# KROLL LECTURE

*Kroll Lecture*

# INFLUENCE OF IMPURITIES ON THE MECHANICAL PROPERTIES OF TITANIUM AND TITANIUM ALLOYS

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## Introduction

The development of Titanium industry in the world is due to the imagination and the obstinacy of an exceptional engineer Dr. W.J.Kroll. Born in Luxembourg in 1908, he received his initial formation in the famous Technische Hochschule of Berlin-Charlottenburg. This formation certainly was decisive for the orientation of his career. Indeed, all his long life was devoted to the same objective, namely the purification of many metals. Before him, many metals were reputed as brittle at room temperature. Dr. Kroll was rapidly convinced that the brittleness was due to small contents in some impurities, mainly oxygen, nitrogen, carbon or hydrogen. The tables 1 and 2 sum up the successive stages of the astonishing activity of Dr. Kroll not only in his personal laboratory of Luxembourg, but also in different institutions. Because of the enormous difficulties created by the 2nd World War, he decided to emigrate in U.S.A. where he succeeded to convince some great american companies or state institutions to support his researches. Dr. Kroll was not only a metallurgist, but also a chemist, a physicist and, above all, an engineer which transfered his laboratory results to the Ti-or Zr-production on the industrial scale.

If we consider only the field of Ti-researches of Dr. Kroll, we are impressed by the competition between different chemists and metallurgists for elaborating <u>ductile</u> titanium. The table 3 sums up the successive stages of processes proposed by some famous metallurgists from Berzelius to Van Arkel.

In spite of the high level of purification obtained by the Kroll's process, some progresses must yet be made for improving the titanium purification by decreasing the content not only in interstitial elements (O , N , H ) but also in substitutional impurities, such as Fe, S, P, Si and so on. It was the reason why Prof. Zwicker suggested that my introductory lecture in honor of the Dr. Kroll's memory was devoted to the theme:

> "Influence of impurities on the mechanical properties of Titanium".

Firstly, I want apologize for presenting only the results obtained in my laboratory of Orsay's University. This presentation could appear too restrictive and pretentious, but the time is too short to give a general survey of the results of many authors. Even thus I must limit my lecture to the influence of impurities on the creep behaviour of impure titanium and incidently to the dynamic strain ageing and to tensile properties at different temperatures.

Table 1

# THE SCIENTIFIC CARREER OF DR. WILLIAM JUSTIN KROLL 1839 - 1973

| Period | Country and Institution | Nature of Activity |
|---|---|---|
| 1910-1917 | Technische Hochschule Berlin-Charlottenburg (Germany) | Born Nov. 24th 1889 in Esch/Alzette, Luxemburg<br>Bachelor's degree in metallurgy of iron |
| 1918 | | Thesis on amorphous pure boron |
| 1918-1919 | Kall/Eifel (Germany) Metallgesellschaft Frankfurt/Main | CaPb refining for bearing alloys, debismuthizing of Pb with Ca, elimination of Sb and As in Sn alloys by Al, elimination of Sb and As in solders by Zn |
| 1919 | Vienna (Austria) | Extraction of Sn, Ag and Au from antimonial bronze residues from church bells |
| 1920-1921 | Hungary, hungarian government, Manfred Weiss CSEPEL works | Construction of a non ferrous metallurgy plant |
| 1922 | Baden-Baden (Germany) I.G. Farben Industry | Development of a low expansion piston alloy Al + 23 % Si (ALUSIL)<br>Mg base alloy with 6 % Ce |
| 1923-1940 | Luxemburg, his own research laboratory | • Connection with the American Smelting and Refining Co.<br>- for debismuthizing Pb by CaC$_2$ under flux of NaCl/CaCl$_2$<br>- for dezincing Pb<br>• Age hardening of AlZnLi and of MgGeAl-alloy: discovery of Si to exchange Ge in transistors<br>• Production of Be by reduction of anhydrous Be-fluoride with Mg<br>• Contract with SIEMENS & HALSKE<br>- for Be-electrolysis<br>- for production of a few kg of Ba by vacuum reduction of BaO by Al<br>• Production of high purity Calcium by subliming in vacuo and casting under Argon |

