PHASE TRANSFORMATIONS OF TITANIUM AND SOME TITANIUM ALLOYS. KINETICS AND MORPHOLOGY OF PHASE TRANSFORMATION. APPLICATION TO HEAT TREATMENT.

E. Etchessahar*, J.P. Auffredic**, J. Debuigne*

* Laboratoire de Métallurgie. Institut National des Sciences Appliquées Rennes (France)

** Laboratoire de Cristallochimie. Université de Rennes (France).

ALLOTROPIC TRANSFORMATION OF TITANIUM

The allotropic transformation of titanium which connects the h.c.p. low temperature phase to the c.c. high temperature phase, is very sensitive to the impurities contents of the metal. Titanium has a particularly high reactivity towards oxygen and nitrogen, whose solid solutions cause a very sharp rise of the transition temperature.

Dilatometric study of metals of different purity levels

The kinetic investigations about the allotropic transition necessitate very pure base materials and high vacuum technique, in order to minimize contamination. The dilatometric experiences were conducted in a direct type apparatus built in our laboratory (1)(2). Its working conditions are : high vacuum (10^{-6} to 10^{-7} Pa) at maximum temperatures of 1050 to 1100° C. A high sensibility i.e. a maximal commonly usable amplification coefficient of 25.10^3. A particularly high stability of the base line allows very long time studies of cumulative annealing type. It is therefore possible to have very fine studies of the samples' evolution in the neighbourhood of the phase transition, enabling precise definitions of transition temperatures.

The present study was carried out using thermal cycling at different speeds of temperature variations vs time and, on the other hand, using the cummulative annealing method. The metals used are R.C.P. Titanium (3) and Van Arkel Titanium (4), their chemical analysis are given in Table 1.

Table 1 : Analysis (in 10^{-6} atomic)

Materials	O	O+N	C	Hf	Al	Fe	Ni	Zr
R.C.P. Titanium	900-1800	-	280	-	10-200	150-250	50-70	10-40
Van Arkel Titanium	100-150	-	-	-	-	70-100	-	-

Thermal cycles. The temperatures of the beginning of transformation during heating of the Van Arkel Titanium are 882 -884 - 886° C for heating speeds of 50, 150 and 300° C/h. On the other hand, the $\beta \rightarrow \alpha$ transformation temperature is unique, i.e. 881° C for the three cooling speeds. The amplitudes of the dimensional variations vary from cycle to cycle in proportions like 1 to 5. The $\alpha \rightarrow \beta$ and $\beta \rightarrow \alpha$ transformations show composite phenomenons : contraction, expansion, sudden variation of slope. Such a dilatogram is given in figure 1.

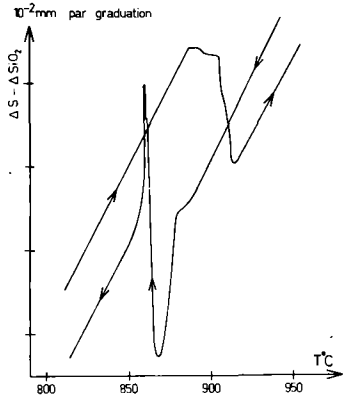


Fig. 1 : Phase transition of titanium

Thermal cyclings of less pure titanium at speeds of 300° C/h and 150°C/h, give the beginning of a α → β transition at 886° C and of β → α at 881° C. The thermal spreading of the transformation has an approximate amplitude of 25 to 30° C. The dilatations and contractions at transformation vary in great proportions (1 : 20) from cycle to cycle, these phenomenons are always composite.

Cumulative annealings. During heating as well as during cooling, the α ↔ β transformation of Van Arkel titanium (figures 2, 3) is an isothermal transformation at 882 ± 2° C which is composed of a slow dilatation and a slow contraction. The transformation time is 36 h. at heating and 28 h. at cooling. The α → β transformation of R.C.P. titanium begins at 884° C and spreads over approximately 17° C at cooling, the β → α transformation runs in the same limits.

