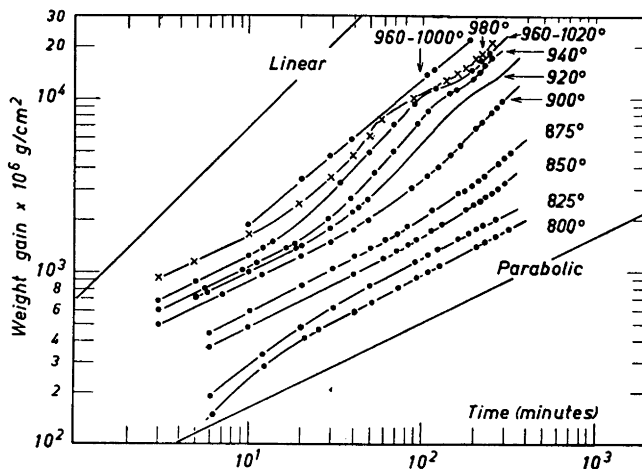


Fig. 4. Oxidation of RC-55 titanium (800–1 020°C).

Kroll titanium. The results on the oxidation of Kroll titanium (cold-rolled and annealed for 10 min in high vacuum of $< 10^{-4}$ mm Hg before the oxidation run) show the same characteristics as for melted van Arkel titanium. As seen in Figs. 2 and 3 the oxidation follows a parabolic rate law between 600 and 800°C, while there are changes from initial parabolic rate laws in the temperature region 850–950°C. It is interesting to note that while van Arkel titanium oxidizes according to an approximately linear rate law at 1 000°C, the oxidation of Kroll titanium again follows an approximately parabolic rate law at this temperature.

The colour of the oxide scales were grey blue, sometimes mottled blue grey white at temperatures above 850°C; at lower temperatures the appearance of the oxide was as for van Arkel titanium.

RC-55. For the sake of comparison it was also of interest to study the oxidation behaviour of a type of commercial titanium. It was also felt that a plate of such titanium would be rather homogeneous both as far as the impurity concentrations and structure of titanium were concerned.

The studies were carried out on RC-55 (max. 0.2% C) samples (annealed for 10 min at $p_{O_2} = 10^{-4}$ mm Hg at the oxidation temperature) in the temperature region 800–1 000°C. The results are shown in Fig. 4. Compared to the unannealed Kroll titanium the oxidation rates are higher by 50–100%. Furthermore, one may say that at all temperatures the oxidation initially follows a parabolic rate law which changes into an approximately linear rate law. There seems to be no definite increase in the oxidation rate between 950 and 1 000°C.

The oxidation of RC-55 gave grey oxide scales at 800°C; above 850°C the colour was yellow and mottled brown-yellow.

The effect of the partial pressure of oxygen on the rate of oxidation. Considering studies of oxidation of metals and alloys in general, the effect of the partial

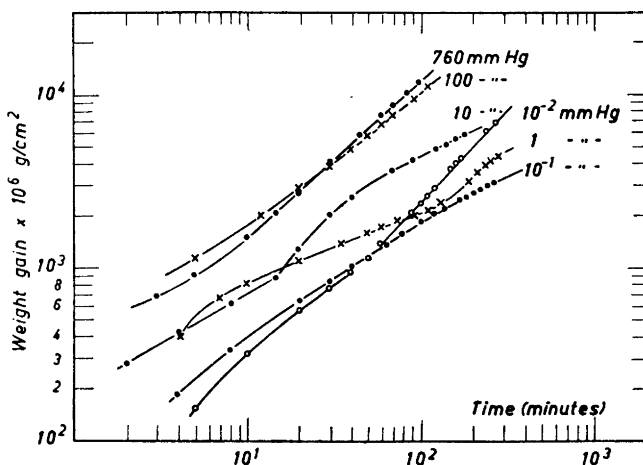


Fig. 5. The effect of oxygen pressure on the oxidation of van Arkel titanium at 1000°C.

pressure of oxygen on the oxidation rate is of importance in elucidating the mechanism of oxidation. In the case of oxidation of titanium with formation of a compact TiO_2 -scale one should on the basis of the general theory of oxidation not expect any effect of the oxygen pressure on the oxidation rate. This should, however, not hold in case of approximately linear rate laws as found for titanium above 900°C. Furthermore, it was of interest to study this effect as the competition between the oxide layer formation and oxygen solution effect probably plays an important role in the oxidation reaction. It is well known that when titanium with TiO_2 films is treated in high vacuum at high

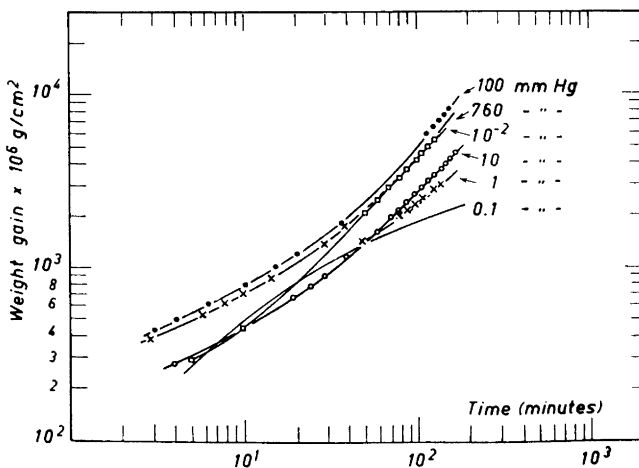


Fig. 6. The effect of oxygen pressure on the oxidation of van Arkel titanium at 900°C.

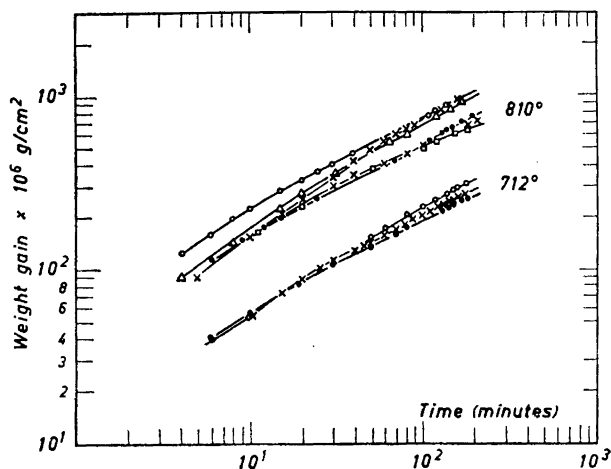


Fig. 7. The effect of oxygen pressure on the oxidation of van Arkel titanium at 810 and 712°C.

△	760 mm Hg and 1 mm Hg		×	760 mm Hg
○	100 » »	712°	●	100 » »
●	10 » »		○	1 » »
810°				
□	10 ⁻¹ mm Hg			
×	10 ⁻² » »			
+	10 ⁻³ » »			

temperatures (> 700—800°C), the oxide film dissolves in the titanium, forming a solution of oxygen in titanium. There should consequently exist a temperature dependent critical pressure below which no oxide layer is formed during the initial period of the reaction.