Table 2

| Period | Country and Institution | Nature of Activity |
|---|---|---|
| 1923-1940 | Luxemburg, his own research laboratory | • Use of H.P. Ca for oxide reductions in a bomb producing fused granules of Cr and V and moreover powders of Ti, Zr, U and Th<br>• Vacuum purification of Si, Cu, Fe, Cr, Be and alloys of Cu, Sn, Pb |
| Sept.1930 | Luxemburg, his own research laboratory | First notes on Titanium<br>• Reduction of $TiCl_4$ by Na: method of NILOSN & PETTERSON |
| May 1935 | Report to Siemens & Halske in Aug. 27, 1937 | • Reduction of $TiO_2$ by pure Ca |
| Juin 1937 | | • Pressureless reduction of $TiCl_4$ by Ca under Argon |
| July 30th 1937 | | • Pressureless reduction of $TiCl_4$ by Mg under Argon |
| July 13th 1938 | | • First $ZrCl_4$ reduction with Mg under Argon and vacuum separation of the sponge from the $MgCl_2$ |
| 1923-1940 | Luxemburg, his own research lab. | • Arc Melting of Ti-sponge with pure Ar of a pressure high enough to avoid glow discharge |
| Fall of 1938 | Visit to USA | • Presentation of various samples of Ti (wires, rod, sheet, arc melted buttons) at six leading companies which showed no interest |
| End of 1938 | Return in Luxemburg, his own laboratory | • Purification by vacuum distillation of Cr, Mg, Be, Fe, Sn, Zn, Pb and their alloys |
| Febr. 10th 1940-1945 | Return in USA, Union Carbide Res. Lab. in Niagara Falls (consultant) | • Fusion-electrolysis with soluble and insoluble anodes to produce Fe-, Cr-, Mn-powders<br>• Production of anhydrous chlorides of Mn and Zr<br>• Separation of Ta and Nb in oxides by $H_2$ reduction + chlorination<br>• Production of Na from NaCl in the mixture with Si and Lime in vacuum |
| December 1945-1950 | USA, U.S. Bureau of Mines: consultant in the ALBANY, Oregon Station | • In charge of the Zr Project: the first strip of Zr rolled in August 1946<br>• Working up of $MgCl_2$ extraction by vacuum distillation<br>• Production of anhydrous $ZrCl_4$ and elimination of $FeCl_3$<br>• Development of Zr-sponge melting-process in graphite crucible<br>• Minor work<br>- on the Li production by vacuum reduction of $Li_2O$ in presence of CaO with Al<br>- on the temperatures of reaction of C with various oxides in vacuo<br>- on the production of ductile Cr by reduction of $CrCl_3$ with Mg |
| 1950-1961 | USA, Corvallis, Oregon | • Production of some Ti alloys with additions of Zr-, V- and Cr- groups, such as Zr,Hf,Th,V, Cb,Ta,Cr and V. Canadian patent based on the solubility of metal chlorides ($TaCl_5$,$CbCl_5$) in $TiCl_4$ |
| 1961-1973 | Belgium, Rhode-St-Genèse | • Retirement in the home of his brother devoted to study the history of metallurgy<br>• Died on March 30th 1973 |

## Table 3

## Historical Data about Marked Progress in Titanium Reduction Methods

| Year | Author | Method | Quality of metal obtained | | |
|---|---|---|---|---|---|
| | | | Hot | Ductile Cold | Brittle |
| 1825 | Berzelius | $K_2TiF_6$ reduced with K | | | x |
| 1855 | St. Claire-Deville | $TiCl_4$ vapors passed over NA | | | x |
| 1887 | Nillson and Petterson | $TiCl_4$ reacted with Na in a bomb | | | x |
| 1982 | Seubert and Schmidt | Mg filing reacted with $TiCl_4$ under $CO_2$ | | | x |
| 1910 | Hunter | $TiCl_4$ reacted with Na in a bomb like Nillson-Petterson | x | | |
| 1914 | Lely and Hamburger | $TiCl_4$ reduced with Na in a bomb like Nillson Petterson | | x | |
| 1919 | Weiss | Dissociation of halides on a hot filament | | x | |
| 1921 | Billy | $TiCl_4$ reduced with Na under hydrogen. $TiH_2$ produced was degassed in vacuum | | | ? |
| 1925 | Van Arkel and de Boer | $TiI_4$ dissociated on a hot filament | | x | |
| 1939 | Freudenberg | Reduced $TiCl_4$ with Na in a chloride flux under hydrogen of atmospheric pressure | | | x |
| 1940+) | Kroll | Reduced $TiCl_4$ with fused Mg under argon of atmospheric pressure | | x | |

+) Process first used in 1937

## Strain-Ageing Phenomenon in Impure Titanium

Some years ago, E.de Paula e Silva, G. Béranger (1,2) and myself presented a comparative study of the dynamic strain ageing observed in titanium and zirconium. Let us remember that an age-hardening is observed under the simultaneous influence of a previous deformation and the temperature. For instance, during the tensile test of a sample, the loading is interrupted after some plastic strain of the material. The load is maintained during fixed time, then the sample is loaded again. The tensile curve shows a stress increment $\Delta\sigma$ (Fig. 1) which depends mainly on four parameters:

- the deformation temperature (Fig. 2)
- the ageing time (Fig. 3)
- the amount of strain before ageing (Fig. 4)
- the impurities content.