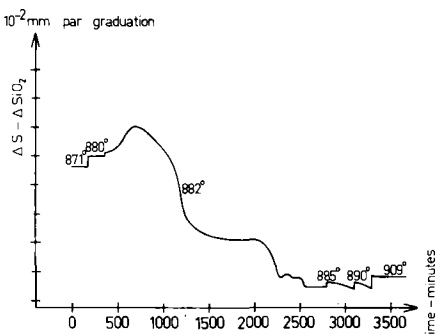


Figure 2 : α → β transformation

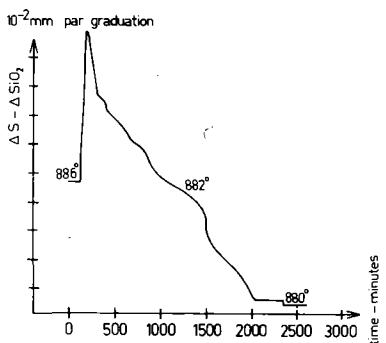


Figure 3 : β → α transformation

As a whole, the influence of impurities is globally α-gen and therefore, the phase transition temperature is raised in the limit of two degrees and an α + β two phase domain appears with a width of 17° C. In this domain, a determined transformation rate corresponds to each temperature, as we showed previously in another study on the phase transition of zirconium (1)(5).

Possible influence of retrograde solubilities of some impurities.

Recently, J. Matyka et al. (6) established experimentally the retrograde solubility of iron in titanium. Our thermodynamic exploitation of the results (7) convinced us of the retrograde solubility of other impurities.

The examination of figure 4 concerning the titanium-rich side of iron-titanium phase diagram with superposition of vertical lines corresponding to the three grades of titanium sutdies (with respect to their iron concentrations) gives evidences for differences in the developments of phase transformation (nature of phase embryos, phase germination, kinetics of phase transformation). The comparison with the dilatometric curves is very instructive. On the other hand, if we consider other solutes with retrograde solubilities, we have a

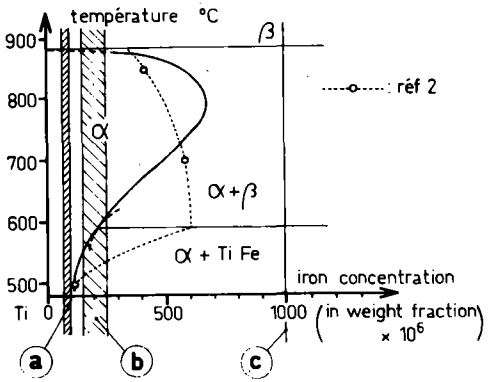


Figure 4 : Iron-titanium phase diagram

rather complicated problem in accounting for the details of their influence.

In industrial alloys, the kinetics of transformations may also be sufficiently influenced by the impurities to generate some variations in the results of identical heat treatments on different grades of the same type of alloy.

ALLOTROPIC TRANSFORMATION OF TITANIUM ZIRCONIUM ALLOYS

The outlines of the titanium-zirconium binary diagram were given as early as 1930 and since, only modifications in the limits of the two phase α + β were given. This diagram is shown on figure 5.

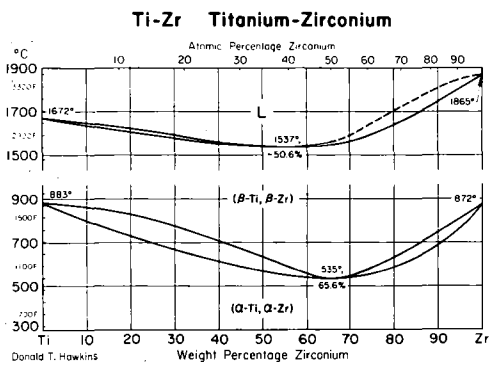


Figure 5 : titanium-zirconium binary diagram

The indifferent point β solid-α solid concerns the equiatomic composition. While the different authors agree with the general features of the diagram, they don't agree with the position of the indifferent point β solid-α solid ; Fast (8), Hayes et al. (9) give their point at 545° C, Duvez (10) at 485° C ; Farrar and Adler (11) at 535° C.