The effect of oxygen pressure was studied at 1 000, 900, 800, and 700°C by oxidizing annealed (30 min at 800°C at $p_{O_2} < 10^{-4}$ mm Hg) van Arkel titanium at oxygen pressures of 760, 100, 10, 1, 10^{-1} , 10^{-2} , and 10^{-3} mm Hg. The results shown in Figs. 5, 6, and 7 were somewhat unexpected, but brought forth new interesting data with regard to the basic processes of the reaction.

Generally one may say that the oxidation is oxygen pressure dependent under conditions of approximately linear rate laws, *e.g.* at 900 and 1 000°C, while the oxidation is oxygen pressure independent under conditions of parabolic rate laws, *e.g.* at 700 and 800°C. At 900 and 1 000°C it is seen that the oxidation behaviour is rather irregular at oxygen pressures below 100 mm Hg. The most interesting conclusions, however, which can be drawn from the curves, is that the oxidation rate does not decrease regularly with decreasing oxygen pressure; rather there exists a certain oxygen pressure ($\sim 10^{-1}$ mm Hg) below which the oxidation rate again increases. The reason for the dependence of the oxidation rate on the oxygen pressure at temperatures above 900°C is probably due to the competition between oxide layer formation and oxygen solution effects.

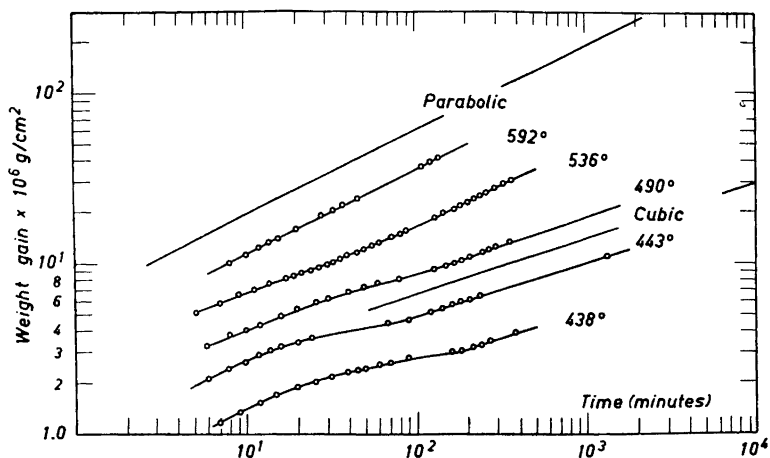


Fig. 8. Oxidation of Kroll titanium in dry air (400–600°C).

It was also interesting to note the effect of oxygen pressure on the appearance and colour of the oxide scale. At 1 000°C the colour changed from light-yellow to white in going from 760 to 0.1 mm Hg. At 10^{-2} and 10^{-3} the colour of the oxide was metallic bluegrey and grey, respectively. At 900°C the colour remained white down to 0.1 mm Hg; below this pressure the colour changed to bluegrey and grey. At 800°C the colour remained light grey in going from 760 to 0.1 mm Hg; at 10^{-2} and 10^{-3} mm Hg the colour was grey white and mottled blue grey, respectively. At 700°C the colour of the surface was dark grey in the pressure range 760 — 1 mm Hg, but the appearance became increasingly metallic with decreasing pressure. At and below 10^{-1} mm Hg the surface was mottled white dark grey.

Low temperature oxidation studies. Low temperature oxidation experiments were made in the temperature region 300–600°C. The characteristic feature of the oxidation reaction in this temperature region is that the oxidation follows non-parabolic rate laws; a logarithmic rate law was found up to about 300°C, while a cubic rate law was obeyed in the temperature region 300–600°C. There are no definite transition temperatures, but rather transition intervals where both rate laws may be found, depending upon the length of oxidation.

The studies were carried out on both cold-rolled, unannealed Kroll titanium and high vacuum annealed (30 min at 800°C) van Arkel titanium. The results are shown in Figs. 8 and 9. The general characteristics of the oxidation reaction are the same for both types of titanium. The logarithmic rate law was found below about 300°C for the length of oxidation of about 5 h, and the cubic rate law was found between 300 and 600°C, while the reaction obeyed a parabolic rate law above approximately 600°C. Furthermore, the duration of the logarithmic rate law period decreased with increasing temperature. Correspondingly the duration of the cubic rate law decreased with

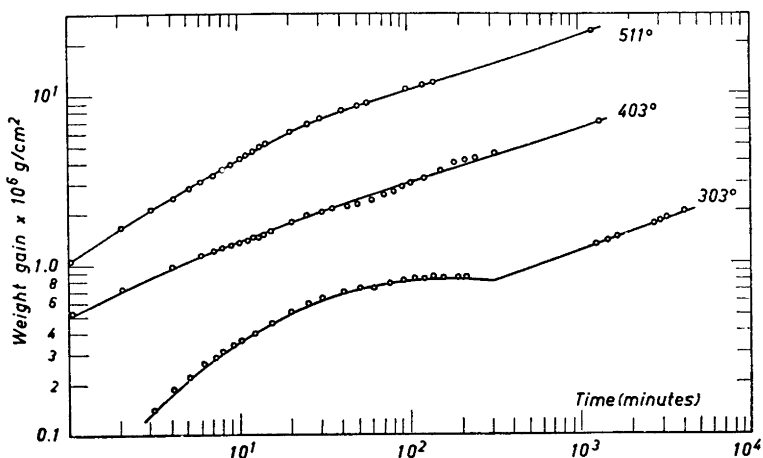


Fig. 9. Oxidation of annealed (30 min at 800°C and $p_{O_2} < 10^{-4}$ mm Hg) van Arkel titanium in dry air (300–500°C.)

increasing temperature at around 500–600°C, until the cubic rate law could no longer be observed and the reaction followed a parabolic rate law at still higher temperatures.

Kofstad and Hauffe²³ have previously proposed that the cubic rate law as found in oxidation of titanium is associated with oxygen solution effects in the titanium metal. With this as a working hypothesis a series of experiments were initiated to investigate the effect of increasing oxygen content on the rate of reaction and the rate law at definite temperatures. According to this hypothesis the duration of the cubic rate law should decrease with increasing oxygen content, and it should eventually disappear for heavy oxygen-saturated titanium. The preliminary studies along these lines substantiated these conclusions.