The amplitude of the strain-ageing is characterized with a greater precision by the ratio $\sigma_3-\sigma_2/\sigma_1$ (Fig. 5). The Figure 2 shows, that this ratio presents for a constant time of ageing (i.e. 5 min.) a maximum value in function of the temperature of tensile test and ageing (300 °C).

On account of the short time of ageing which permits to observe the $\Delta\sigma$ increment, this phenomenon cannot be explained by the Cottrell mechanism of trapping oxygen atoms by dislocations. This mechanism assumed that the oxygen interstitial atoms might diffuse on very long distances. This diffusion process is unlikly at low temperatures and for short times of ageing. At this time we interpreted the strain-ageing of titanium by some ordering process of oxygen atoms at short distance by a mechanism suggested by Snoek (3) and Schoeck (4). Some pairs of interstitial oxygen atoms would be ordered along a direction parallel to the c-axis of the hexagonal lattice of α-Ti (Fig. 6). This ordering of oxygen atoms would be favorized by the anisotropic deformation of the Ti-lattice due to the insertion of oxygen atoms. This anisotropic distorsion of the Ti-lattice can be estimated by the variation of a, c and c/a parameters of α-Ti in function of the oxygen content (Fig.7a-c) (5,6).

## Variation of the Tensile Properties with the Temperature

In a second stage of these researches, the creep behaviour of different grades of titanium (commercially pure titanium and titanium purified by the Van Arkel-process) was studied at increasing temperatures. The table 4 gives the impurities content (in ppm) of commercial Ti and purified Van Arkel-titanium.

Table 4

| | $O_2$ | $H_2$ | $N_2$ | C | Fe |
|---|---|---|---|---|---|
| Commercial Ti | 940 | 20 | 240 | 100 | 400 |
| Van Arkel Ti | 25 | - | 30 | 10 | 25 |

Also a commercial alloy used in the aircraft industry was compared. This alloy is called IMI 685 and contains mainly 6 % Al; 5 % Zr;

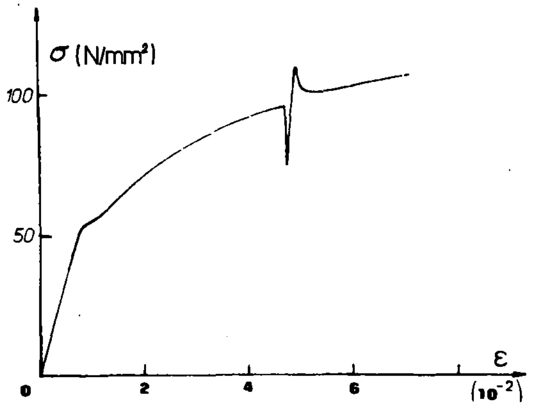

Fig. 1: Stress-strain curve of commercially pure titanium at 295° C, showing the strain-ageing after an interruption at 5 % deformation.

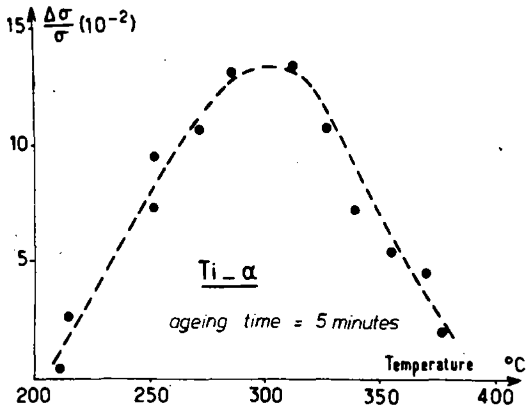

Fig. 2: Variation of $\Delta\sigma/\sigma$ (commercially pure titanium) with the temperature measured by tensile test.

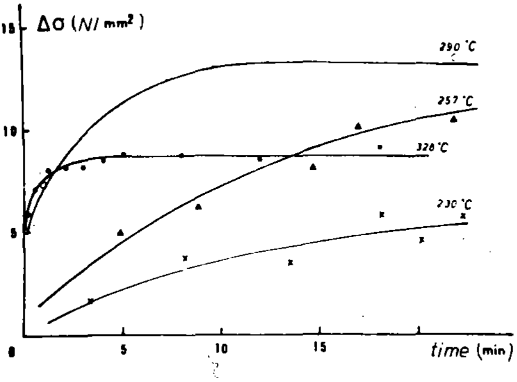

Fig. 3: Variation of $\Delta\sigma$ with the ageing time at different temperatures.