The precise determination of the indifferent point appears as a fundamental requirement before developping other investigations in this binary system.

Experimental methods

The phase transition of equiatomic Ti-Zr alloys was studied by high vacuum dilatometry in the apparatus previously described and by microcalorimetry in a high temperature Calvet microcalorimeter equiped with special calorimetric cells. The calibration of this calorimeter was obtained by Joule-effect either "in situ" or in special calibration run when the equipment occupied too great a space to allow "in situ" calibration.

Three Ti-Zr alloys at different impurity levels, were studied. The first one, Ti-Zr 1, is at industrial purity level, the other two, Ti-Zr 2 and Ti-Zr 3 were synthetized under very pure Argon. The impurities concentrations of starting metals, are given in table 2.

Table 2

Samples	Materials	Composition at 10^{-6}										
		O	N	C	Cr	Hf	Al	Fe	Ni	H	Zr	Ti
Ti Zr 1	Ti Zr	3130	500			4000						
Ti Zr 2	Ti	900 1800		280			10 200	150 250	50 70		10 40	
	Zr	2250	293	1520	105	102				23600		38
Ti Zr 3	Ti	100						70				
	Zr	8	8			27	0	2				

Dilatometry

Thermal cycles. At the same speed of thermal cycling, differences appear in the transition temperatures from one alloy to another. Table 3 gives the experimental results. We note that with increasing purity of the alloys an increasing hysteresis appears, between the beginning of the $\alpha \rightarrow \beta$ transition and the beginning of the $\beta \rightarrow \alpha$ transition.

Table 3

Alloys	$\alpha \rightarrow \beta$		$\beta \rightarrow \alpha$		Hysteresis (°C)
	transition beginning (°C)	transition end (°C)	transition beginning (°C)	transition end (°C)	
Ti Zr 1	616	642	586	567	30
Ti Zr 2	616	641	583	568	33
Ti Zr 3	621	642	581	562	40

The dilatometric amplitudes at the transition are similar for the $\alpha \rightarrow \beta$ and for the $\beta \rightarrow \alpha$ transition when the maximum temperature of the sample does not exceed by more than a hundred degrees the temperature of transformation. On the contrary, when the maximum temperatures of the sample are higher, systematic variations of the dilatometric amplitudes take place. Above 940° C, the dilatometric amplitudes at the phase transition are maximum for identical annealing

times. The variations of these amplitudes at transition were studied using four dilatometric cycles $\alpha \rightarrow \beta$ and $\beta \rightarrow \alpha$ caracterized by a heating and cooling speed of 300° C/h. Before the experience, the sample was annealed at 940° C during 20 minutes. The dilatograms are given figure 6.