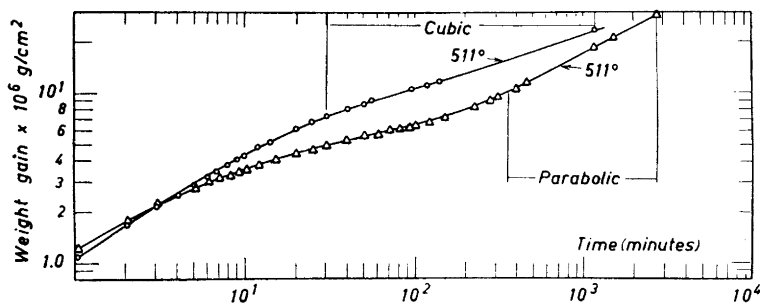


Fig. 10. Oxidation of van Arkel titanium (O) and titanium containing 4 at. % oxygen (Δ) at 511°C.

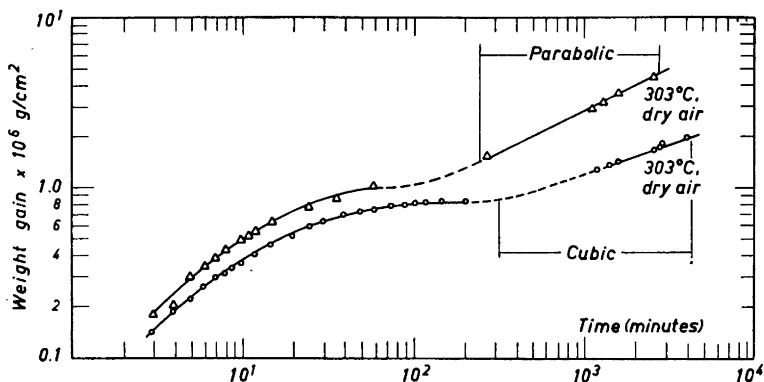


Fig. 11. The effect of oxidation-high vacuum cycles on the oxidation of van Arkel titanium (O) at 303°C. Prior to the oxidation run at 303°C, the oxygen-enriched specimen (Δ) was oxidized for 4 000 min at 403°C with subsequent annealing for 10 min in high vacuum at 800°C.

In Fig. 10 is shown the difference in oxidation behaviour at 511°C between van Arkel titanium containing 4 at. % oxygen and van Arkel titanium which was made by oxidizing the titanium and treating the specimens in high vacuum ($p_{O_2} = 10^{-5}$ mm Hg) for 24 h. As seen, the van Arkel titanium follows a cubic rate law after about 30 min of oxidation, while the 4 at. % O-Ti alloy oxidizes somewhat slower and follows a parabolic rate law after about 300 min.

Similar experiments at 403 and 303°C gave corresponding results. In these experiments high vacuum annealed van Arkel titanium specimens were oxidized for several days at 403°C, *e.g.* in the cubic rate law region. During these treatments thin films of TiO_2 were formed, but by treating the specimens in high vacuum at 800°C for 10 min the oxide films dissolved in the titanium. The oxidation-high vacuum annealing cycles were continued up to 5 times, and the oxidation was thus measured on titanium samples with increasing oxygen content. It is clear that such short annealing periods in no way distributed the oxygen uniformly through the sample. On the other hand, the outer layer of the titanium metal became more and more saturated after each oxidation-high vacuum cycle. The oxidation experiments consequently gave qualitative results as to the effect of oxygen concentration on the oxidation reaction. Qualitatively the effect of these oxidation-high vacuum annealing cycles in the cubic rate law region was to reduce the duration of the cubic law period. Furthermore, the cubic rate law would also completely disappear for samples which had previously been oxidized for the necessary length of time. Thus the cubic rate law could not be observed for specimens which had previously been oxidized for 2 600 min at 400°C with subsequent annealing for 10 min in high vacuum at 800°C.

Similarly, at 300°C the oxidation of van Arkel titanium followed the logarithmic rate law for the first 300 min, whereupon it changed into a cubic rate law. Oxidizing previously oxidation-high vacuum annealed specimens,



Fig. 12. Oxide surface of Kroll titanium oxidized for 10 min at 890°C and $p_{O_2} = 1$ atm. 3 500 \times .



Fig. 13. Oxide surface of Kroll titanium oxidized for 60 min at 890°C and $p_{O_2} = 1$ atm. 8 200 \times .

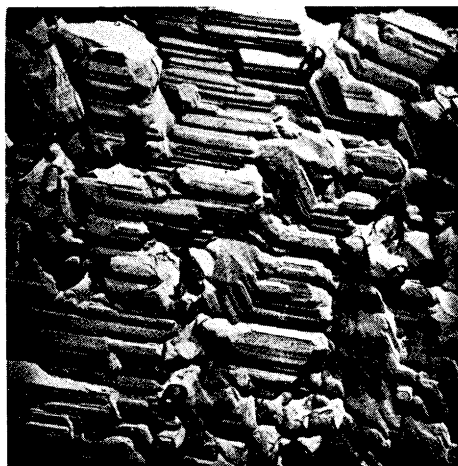


Fig. 14. Oxide surface of Kroll titanium oxidized for 20 h at 890°C and $p_{O_2} = 1$ atm. 8 200 \times .



Fig. 15. Oxide surface of Kroll titanium oxidized for 10 min at 1 000°C and $p_{O_2} = 1$ atm. 3 500 \times .

the cubic rate law disappeared. After an initial logarithmic period the oxidation followed a parabolic rate law as shown in Fig. 11. The surface of the specimens showed blue or yellow interference colours when oxidized in the cubic and logarithmic rate law regions.

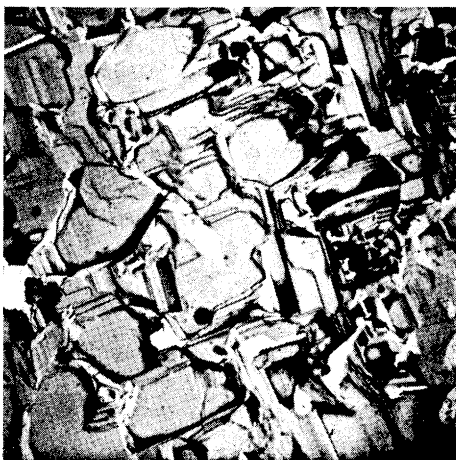


Fig. 16. Oxide surface of Kroll titanium oxidized for 60 min at 1 000°C and $p_{O_2} = 1$ atm. 3 500 \times .



Fig. 17. Oxide surface of Kroll titanium oxidized for 21 h at 1 000°C and $p_{O_2} = 1$ atm. 3 500 \times .

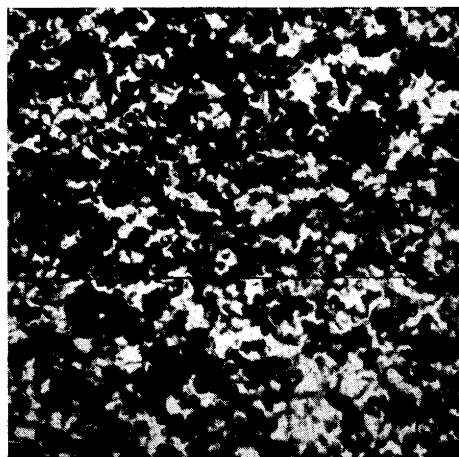


Fig. 18. Back side of detached oxide scale. Kroll titanium oxidized for 20 h at 890°C. 12 500 \times .