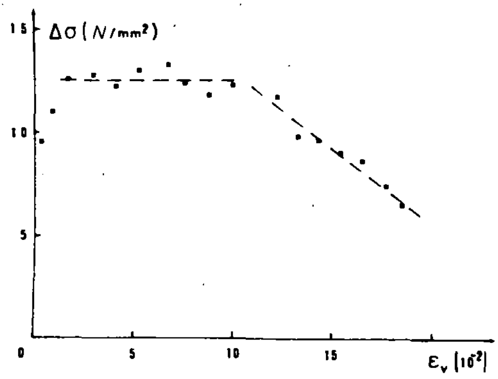

Fig. 4: Variation of Δσ with the amount of strain before ageing.

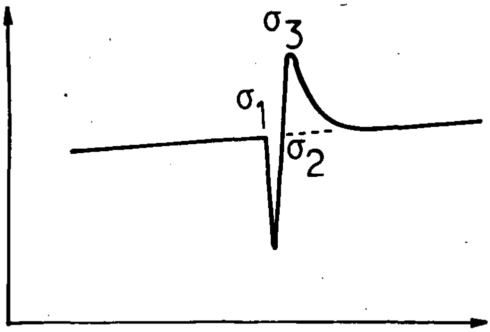

Fig. 5: Principle of the measurement of the strain-ageing effect.

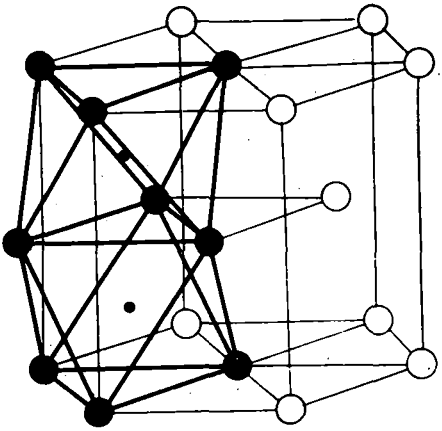

Fig. 6: Position of the interstitial atoms in the hexagonal titanium lattice.

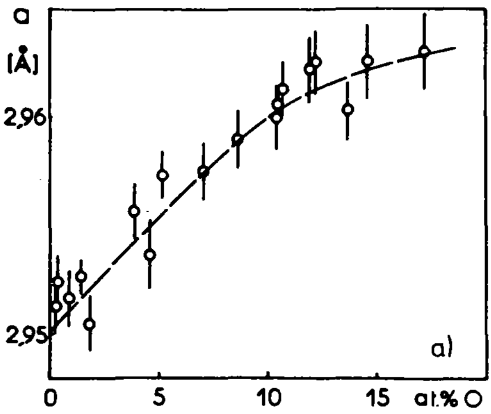

Fig. 7a

Fig. 7b

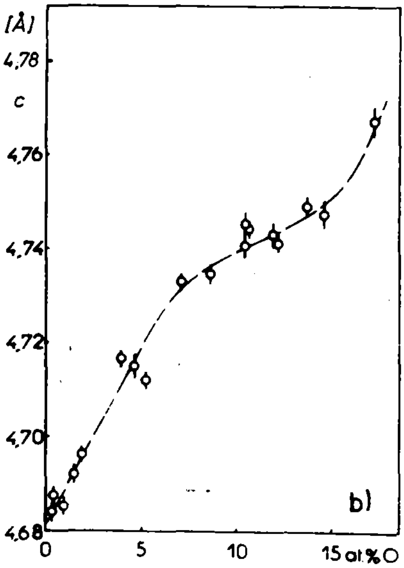

Fig. 7c

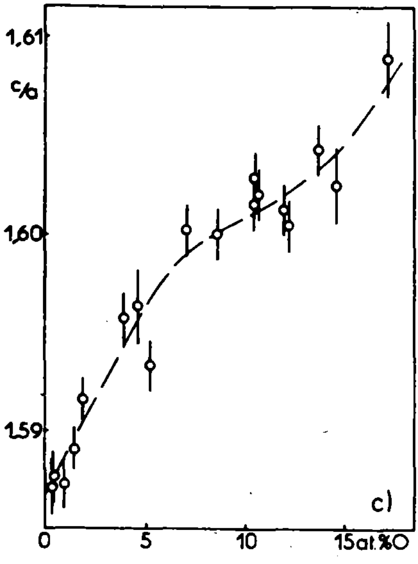

Fig. 7 a-c: Influence of the oxygen content on the lattice parameters a, c and c/a.

0,5 % Mo and 0,25 % Si. Firstly some tensile tests on the commercial titanium at different temperatures permitted to determine the load to be applied during the creep test in order to avoid some plastic deformation in the beginning of the creep test. The figure 8a-d show the variations of uniform and fracture elongation in function of the increasing temperature (7).