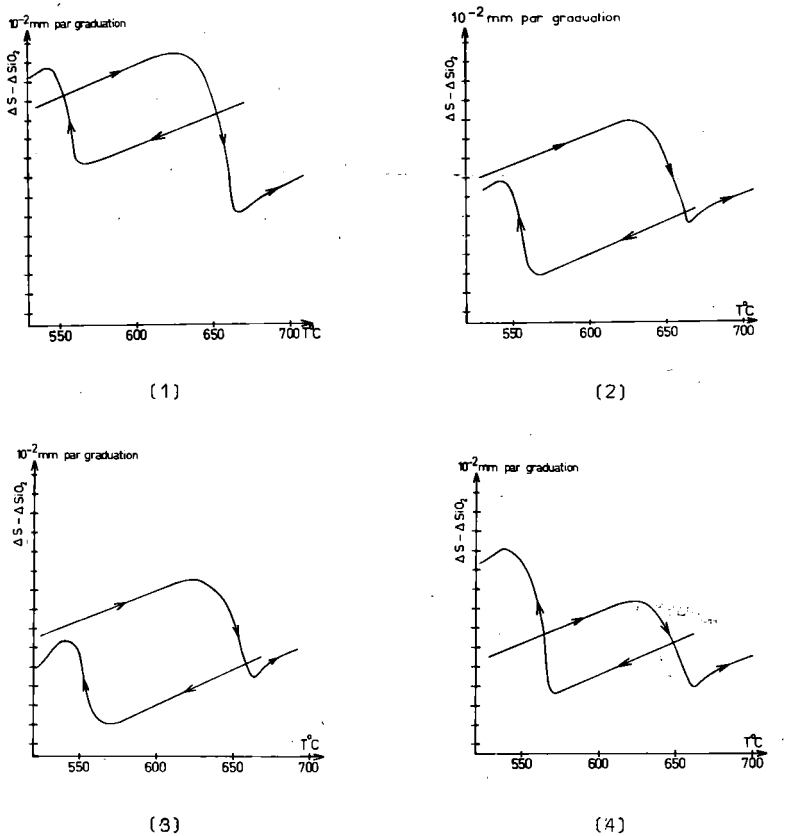


Figure 6 : amplitudes at transition

Cycle 1 : after the $\alpha \rightarrow \beta$ transition, the sample is annealed at 700° C during 20 minutes. At cooling, the amplitude of the $\beta \rightarrow \alpha$ transition is much lower than that observed at heating.

Cycle 2 : The amplitude of the $\alpha \rightarrow \beta$ transition is comparable to that of the $\beta \rightarrow \alpha$ transition in the first cycle. After a 20 minutes β-phase annealing at 700° C, the amplitude of the $\beta \rightarrow \alpha$ transition is within the same range of values as the amplitude observed at heating for the $\alpha \rightarrow \beta$ transition.

Cycle 3 : The transition amplitudes at heating and cooling are in the same range.

Cycle 4 : In this cycle, the β-phase annealing temperature is 900° C for 20 minutes ; a consequence of such an annealing is the increase of amplitude of the $\beta \rightarrow \alpha$ transition. This amplitude may be compared with that of dilatations observed during transitions in the previous dilatograms.

This phenomenon makes evident the influence of the β-phase annealing temperature and is observed whatever the purity of the alloy. In experimental conditions similar to those of Cycle 4 in figure 5, the amplitude ratios for α → β and β → α transformations are always in the same range.

Ti Zr 1 alloy : α → β amplitude ≃ 58 % of β → α amplitude

Ti Zr 2 alloy : α → β amplitude ≃ 60 % of β → α amplitude

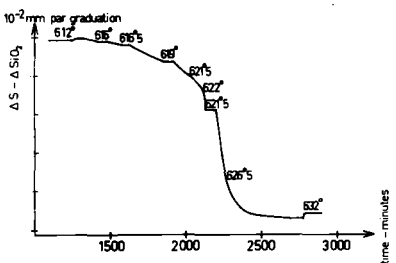
Ti Zr 3 alloy : α → β amplitude ≃ 57 % of β → α amplitude

This phenomenon, common to the three alloys of different purity levels, is certainly specific of the type of transformations involved and we suggest a noteable effect of stresses generated in the metals during the phase transition.

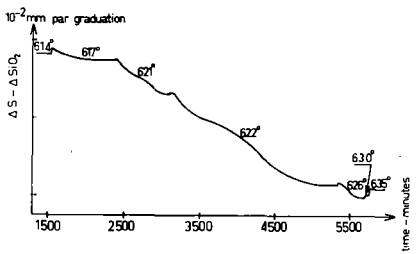
Cumulative annealing

This study was made for the different alloys.