Structural investigations. A number of X-ray diffraction diagrams taken of specimens oxidized in pure oxygen indicated only rutile in the oxide scale.*

* Only in one case was the presence of TiO and Ti_2O_3 established with certainty. During a run oxidizing van Arkel titanium at 900°C and low pressures, the oxygen was accidentally saturated with water vapor. The subsequent X-ray diagram showed that the oxide scale, which was black, consisted solely of TiO and Ti_2O_3 . This means that any TiO and Ti_2O_3 formed were only present in amounts smaller than a few percent.



Fig. 19. Van Arkel titanium oxidized for 5 h at 700°C. 375 ×.



Fig. 20. Van Arkel titanium oxidized for 5 h at 800°C. 375 ×.

Specimens of Kroll titanium oxidized at 900 and 1 000°C for different length of time were also investigated by electron microscopy techniques. The specimens were cold-rolled and oxidized without high vacuum annealing. This procedure resulted in a preferred orientation in the titanium metal structure, and this again had its effect on the oxide scale. The results are shown in Figs. 12—18.

After 2 min of oxidation the crystals were at both temperatures small and spherical, but in some spots there was a tendency to a preferred orientation. Especially for the specimens oxidized at 900°C the crystals began to take on a lengthened form with normally developed crystal faces. After 10 min of oxidation the 900°C specimens differed from those at 1 000°C in that the rutile crystals were parallel and stretched lengthways, and they showed a decidedly preferred orientation over large parts of the surface. At 1 000°C the crystals were much larger and there was a much smaller tendency to preferred orientation. After one hour of oxidation the specimens at 900°C did not differ appreciable from those oxidized for 10 min, while the specimens oxidized at 1 000°C showed that the tendency to preferred orientation became less pronounced and there was evidence of surface diffusion and crystal growth.



Fig. 21. RC-55 titanium oxidized for 5 h at 825°C. 75 \times .

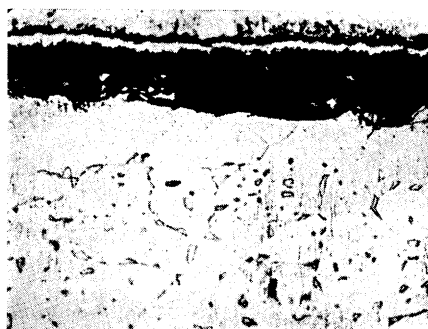


Fig. 22. Fig. 21. at a higher magnification. 325 \times .

Specimens oxidized longer than one hour at 1 000°C showed large crystal growth steps and less preferred orientation. At 900°C the crystals remained relatively small. Even for an oxidation period of 27 h did crystals show a high degree of preferred orientation. At both temperatures the formation of elbow twins was a common phenomenon.

By removing the oxide scale with tape, the back side of the oxide layer was investigated. These investigations showed small, spherically formed crystals without crystal faces for both temperatures and for different lengths of oxidation.

Metallographic examination of a large number of specimens has given the following visual picture of the oxide scale and the metal beneath for oxidation of titanium above 700°C.

The first oxide layer which can be observed, appears to be dense and even, and to be in very close contact with the underlying metal. Growing in thickness, there can be observed a formation of thin layers parallel to the surface. The density seems to decrease as there appears a large number of elongated holes in the oxide layer which hardly can be a result of polishing alone, although polishing may increase their size and give an exaggerated impression of the amount of total porosity.

When the oxide has reached a rather large thickness, it is comparatively easy to polish and to retain, while at some earlier stage it breaks and is partly removed during polishing.

The oxide layer seems to consist of one phase only; a slightly different tone sometimes observed near the interface oxide/metal is believed only to be an optical effect due to internal reflection. Examination under polarized light (crossed Nicols) shows no sign of the presence of more than one phase.

Already shortly after the first traces of an oxide layer can be observed microscopically, a sort of boundary can be seen to move slowly inwards into the metal core in cold-rolled, unannealed specimens. The area between this boundary and the oxide layer is characterized by a larger grain size, and the grains are more or less columnar with their largest extension perpendicular to the surface. This area is very brittle, and when it reaches a certain thickness, fragments start to break out during polishing. This is shortly before the oxide layer has become thick enough to stand up against the strain of polishing, which means that at any stage of oxidation, there will be hard particles breaking out making the polishing very difficult. Further the holes or grooves formed collect debris and liquids which stain the specimen during drying.

The metal core inside this moving boundary has a much smaller grain-size, and the grains show a more random orientation. It is suggested that this moving boundary represents the delineation between an outer area with a very high oxygen content and an inner core containing only the original or a very low amount of oxygen. Further the boundary is believed at any time to be situated in that part of the metal where the micro-hardness testing shows the very steep change in hardness.

There naturally is a distinct difference in microstructure between the specimens which were oxidized in cold-rolled condition and the specimens which were annealed before oxidation. The last-named shows very much larger grains, very often extending right through the whole cross-section of the specimen. Grain growth during oxidation of such specimens therefore becomes unimportant, and a formation of columnar crystals can hardly be observed.

As most of the photographs show several details, their description has been postponed. In Figs. 19 and 20 are shown the oxide scales formed after oxidation of van Arkel titanium in 1 atm. O_2 for 5 h at 700 and 800°C, respectively. The dark spots near the oxide/metal interface in Fig. 21 are due to holes from the breaking out of hard and brittle particles during polishing.

Fig. 21 (RC-55 titanium oxidized for 300 min at 825°C) shows on both sides of the specimen a comparatively well conserved oxide layer under the plating. Beneath the oxide scale follows a groove where most of the brittle metal has been removed during the polishing. The inner part of this brittle layer still remains in place, and the boundary between this layer and the rest of the core has revealed a different structure after etching. Fig. 22 shows a detail at higher magnification.

Micro-hardness measurements were made on transverse sections of a series of specimens oxidized for various lengths of time (10 min, 5 h, and 24 h) and at different temperatures. Some of the specimens were oxidized in the cold-rolled condition, others after annealing for 20 min at 1 000°C.

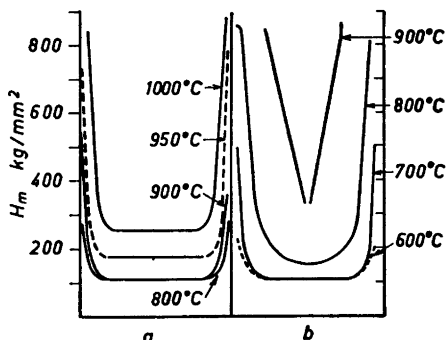


Fig. 23a. The effect of temperature on the oxygen penetration into Kroll titanium after oxidation for 10 min.