The shape of the tensile curves presents different features with the increasing temperatures:

- in the range A (from 100 to 150° C), the curve presents some brutal discontinuities due to the formation of mechanical twins (Fig. 8a),
- in the range B (from 200 to 300° C), the curve presents an yield point. This fact is generally attributed to an interaction between interstitial atoms and dislocations (Fig. 8b).
- in the range C (from 300 to 400° C), the Portevin-Le Chatelier effect appears progressively (Fig. 8c).

Creep Behaviour at Different Temperatures

These preliminary tensile tests permitted two kinds of creep tests:

- In the first run of tests, the applied stress was equal to 90 % of the conventional yield stress ($\sigma_{0,2}$) measured at each temperature of the tensile test.
- In the second run, a constant stress was applied to the creep sample and was fixed to 90 % of the $\sigma_{0,2}$ yield strength measured for a tensile test at 200° C.

The creep behaviour of commercial titanium was characterized by the sample elongation after 100 h of creep (3).

- For the first run of tests, the figure 9 shows two different behaviours according to the creep temperature
  - . at low temperatures, the creep elongation increases normaly with the temperature until 150° C, then rapidly decreases between 150 and 300° C,
  - . it is only above 350° C that the creep elongation increases again with the increasing temperature.
- For the second run of tests with a constant load of 132,3 N/mm$^2$, the curve of creep elongation, for 100 h of tests, presents the same feature (Fig. 10).

On account of the rapid elongation during the initial loading of the creep sample, we preferred to plot the difference of elongation between a time of 15 min. and 100 h of creep. Then, the anomalous creep behaviour of impure titanium around 300° C appears more clearly. The figure 11 shows

- the increasing creep elongation from 25 to 150° C,
- the rapid decrease of creep elongation between 150° C and 300° C: the deformation indeed is blocked around 300° C,
- the creep elongation increases again above 300° C.

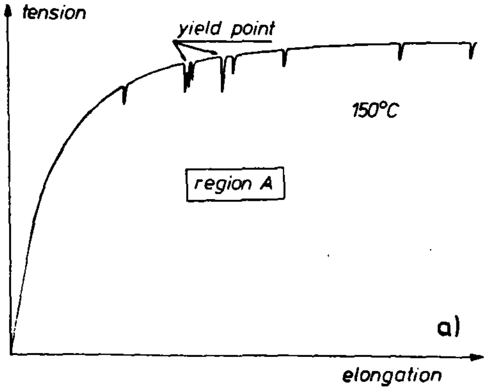

Fig. 8a

Fig. 8a-c: Characteristic stress-strain curves in different temperature regions A, B and C (see also Fig. 11)

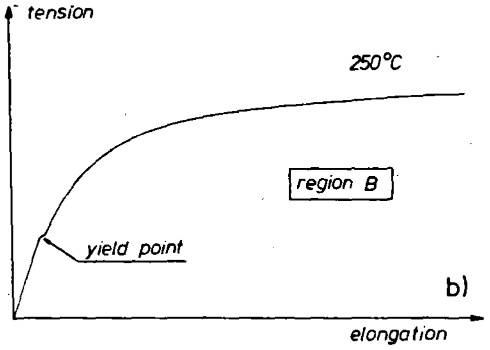

Fig. 8b

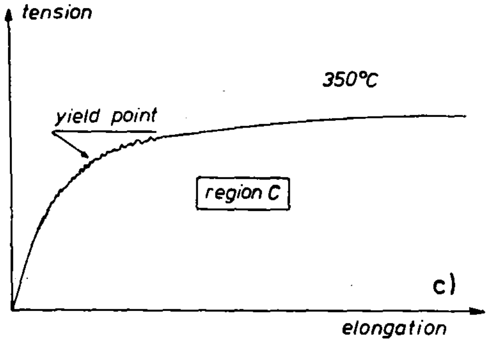

Fig. 8c

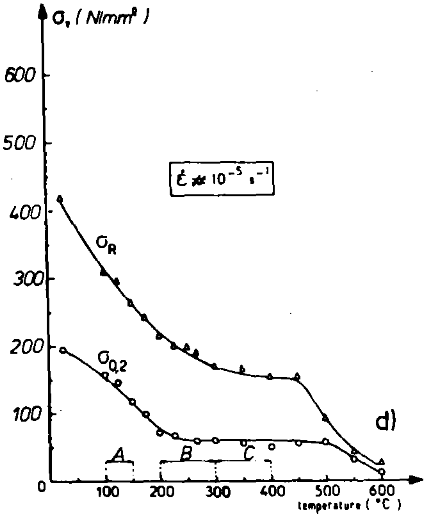

Fig. 8d: Influence of the temperature on the yield strength and the ultimate tensile strength.