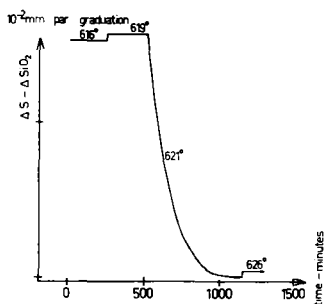
α → β transition (figure 7



Ti Zr 1 sample



Ti Zr 2 sample



Ti Zr 3 sample

Figure 7 : cumulative annealings
α → β transition

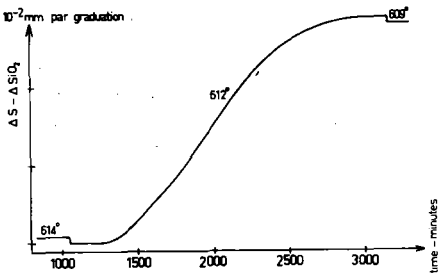
For the less pure alloy (Ti Zr 1), the phase transition begins at 616° C and extends over 10° C, is slow and for each temperature in this domain, corresponds a determined transformation rate.

The transformation of Ti Zr 2 begins at 617° C and is comparable to that of alloy 1.

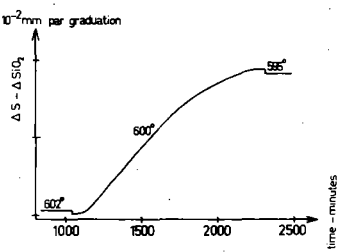
The transformation of Ti Zr 3 alloy, the purer one, is much more rapid and is isotherm at 621° C. The transformation time is approximately 490 minutes.

After $\alpha \rightarrow \beta$ transformation, the final temperature is 940° C for the three alloys, which are annealed for 30 minutes at this temperature before cooling.

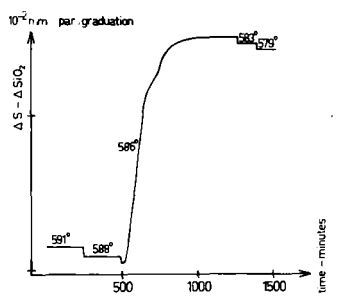
$\beta \rightarrow \alpha$ transition (figure 8)



Ti Zr 1 sample



Ti Zr 2 sample



Ti Zr 3 sample

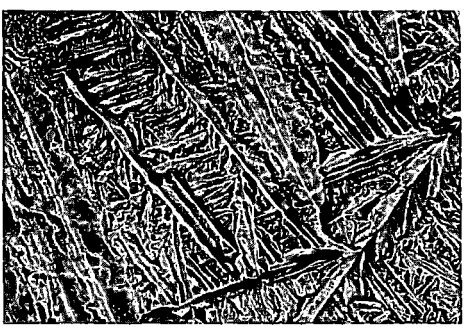


Figure 8 : cumulative annealings, $\beta \rightarrow \alpha$ transition

This transformation is isothermal at 612° C for Ti Zr 1 alloy ; it is slow and lasts approximately 28 hours. For alloy 2, it is also isothermal but at 600° C and lasts approximately 20 hours. The purer alloy, Ti Zr 3, shows an isothermal transition at 586° C during approximately 7 hours 30 minutes. This kinetics, in spite of its slowness, is the quickest obtained.

Figure 8 (4) shows a metallography of the surface of Ti Zr 3, after isothermal $\beta \rightarrow \alpha$ transition ; in the acicular structure observed, the needles have not altered and show the relief effect due to $\beta \rightarrow \alpha$ transformation. These are the last martensitically transformed zones.

Calorimetric study

Experimental procedures. To prevent pollution, the sample is at the bottom of a closed zirconium cylinder which is placed in a silica specimen holder moving with smooth friction in the calorimetric cell. This cell is a transparent silica tube closed by a double Wilson's joint metallic head, with a metallic valve and a manometer to measure pressure inside the cell. In a first time, the cell alone is disgassed under vacuum at 900° C ; during this operation, the zirconium cylinder is annealed at 800° C in ultra high vacuum.

After this, the different elements are assembled and introduced in the calorimetric cell, where titanium getters are also placed.

The calorimetric cell is then connected to a high vacuum ionic pump for disgassing at 400° C before introduction of highly purified argon. Finally, the titanium getters are inductively heated at 1000° C during 48 hours.