Fig. 23b. The effect of temperature on the oxygen penetration into van Arkel titanium after 5 h of oxidation.

In Fig. 23 a and b are shown the effect of temperature on the oxygen penetration into the titanium metal after oxidation for 10 min and 5 h, respectively. The data shown in Fig. 23 a were obtained by oxidizing Kroll titanium in the cold-rolled condition for 10 min, while Fig. 23 b gives the result of oxidation of van Arkel titanium. All the plates had a thickness of 0.03 cm before the start of oxidation. The results show clearly that oxygen penetration into titanium metal plays an important role in the oxidation reaction.

As seen, the oxygen is concentrated near the metal/oxide interface after oxidation at temperatures below 700°C, while the oxygen penetrates to the core of the specimens by oxidizing at 800°C and above. Especially may be noted the large oxygen penetration above 900°C when the titanium exists in its β -modification. This result is in agreement with the fact that the rate of diffusion of oxygen is much larger in the β - than in the α -phase, even though the solubility of oxygen is higher in the β -modification.

In Fig. 24 is shown the effect of length of oxidation on the oxygen penetration into the van Arkel titanium at 800°C. At this temperature titanium exists in its α -modification with a relatively low rate of oxygen diffusion compared to that of β -titanium, and consequently the inner part is only slowly saturated with oxygen. Most of the oxygen is concentrated at or near the metal/oxide interface, the slope of the oxygen penetration curve is decreasing sharply when going from the metal/oxide interface into the metal.

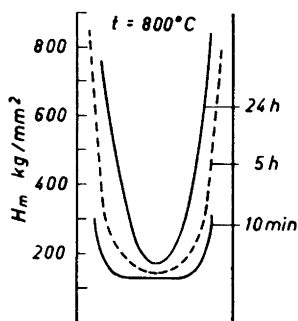


Fig. 24. The effect of length of oxidation on the oxygen penetration into van Arkel titanium after oxidation at 800°C.

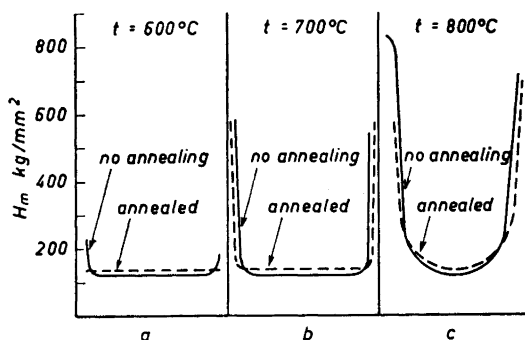


Fig. 25. *a, b, c.* The effect of annealing (20 mins at 1 000°C and $p_{O_2} < 10^{-4}$ mm Hg) before the oxidation run on the oxygen penetration into van Arkel titanium after 5 h of oxidation at 600, 700, and 800°C, respectively.

Figs. 25 *a, b,* and *c* show the effect of the oxygen penetration curves for van Arkel titanium after 5 h oxidation at 600, 700, and 800°C, respectively. All the specimens did have a thin outer zone enriched with oxygen, which was introduced in the metal during annealing between rolling runs. Half of the specimens were oxidized as such, and the other half annealed for 20 min at 1 000°C at $p_{O_2} = 10^{-4}$ mm Hg before the start of the oxidation. The results clearly show the effect of this annealing. Qualitatively one may say that during the annealing the oxygen in the outer zone has diffused into the specimen, and has become distributed throughout the specimen. The hardness throughout the sample is thereby increased as shown by the raising of the oxygen penetration curves in the annealed specimens compared to the unannealed. Correspondingly, the steep parts of the oxygen penetration curves are displaced further into the metal in the case of the unannealed specimens.

It is very reasonable that the effect of annealing has a decisive effect on the oxidation characteristics as the kinetics of the oxygen penetration into the metal very possibly plays an important role in the oxidation reaction. When titanium is oxidized in the cubic rate law region (300—600°C), there is some evidence that the kinetics of oxygen diffusion into the metal is responsible for the cubic rate law. Furthermore, the concentration of oxygen in the outer layer also determines the duration of the cubic rate law period.

DISCUSSION

All the above described results clearly indicate that the mechanism of oxidation of titanium is very complex, and no simple interpretation can be given to the diverse phenomena observed at different temperatures and oxygen pressures. The main reason for this state of affairs is partly due to the high oxygen solubility and the resulting interplay and competition between oxide film formation and oxygen dissolution effects.

Oxidation mechanism

a. Oxide scale. From a thermodynamic reasoning and comparing with iron, one might in the case of oxidation of titanium expect to find a sequence of oxides in the oxide scale with TiO near the metal/oxide phase boundary, Ti_2O_3 in an intermediate region, and TiO_2 at the outer part of the oxide scale. Assuming a compact oxide scale, the amounts of each oxide would on the basis of the Wagner theory of oxidation be dependent upon the rate of formation of the independent oxides, *e.g.* upon their respective defect structures and the rate of ion diffusion through each phase.

Actually, when oxidizing titanium in oxygen, both the X-ray diffraction and metallographic studies show that the oxide scale only consists of one phase, which is rutile. Considering the accuracy of these methods, one may conclude that any TiO and Ti_2O_3 formed are present only in amounts smaller than a few percent.

TiO_2 is a n-type semiconductor and has an oxygen deficient structure²⁵. It is generally accepted that this oxygen deficiency results in oxygen ion vacancies rather than interstitial titanium ions in the rutile lattice²⁶.

b. Diffusion. The oxygen ion vacancies may facilitate a higher rate of diffusion for oxygen than for titanium in TiO_2 , and consequently the inward diffusion of oxygen from the outer layer of the oxide might be expected to determine the rate of oxidation of titanium.

Almost all investigators studying the oxidation of titanium below 1 000°C have on the basis of various evidence (marker studies, scratches, and surface markings on the metal specimens) suggested that this mechanism is correct^{5,12,21}. Recent marker studies by Kinna and Knorr at 1 000 and 1 200°C indicate that in addition to oxygen ion diffusion, diffusion of titanium ions also plays an important role during the oxidation²².

There has in this investigation not been made any direct attempts as to establish whether oxygen or titanium ions migrate through the oxide scale. The metallographic and electron microscopy studies do indicate, however, that an overwhelming oxygen diffusion takes place during oxidation below at least 900°C. As the oxide layers grow in thickness, there can in the oxide layer be observed a formation of thin layers parallel to the surface, which indicate that the growth of the oxide layer takes place at the metal/oxide interface. The electron microscope pictures of titanium oxidized for different lengths of time (up to 27 h) at 900°C show a high degree of preferred orientation, which do not change appreciably with the duration of the oxidation. This shows that the crystal growth and corresponding surface diffusion of titanium ions is small at this temperature. Hence titanium ions seem to be relatively immobile at this temperature. This could mean that migration of titanium ions through the oxide scale can hardly be responsible for the oxidation of titanium. At 1 000°C the surface of the oxide scale showed a much smaller tendency to preferred orientation than at 900°C; specimens oxidized longer than one hour at 1 000°C showed large crystal growth steps and few signs of preferred orientation. Thus, at this temperature the surface diffusion of titanium ions seems more pronounced. It is of course to expect that surface diffusion is much faster than volume diffusion, but the observation is at least

in qualitative agreement with the results of Kinna and Knorr, who find that both titanium and oxygen ions migrate through the oxide scale during oxidation at 1 000°C and above.