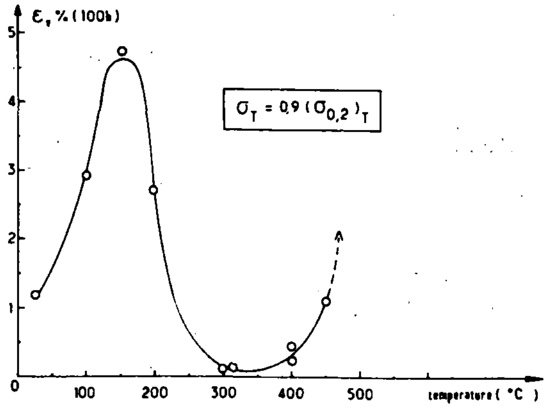

Fig. 9: Variation of the creep deformation measured after 100 h under a stress of 90 % of the yield strength with the temperature.

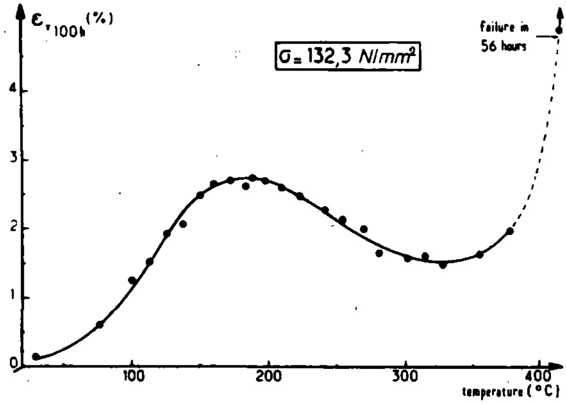

Fig. 10: Influence of the temperature on the creep deformation measured after 100 h under a stress of 132,3 N/mm$^2$.

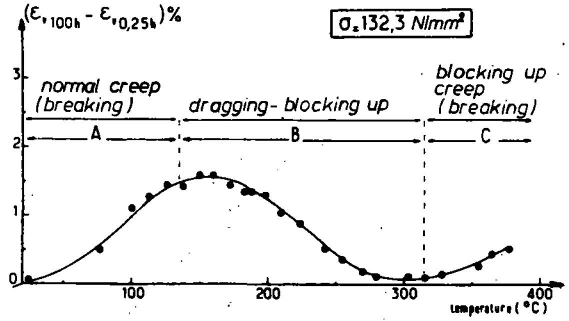

Fig. 11: Influence of the temperature on the creep deformation measured between 0,25 h and 100 h under a stress of 132,3 N/mm$^2$.

Above 300° C, the creep curve presents successive steps which recalls the "incubation creep" observed for different materials such as Fe by Arsenault and Weertman (9); Ni by Jenkins (10); Mo by Beardmore (11); Zr by Warda and Techtsonian (12).

The figure 12 shows some recorded curves of creep at different temperatures in linear coordinates representation. But the plot of the creep elongation versus the logarithm of time permits to distinguish more clearly stages of deformation (Fig. 13):

- In the first stage, the experimental data fit a classical logarithm law such as

  $$\varepsilon = a \log t + b$$

  This logarithmic law is obeyed until a time $t_f$.
- In a intermediate stage, the curve of $\varepsilon$ versus log t has a decreasing slope until a time $t_b$.
- In the last stage, above $t_b$, the creep strain is completely blocked.

Then each creep curve recorded at different temperatures may be characterized by two parameters $t_f$ and $t_b$ which decrease all the more fast as the temperature is higher (Fig. 14).

It is instructive to compare the creep behaviour of the IMI alloy because the phenomenon of "breaking" and "blocking" of creep are more pronounced. The figures 15 and 16 represent respectively some isothermal creep curves between 100 and 350°C in linear and semi-logarithmic coordinates. The figure 17 represents the variations of $t_f$ and $t_b$ versus the temperature.

At last the creep behaviour of commercial titanium was compared to the behaviour of Van Arkel-titanium. The figure 18 shows the variations of $\varepsilon_{(100\ h)}$ and $\varepsilon_{(100h-0,25h)}$ in function of the creep temperature. The shape of these curves are roughly similar to the curves of the commercial titanium. However, the total blocking of creep is observed at a lower temperature (230° C instead of 300° C).