These operations avoid pollution of the sample during the calorimetric determination which proceeds under static argon.

Thermal cycles. The $\alpha \rightarrow \beta$ transition is endothermic and the $\beta \rightarrow \alpha$ transition is exothermic for the three alloys studied.

Tables 4, 5, 6 give the experimental results on the three alloys submitted to three successive thermal cycles. The temperatures of the beginning and of the end of the transition are respectively noted θ_i and θ_f: θ_{Mx} being the temperature of the maximum of the endo or exothermic calorimetric peak. ΔH is the heat of transition. The calorimetric curves for each of the three alloys are given on figures 9, 10, 11, the roman numbers I, II and III are for the successive thermal cycles.

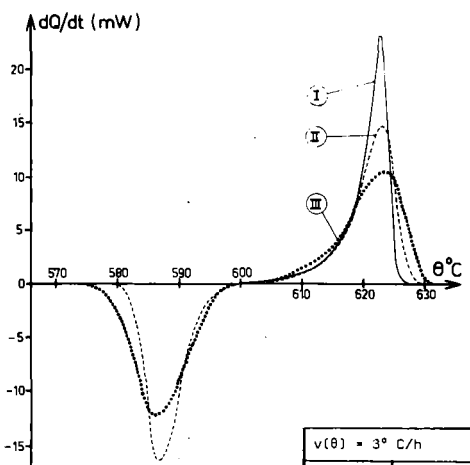


Figure 9 :

Calorimetric curves, sample n° 1

Table 4 : transformation results

Ti Zr, sample 1

v(θ) = 3° C/h			Ti Zr 1 alloy					m = 3,40884 g
Cycle n°	α → β				β → α			
	θi (°C)	θ_{Mx} (°C)	θf (°C)	ΔH (J/mole)	θi (°C)	θ_{Mx} (°C)	θf (°C)	ΔH (J/mole)
I	602	623	627	2617				
II	603	624	629	2530	601,5	587	577	2559
III	603	623	631	2500	601	585	572	2530

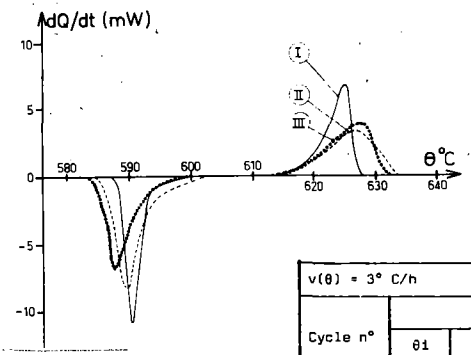


Figure 10 :

Calorimetric curves, sample n° 2

←

Table 5 : transformation results

Ti Zr, sample 2 ↓

v(θ) = 3° C/h			Ti Zr 2 alloy					m = 1,09792 g
Cycle n°	α → β				β → α			
	θi (°C)	θ_{Mx} (°C)	θf (°C)	ΔH (J/mole)	θi (°C)	θ_{Mx} (°C)	θf (°C)	ΔH (J/mole)
I	614	625	628	2239	600	590	587	2297
II	612	626	634	2326	602	590	585	2413
III	613	628	633	2268	600	588	583	2326

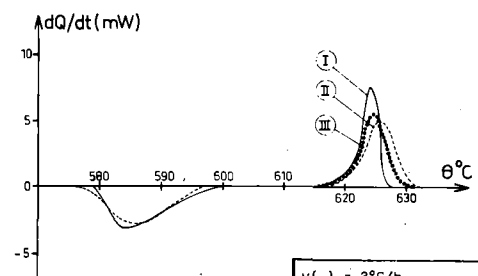


Figure 11 :