The relative importance of oxygen ion and titanium ion diffusion through the oxide scale during oxidation of titanium may be described by the following qualitative considerations: Even though the defect structure of rutile favours a predominant oxygen ion diffusion, the titanium ions are of course not frozen in their lattice positions. The question of titanium ion diffusion is also a matter of thermal energy of the ions and potential energy barriers between neighbouring lattice positions. One could perhaps conclude that the activation energy for oxygen ion diffusion is much smaller than the activation energy for titanium ion diffusion in TiO_2 . But this situation only implies that the oxygen ion diffusion is the most probable diffusion process in TiO_2 at lower temperatures, but titanium ion diffusion becomes increasingly important with increasing temperature.

For considerations of the oxidation mechanism of the titanium oxidation below 1 000°C, it will be assumed that the oxygen-ion diffusion determines the oxidation reaction.

c. Rate laws. The reported studies on the oxidation rates and the rate laws of oxidation at different temperatures are all in general agreement with data previously reported by other investigators and as reviewed by Kofstad and Hauffe²³. The rate laws found in this investigation may be represented as follows: The oxidation follows a logarithmic rate equation up to approximately 300°C, a cubic rate law is found in the temperature region 300—600°C, a parabolic rate equation is obeyed between 600 and 850, while no clearcut rate law is found above 850°C. The rate laws observed at high temperatures (> 850°C) may often be described as an initial parabolic rate law followed by a linear rate law, while in other cases the rate law may be interpreted as a mixture of linear and parabolic rate laws.

It should be pointed out that there are no definite temperatures at which the oxidation changes rate law; rather there are temperature intervals where different rate laws may be observed depending upon the duration of the oxidation. At 300°C for example, the logarithmic rate law is conformed with for approximately 300 min whereupon the rate changes into a cubic rate law. With increasing temperature, the duration of the logarithmic rate law period becomes increasingly shorter. Similarly at approximately 550°C the oxidation will for a relatively short period obey the cubic rate law, when after longer periods the oxidation will follow a parabolic rate law. In the parabolic rate law region between 600 and 850°C the oxidation will eventually increase abruptly at very long oxidation periods and change into approximately a linear rate law. The time during which the parabolic rate equation is obeyed, becomes shorter with increasing temperatures until at 900°C the oxidation follows approximately a linear rate law after 10 min of oxidation.

The interpretation of the mechanism of oxidation of titanium is complicated by the high solubility of oxygen in titanium. It is thus not only necessary to consider the formation of an oxide layer and the rate of diffusion of ions through this layer, but also the dissolution of oxygen in titanium, *e.g.* the rate of diffusion of oxygen through oxygen-enriched titanium.

There is no unequivocal interpretation of the logarithmic rate law. It is, however, well known that the oxidation of many metals follows a logarithmic rate equation. This type of relationship is often interpreted in terms of electric field effects across very thin oxide films (up to 50 Å)²⁷. After the oxygen is adsorbed on the oxide surface, they combine with electrons and from chemisorbed oxygen ions because of the relatively high electron affinity of oxygen. The chemisorption gives rise to an electric field across the oxide film. According to Hauffe²⁴ the transfer of electrons across the oxide film is the rate-determining step in the reaction during the logarithmic rate law period.

Another derivation of the logarithmic rate law at low temperatures for oxide films thicker than 50 Å, is due to Evans²⁸, who makes use of the assumption that the effective area undergoing oxidation is not constant. This situation may be due to disarrayed oxide films, for instance at the junction of grains or the intersection of slip planes. If oxygen at such points can reach the metal, oxidation is likely to penetrate inwards along such paths of disarray, producing localized oxidation and thereby not a uniform film thickening. This situation may also arise in cases where there is a zone mixed with, or consisting of metal and interpenetrating metal and oxide as observed by Vernon, Calman, Clews, and Nurse oxidizing iron below 200°C²⁹.

Other interpretations of the logarithmic rate law have been proposed by Rideal and Jones³⁰, Uhlig³¹, and Landsberg³².

At the present time it is difficult to decide as to the correct mechanism in the logarithmic region in the case of titanium oxidation. According to the reported data the logarithmic rate law is obeyed until the weight gain/cm² equals about 1×10^{-6} g, which corresponds to a film thickness of approximately 60 Å. On the other hand, the data of Gulbransen and Andrew²³ may be interpreted as obeying a logarithmic rate law up to a weight gain of at least 6×10^{-6} g/cm² corresponding to a film thickness of at least 360 Å. Further investigations of this problems are therefore necessary. In this respect it would also be of importance to study the effect of oxygen pressure on the rate of oxidation.

It is reasonable to assume that the logarithmic rate law is associated with an oxide film formation, as it is very unlikely that a diffusion of oxygen into the metal would yield such a rate law. The rate of dissolution and diffusion of oxygen in titanium is consequently very small compared to the rate of film formation during the logarithmic rate law period.

With regard to the cubic rate law in general a few attempts have been made to work out a theoretical treatment. Mott³⁷ predicted the cubic rate from theoretical studies in connection with the logarithmic equation. A derivation of this rate law has also been made by Hauffe, Engell, and Ilschner in order to interpret the oxidation of nickel at 400°C³³. The derivations of both Mott and Hauffe presupposes a p-type oxide film, and as TiO₂ is an n-type conductor, these approaches are not applicable in the case of oxidation of titanium.

In view of the fact that the cubic rate law is followed up to about 600°C, where the oxidation is appreciable, it seems that it cannot be interpreted in terms of electric field effects across the oxide layer. These approaches assume a relatively thin oxide film with a maximum thickness of a few hundred Ångströms, a condition which is not well satisfied in the case of titanium

oxidating at 500–600°C. On this basis Kofstad and Hauffe²³ suggested that the cubic rate law was due to another mechanism.

In view of the high solubility of oxygen in titanium it was reasonable to suggest an interpretation of the cubic rate law in terms of diffusion of oxygen through the outer layer of the oxygen-enriched titanium. Using this as a working hypothesis several studies were made, which substantiated this assumption.

In this connection it is interesting to note that the oxidation of zirconium also follows a cubic rate law between 350 and 950°C³⁴. As in the case of titanium, it is here also evident that electric field effects cannot explain this high temperature oxidation mechanism. Zirconium and titanium are very much alike in having a very high oxygen solubility, and it is possible that this effect is responsible for the cubic rate law. Furthermore, there is evidence that the rate of diffusion of oxygen in titanium is dependent upon the oxygen concentration in titanium³⁵.