After all, these results suggest that these creep anomalies are due to the impurities content even in the case of the purest titanium produced by the Van Arkel-process. For this reason, more recently, C. Servant, C. Quesne and C. Sévérac (13) tried to purifiy "artificially" impure titanium by the precipitation of the impurities by very slow cooling treatments from high temperatures or by very long heat treatments at low temperatures. This efficiency of these precipitation treatments was proved by the identification of different precipitated compounds by electronic microdiffraction.

These observations permitted to identify some localized precipitates, as sulpho-phosphides, silicides (14) and above all some

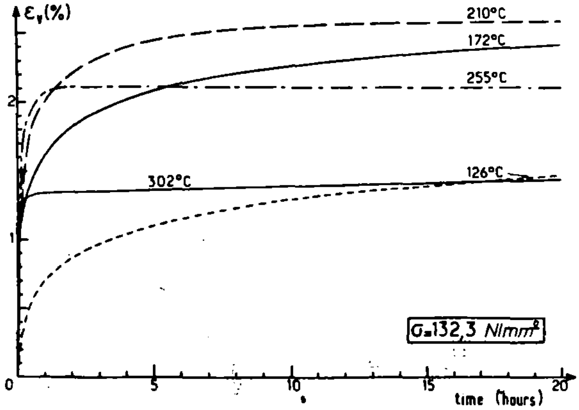

Fig. 12: Creep curves at different temperatures ($\sigma$=132,3 N/mm$^2$)

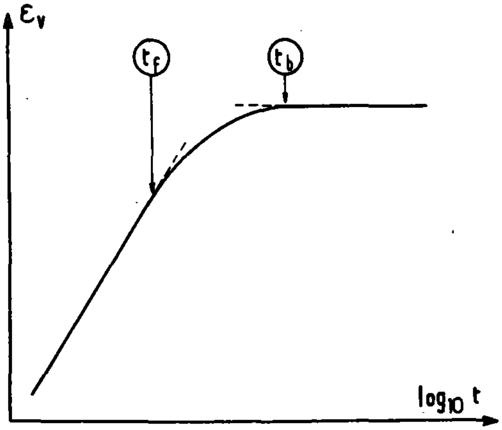

Fig. 13: Principle of determination of the parameters $t_f$ and $t_b$.

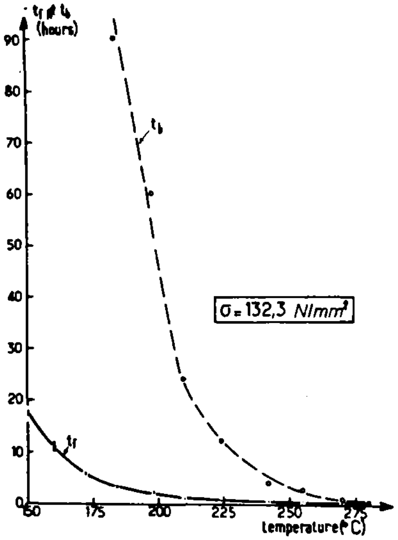

Fig. 14: Influence of the temperature on the parameters $t_f$ and $t_b$ with commercially pure titanium ($\sigma$=132,3 N/mm$^2$).

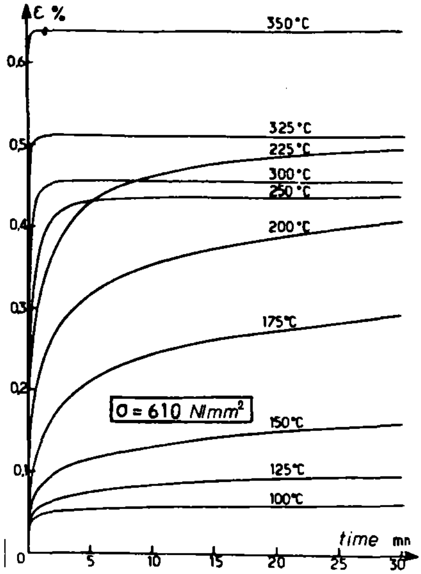

Fig. 15: Creep curve for TiAl6Zr5Mo0,5 between 100° C and 350° C ($\sigma$= 610 N/mm$^2$).

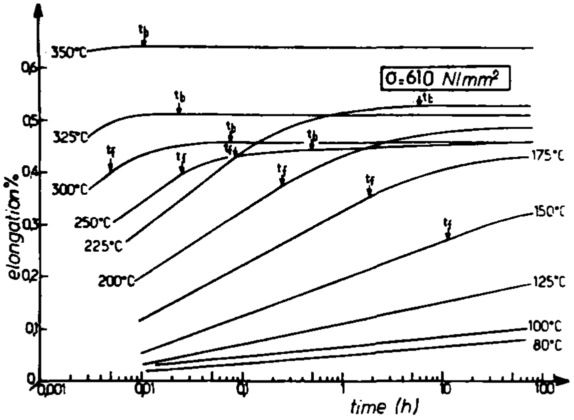

Fig. 16: Determination of the parameter $t_f$ and $t_b$ at different temperatures for TiAl6Zr5Mo0,5.