Calorimetric curves, sample n° 3

←

Table 6 : transformation results

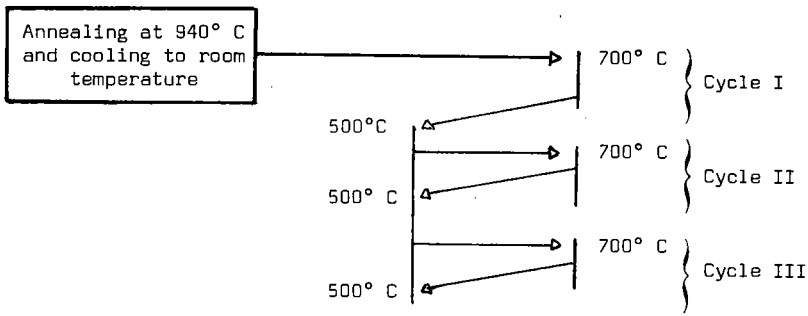
Ti Zr, sample 3 ↓

v( ) = 3°C/h			Ti Zr 3 alloy					m = 0,87233 g
Cycle n°	α → β				β → α			
	θi (°C)	θ_{Mx} (°C)	θf (°C)	ΔH (J/mole)	θi (°C)	θ_{Mx} (°C)	θf (°C)	ΔH (J/mole)
I	616	624	628	2443	599	584	579	2529
II	615	626	632	2443	597	586	576	2558
III	616	624	632	2413				

All three samples have the same thermal history before the microcalorimetric study : an annealing at 940° C for 30 minutes in high vacuum (10^{-6} Pa) and then a cooling at a speed of 300° C.h^{-1} to room temperature.

- No significative variations were observed in the values of transformation heat at heating or cooling, the average value of ΔH = 2425 ± 131 J/mole.
- The temperatures of the beginning of the α → β transition lower with the increase of impurities content and the hysteresis between both temperatures at beginning of α → β transition and beginning of β → α transition increase with lowering of impurities content.
- In a general way, it can also be pointed out that the kinetics of either α → β or β → α transformation of the second and third cycle is noticeably different

from that we had in the first cycle. In this case, the curves maximum was noticeably higher. The thermal history of a sample submitted to three successive cycles is :



The ultimate temperature of heat treatment influences the shape and the spreading of the thermal peak. For the same alloy, the spreading of the peak is minimum for an experience after an annealing at 940° C, on the other hand the ultimate annealing temperature has no influence on the value of heats of the $\alpha \rightarrow \beta$ and $\beta \rightarrow \alpha$ transformations.

These features are probably due to stresses generated in the sample during thermal cyclings. These stresses can be annealed at an appropriate temperature as shown on figure 12, where the temperature raise of the sixth cycle on Ti Zr 3 after annealing at 940° C in ultra-high vacuum is represented.

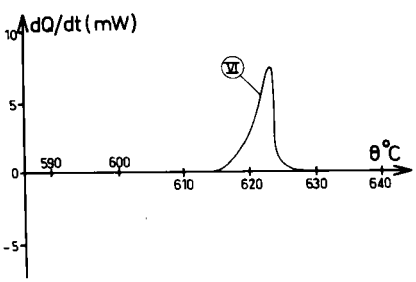


Figure 12 : Ti Zr 3, sixth cycle

The influence of sample pollution. The goal is to study the influence on the $\alpha \underset{\rightarrow}{\leftarrow} \beta$ phase transition of Ti-Zr equiatomic, of pollution due to the contact of the sample with silica in the apparatus. In this experience, we do not use a zirconium container and consequently, the sample is put directly in the transparent silica container. The sample used is of the same grade as Ti Zr 1 ; the five thermal cycles given on figure 13 and table 7 show evidence of a clear modification of the calorimetric curves.

During heating and from the first cycle a 45° C magnitude is measured for the lowering of the transformation beginning temperature. The calorimetric curve shows two non-separated peaks, the first one having the lowest heigth and spreading over 67° C. In the course of the five cycles, the calorimetric curve shifts steadily towards lower temperatures. The transformation heat average value is $\Delta H_{\alpha \rightarrow \beta}$ = 2916 ± 33 J/mole, then higher than 2425 ± 131 J/mole.