If the cubic rate law is interpreted in terms of oxygen dissolution in the outer layer of the titanium, one could expect an effect of the oxygen concentration in the titanium on the duration of the cubic rate law period. The length of this period should decrease with increasing oxygen content, and it should eventually disappear for heavily oxygen-saturated titanium.

As seen in Figs. 10 and 11, our preliminary studies along these lines substantiated these assumptions. At 511°C (Fig. 14) the cubic rate law period was shorter for the titanium containing 4 at. % O₂ than for pure titanium. Furthermore, the oxidation changed into a parabolic rate law after about 300 min of oxidation in the case of the oxygen-enriched specimen.

Similar experiments at 403 and 303°C showed corresponding effects. At these temperatures the oxidation was performed on specimens which were highly enriched with oxygen in the outer layer of the titanium by oxidizing the specimens and thereupon treating them in high vacuum at 800°C for 10 min in order to dissolve the oxide film. The intention was to shorten the duration of the cubic rate law period, until the cubic rate law disappeared completely for heavily oxygen-saturated specimens. Similarly, at 303°C the oxidation of van Arkel titanium obeyed the logarithmic rate law for the first 300 min and is followed by a cubic rate law, but by oxidizing previously oxidation-high vacuum annealed specimens the cubic rate law disappeared. After an initial logarithmic rate law period the oxidation now followed a parabolic rate law.

On the basis of these studies the following qualitative picture may be given of the oxidation process in the cubic rate law region: The very first part of the reaction involves a chemisorption of oxygen on the titanium, followed by an oxide film formation, the oxide consisting of TiO₂. At the same time the diffusion of oxygen into the titanium metal also takes place: we thus have a competition between oxide film formation and oxygen dissolution in the metal. At low temperatures (~ 300°C) the diffusion of oxygen into the titanium is so small that the oxide film formation is the predominant feature of the reaction. The oxidation accordingly follows a logarithmic rate law which prevails as long as the rate of oxide film formation is very much faster than the rate of oxygen dissolution. The distinctive stamp of

the logarithmic rate law is of course the rapidly decreasing rate of oxidation with increasing time, and at a certain time (which becomes increasingly longer with decreasing temperatures) the rate of dissolution of oxygen will eventually become the predominant feature of the oxidation reaction. At this time interval, the oxidation changes from a logarithmic to a cubic rate law, as observed when titanium is oxidized at 303°C (Fig. 11).

This same situation does of course exist at higher temperatures. At increasing temperatures, however, the rate of oxygen dissolution plays an increasingly predominant role as compared to the oxide film formation obeying the logarithmic rate law. The logarithmic law period consequently becomes shorter with increasing temperatures. In addition, the oxidation neither follows a logarithmic nor a cubic rate law during the first stages of the oxidation in the temperature region 400—500°C. The observed oxidation may be interpreted as a mixture of a logarithmic and a cubic rate law, as both the rate of oxide film formation and oxygen dissolution is of the same order in this time interval. The rate of oxide film formation rapidly decreases, whereupon the diffusion of oxygen becomes the determining mechanism.

If the proposed interpretation of the data is correct, it would imply that the oxide film has an approximately stationary thickness when the oxidation follows the cubic rate law. The oxygen which dissolves in titanium is taken from the TiO_2 scale; however, a decrease in the thickness of the oxide film would immediately be counteracted by an increase in the electric field across the oxide (assuming the mechanism proposed by Mott). This immediately causes a growth of the oxide film until it reaches the stationary thickness. One way of testing this hypothesis would be to measure the growth of the oxide film in the cubic rate law region.

This may be done by continuously following the oxide film formation by means of X-ray or electron diffraction studies. Of importance in elucidating the mechanism in the logarithmic and cubic rate law regions would also be to study the oxidation as a function of the oxygen pressure.

In the results given in Fig. 11 it is shown that the cubic rate law eventually disappears when the outer region of the titanium becomes heavily enriched with oxygen, and the oxidation eventually follows a parabolic rate law even at 300°C. The following interpretation is proposed to explain this phenomenon: The parabolic rate law, as observed for oxygen enriched specimens even at 300°C, is assumed to represent a growth of the oxide film. However, in order that TiO_2 be formed, the chemical potential of oxygen in the TiO_2 phase, $\mu_{(\text{TiO}_2)}$, must be equal to the chemical potential of oxygen dissolved in titanium at the metal/oxide phase boundary, $\mu_{(\text{Ti})}$:

$$\mu_{(\text{TiO}_2)} = \mu_{(\text{Ti})}$$

During the cubic rate law region oxygen dissolves in the titanium, and oxygen consequently continuously migrates away from the region of the titanium in the immediate neighbourhood of the metal/oxide phase boundary. Thus during the cubic rate law period the chemical potential of oxygen in titanium, $\mu_{(\text{Ti})}$, does not reach the value necessary for a further growth of the TiO_2 oxide film. Only when the region of the titanium metal at the metal/oxide interface becomes saturated with oxygen, does the condition exist for a

further growth of the oxide film. When this saturation value is reached, the oxidation does not follow the cubic rate law any longer, rather we get a growth of the oxide scale. The rate determining reaction now becomes the diffusion of oxygen ions through the oxide scale with a corresponding parabolic rate law of oxidation. During the parabolic rate law period the diffusion of oxygen into the titanium metal does of course go on at the same rate, and as the oxygen ion diffusion through the oxide film is the slower process, the oxygen penetrates deeper into the titanium metal core with increasing time, as found by the micro-hardness studies at 800°C (Fig. 24).

The discussion and interpretations presented are of course only qualitative. The interpretations are only given in order to explain the kinetics of the oxidation reaction.

Another interpretation of the parabolic rate law in terms of electric field effects in the oxide film as proposed by Engell and Hauffe³⁶ for oxidation of zinc at 300°C, may also be considered. It is felt, however, that the interpretations presented may serve as a useful working hypothesis for further studies on the elucidation and understanding of the oxidation mechanism in this temperature region.

Several studies can be proposed for testing the hypothesis. Again it would be of invaluable help to study the growth of the oxide film during oxidation with X-ray or electron diffraction techniques. Furthermore, the oxygen pressure dependence of the oxidation would also provide clues as to the oxidation mechanism. According to this hypothesis all the rate laws (logarithmic, cubic and parabolic) should also be observed during oxidation at one temperature such as 300°C, provided that the oxidation is followed for the necessary length of time. This has not been done at this temperature, as the oxidation as shown in Fig. 11 was only followed for about 3 days. In order to obtain the parabolic rate law at this temperature a length of oxidation of several weeks, perhaps months, will be needed when oxidizing an oxygen free titanium specimen.