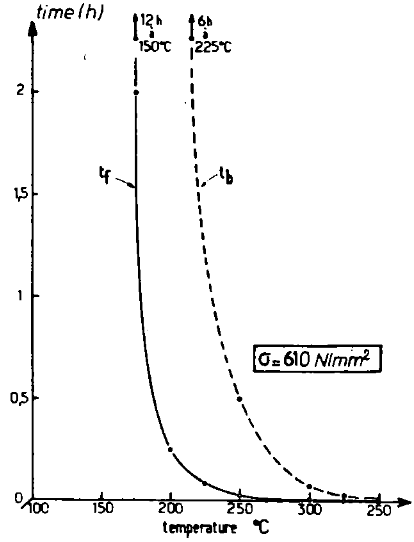

Fig. 17: Influence of the temperature on the parameter $t_f$ and $t_b$ for TiAl6Zr5Mo0,5 ($\sigma$=610 N/mm$^2$).

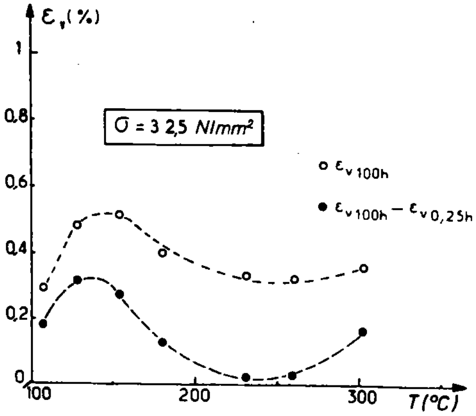

Fig. 18: Influence of the temperature on the creep deformation for Van Arkel-titanium.

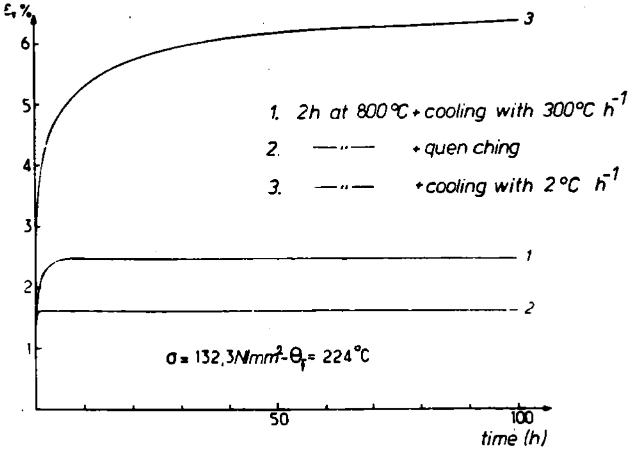

Fig. 19: Creep deformation at 224$^{o}$ C of commercially pure titanium after different heat treatment.

localized ordering of oxygen atoms. The precipitation of these different phases due to a very slow rate of cooling of 2° C per hour from 800° C modifies completely the creep curve at the temperatures below 300° C. The figure 19 shows the disappearance of blocking of the creep. More details on these recent observations are presented by S.J. de Souza (15), C. Quesne, C. Servant, C.Sévérac (16).

These results show clearly the influence of very small contents in impurities on the mechanical properties of titanium. But, at present time, it is difficult to precise definitely the respective influence of interstitial substitutional and substitutional impurities. It is likely that the creep anomalies are correlated to the dynamic strain ageing because the creep anomalies and the maximum amplitude of strain-ageing were observed in the same range of temperatures. Probably the strain- ageing is mainly due to the interstitial atoms of oxygen, because its appearance does not require a long time of ageing.

But the creep anomalies may be caused also by some interactions between interstitial and substitutional impurities. Probably the iron impurity may also influence the creep behaviour of Titanium because the iron solubility in α-Ti is relatively small (17). A proof of this iron influence is given by the results obtained by P. Delarbre (18) in the laboratory of Prof. Zwicker. Delarbre elaborated different Ti-Fe alloys with Fe-contents from 0,01 to 0,13 % and confirmed the blocking of creep elongation, even for 2000 h of creep.

In conclusion, it was the great merit of Dr. Kroll to foresee the importance of impurities on the ductility of Ti and Zr at room temperature. But the recent researches of many metallurgists show the influence of impurities, even at higher temperatures. However, at present time, we cannot distinguish the respective influence of interstitial and substitutional impurities. Some theoretical approach of these problems should be desirable to explain experimental results.

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