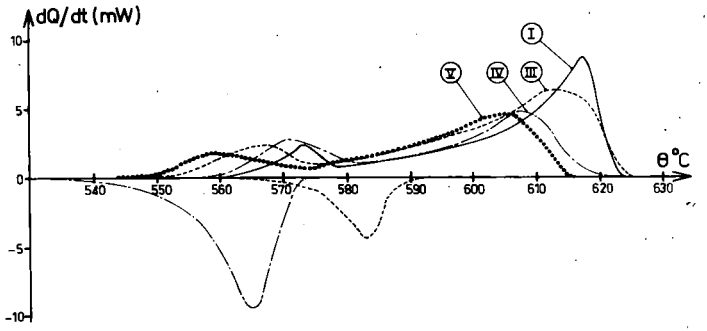


Figure 13 : Ti Zr 1, influence of sample pollution

Table 7

Ti Zr 1 Alloy					m = 3,69519 g					
Cycle n°	α → β					β → α				
	v(θ) (°C/h)	θi (°C)	θ_{Mx} (°C)	θf (°C)	ΔH (J/mole)	v(θ) (°C/h)	θi (°C)	θ_{Mx} (°C)	θf (°C)	ΔH (J/mole)
I	3	557	617	624	2878					
II	4,5	555	614	625	2936	1	594	583	563	2297
III	3	549	607	621	2936	3	575	565	532	2268
IV	3	544	605	618						

During cooling, the β → α transformation gives only one peak on the calorimetric curves, with a shift towards lower temperatures as the successive cycles take place. The evidence of the sample evolution appears by comparison between the values of previously defined caracteristical temperatures for the fourth cycle (θi = 575° C - θm = 565° C - θf = 532° C) with those found in good experimental conditions on the same alloy (see table 3) (θi = 601° C - θm = 585° C - θf = 572° C).

The differences between the calorimetric curves during heating and during cooling for the polluted sample can be explained in the following manner :

. on heating, the partially polluted sample begins to transform (first peak) and then the whole core transforms (second and highest peak).
. on cooling, the hysteresis may be the origin of the two reverse peaks overlapping giving apparently a unique reverse peak.

This viewpoint must be discussed further and, above all, controlled pollution experiments are necessary to complement our results. These experiments are being carried at this time in our laboratory and we think they might explain the results of Farrar and Adler (11)

General conclusion

The results obtained in this study of phase transformation of titanium and of an equiatomic titanium-zirconium solid-solution, both with samples of different grades, show that at slow heating and cooling rates, the transformation is

slow and its characteristics depend on the impurities content. Pulse heating (12) and fast quenching (13) experiments give very high transformation rates. The rate of transformation is probably dependent on the heat flux density input or output. The different variables considered here must be kept in mind when examining industrial heat treatment of titanium and titanium alloys.

References

1. E. Etchessahar : *Thèse de spécialité*, Nantes (1975)

2. E. Etchessahar, J. Debuigne : *Brevet ANVAR 9350.*

3. R.C.P. N° 244 du C.N.R.S. *"Propriétés mécaniques du Titane et de ses Alliages".*

4. J. Bigot, C.E.C.M. Vitry, France

5. E. Etchessahar, J. Debuigne *(to be published)*

6. J. Matyka, F. Faudot, J. Bigot, *Scripta Metallurgica*, vol. 13, p. 645-648 (1979).

7. B. Jounel, J. Debuigne *(to be published)*

8. J.D. Fast : *Rec. Trav. Chim.*, 58 (1939) 973-983.

9. E.T. Hayes, A.H. Roberson, O.G. Paasche : *U.S. Bur. Mines Dept. invest.*, 4826 (nov. 1951)

10. P. Duwez, *J. Inst. Met.* 80 (1951-52) 525-527.

11. P.A. Farrar, S. Adler : *Trans. A.I.M.E.*, 326 (1966) 1061-64.

12. R. Parker : *Met. Trans.* 233 (1965) 1545-1549.

13. M. Cormier, F. Claisse : *J. Less Common Metals* 34 (1974) 181-189.