The same interpretation of the parabolic rate law for oxygen-enriched specimens at temperatures below 500°C, is proposed to be valid for the parabolic rate law region between 600 and 850°C. When oxidizing oxygen-free specimens at these temperatures, the region of titanium metal at the metal/oxide interface becomes saturated so fast with oxygen, that the cubic rate law is not observed. The parabolic rate law is consequently obeyed after a few minutes of oxidation. The diffusion of oxygen through the oxide is the slower and therefore the rate determining step in the reaction. Simultaneously oxygen diffuses into the titanium metal, and it penetrates deeper into the titanium metal core with increasing length of oxidation as shown by the micro-hardness studies of the oxygen penetration during oxidation at 800°C (Fig. 24).

For long periods of oxidation in this temperature region, the oxidation rate increases abruptly, and the rate law changes into an approximately linear rate law. As pointed out by several investigators^{5,12,13} this is a result of the cracking of the oxide scale with subsequent formation of a porous oxide scale. The Pilling-Bedworth ratio is in the case of titanium equal to 1.76, and this

results in stresses in the oxide scale producing cracks and fissures, which causes the linear rate law.

At temperatures of 900°C and above, the oxide scale apparently reaches the critical thickness after a few minutes of oxidation, and the oxidation therefore follows an approximately linear rate law in this temperature region. In addition the effect of the allotropic transformation of titanium at 883°C may have some effect on the oxidation rate in the linear rate law region. Oxygen diffuses faster in β - than in α -titanium, and when there is no protective oxide layer, this increased rate of diffusion in the β -titanium may partially account for the fast oxidation in the linear rate law region. It should be kept in mind, however, that even when oxidizing in the β -region, the outer oxygen-enriched layer of the titanium metal will consist of α -titanium, as dissolved oxygen raises the transition temperature of the α - β transition.

The data on Kroll titanium indicates that the oxidation follows an approximately parabolic rate law at 1 000°C, while the oxidation of van Arkel titanium follows a linear rate law at the same temperature. The reason for this difference is not clear, but one explanation may be that the impurities in the Kroll titanium has a beneficial effect on the mechanical properties of the oxide scale. The reappearance of the parabolic rate law when Kroll titanium is oxidized at 1 000°C, may be interpreted in terms of a sintering effect of the oxide. As pointed out by Jenkins^{12,19}, rutile has a Tamman temperature of about 1 000°C, and one might consequently expect a relatively high rate of sintering at these temperatures. The difference between Kroll and van Arkel titanium, therefore, may be traced back to the larger amounts of impurities present in Kroll titanium. Impurities of magnesium and iron (present in Kroll titanium) would tend to increase the defect structure of TiO_2 , thereby suggesting a higher sintering effect in the case of Kroll titanium. This would decrease the porosity of the oxide scales; furthermore, the growth stresses would be more easily relieved, thereby preventing the formation of cracks in the scale. An investigation of the density of the oxide scale formed would be of help in elucidating this problem.

The electron microscope pictures of the surface of Kroll titanium oxidized at 1 000°C also supports the assumption of a sintering effect at this temperature. The pictures show little preferred orientation of the oxide surface even after 10 min of oxidation, thus indicating that the surface diffusion of ions is relatively fast.

d. Effect of oxygen pressure. The studies of the effect of oxygen pressure on the oxidation rate of van Arkel titanium also brought forth new interesting data with regard to the oxidation mechanism, although further studies are necessary for definite interpretations of the results.

The effect of oxygen pressure was studied at 700, 800, 900, and 1 000°C. Generally one may say that the oxidation is oxygen pressure dependent at 900 and 1 000°, *e.g.* under conditions of approximately linear rate laws, while the oxidation is oxygen pressure independent within the limits of error under conditions of parabolic rate laws at 700 and 800°C. On the basis of the general theory of oxidation, one should in the case of oxidation of titanium with formation of a compact TiO_2 -scale, expect no dependence of oxygen pressure on the oxidation rate²¹. This should, however, not be the case under conditions

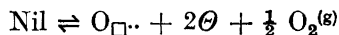
of linear rate laws as found for van Arkel titanium at 900 and 1 000°C, and in which case the rate determining step probably is a phase boundary reaction at the metal/oxide interface. The present results are therefore generally as would be expected.

As the oxidation of titanium is complicated by oxygen dissolution in titanium, one might at low pressures expect to observe an effect due to the competition between the oxide layer formation and oxygen dissolution. This is particularly so, as it is well known that when titanium with TiO_2 films is treated in high vacuum at high temperatures, (> 700—800°C), the oxide film dissolves in the titanium, forming a solution of oxygen in titanium. There should consequently exist a temperature dependent critical pressure below which no oxide layer is formed during the initial period of the reaction. An oxide layer formation would only occur when the outer layer of the titanium becomes saturated with oxygen thereby raising the chemical potential of oxygen to the value permitting formation of TiO_2 .

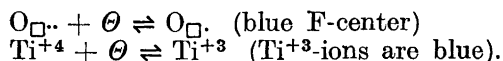
The oxygen pressure dependence at 900 and 1 000°C may be interpreted in terms of these suggestions. At these temperatures it is seen that the oxidation behaviour is rather irregular below 100 mm Hg. The interesting part is that the oxidation rate does not decrease with decreasing pressure below an oxygen pressure of 10^{-1} mm Hg. Rather the oxidation rate again increases when the oxygen pressure is decreased to 10^{-2} and 10^{-3} mm Hg.

Judging from the results at 1 000°C it is evident that the oxide scale has an increasingly protective effect at 10, 1 and 0.1 mm Hg as compared to 1 atm. and 100 mm Hg. The reason for this is not clear, but it is suggested that the lower oxygen pressures increase the oxygen ion vacancies in the TiO_2 . This in turn permits a higher rate of diffusion of ions with a corresponding sintering effect. At pressures below 0.1 mm Hg the competition between oxide film formation and dissolution of oxygen in titanium plays a more dominant role. The tendency to oxide film formation decreases, and at a certain pressure no oxide will be formed. The titanium metal under these conditions is exposed to oxygen atmosphere, and the oxygen migrates directly into the metal. There will be growth of an oxide scale only when the outer layer of the titanium metal is saturated with oxygen.

e. Colour of oxide scales. In this connection it is also interesting to note the change in colour of the oxide scale formed when oxidizing at different pressures. It is well known that rutile may change its colour with changing oxygen content and with small additions of foreign oxides³⁶⁻³⁸. The oxygen deficient structure may with Schottky symbols be expressed as



where Nil designates a structure without defects, the squares are ion vacancies, the dots are positive excess charges, and Θ are free electrons. TiO_2 is an n-conductor and with decreasing oxygen content, electrons may be captured according to one or both of the following equations:



Thus, rutile generally shows an increasingly blue colour with decreasing oxygen content. However, the significance of the observed colour change as a function of oxygen pressure is not clear at the present.

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