

## STUDY OF CHROMIUM SOLUBILITY IN $\alpha$ PURE-TITANIUM

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### Introduction

The binary phase diagrams of group IV metals are badly known especially for low concentrations. This may be due to experimental difficulties for diagram - establishment. First, alloys elaboration and thermal treatments are made difficult by the high reactivity of these materials at high temperature. Another difficulty is due to kinetic problems. As a matter of fact, the allotropic transformation  $\alpha - \beta$  is slowed down by the additional elements and thus there is a great indetermination of the eutectoid temperature. The industrial development of titanium need a thoroughly knowledge of these diagrams. In an previous work, we have studied the iron solubility in  $\alpha$ -titanium and we have determined the apparent diffusion coefficient of iron in this material. The iron important effect on the creep titanium properties was proved (1).

Our present work determines the chromium solubility in  $\alpha$  titanium. The analogy of Ti-Fe and Ti-Cr diagrams leads us to think that chromium solubility, as iron solubility, is retrograde.

### Experimental method

We used titanium prepared by the Van Arkel process (2). The standard analysis is shown in table 1.

Table 1

Van Arkel standard analysis determined by activation methods. The concentrations are evaluated in  $\mu\text{g/g}$ .

| Elements | Content $\mu\text{g/g}$ |         |
|----------|-------------------------|---------|
| O        | 30                      |         |
| N        | <30                     |         |
| C        | <10                     |         |
| Fe       | 26                      | <2(*)   |
| Mn       | <1                      |         |
| Mg       |                         | <1(*)   |
| Si       |                         | 1(*)    |
| Zr       | 17                      | <0.4(*) |
| Cr       | 0.8                     | 0.02(*) |
| Cu       | 14.3                    |         |
| Mo       | 0.1                     | 0.01(*) |
| V        | 6                       | 0.6(*)  |
| Al       | <11                     | 0.6(*)  |

(\*) contents determined by spectrographic analysis.

The solute is chromium which RRR is 265. Various chromium content alloys : 500, 2000, 3000, 3200, 4000, 5000  $\mu\text{g/g}$  are prepared by levitation melting under purified helium. All are prepared from a starting alloy of 30 % in weight chromium content. Accuracy of the chromium content alloys is evaluated at 1 % (3). Thermal treatments are carried under ultra vacuum better

than  $1 \cdot 10^{-8}$  Torr. The anneals are stopped by an air-quenching. As a matter of fact, tests made with different quenching speeds (4) have shown that cooling speed during air-quenching maintained solid solution at high temperature enough.

Chromium evolution in  $\alpha$  titanium is followed by low temperature electrical resistivity. We measure the ratio  $R_{He} = \frac{\rho_{4.2K}}{\rho_{273K}}$ .

### Results and discussion

After cold rolling, the samples are recrystallised at  $720^\circ\text{C}$ . The anneals are made at increasing temperatures, the quality of thermal treatments being verified against check with pure titanium.

The  $R_{He} = f(T)$  curve is drawn on figure 1.

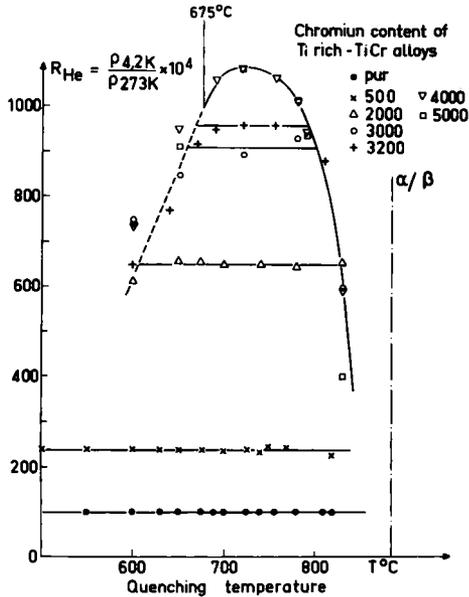


Fig. 1: Electrical resistivity ratio  $R_{He}$  evaluation in relation with anneal temperature, for different Ti-Cr alloys.

$R_{He}$  increased when quenching temperature is increased, then when all the chromium has gone into solid solution, this remains constant and there is a resistivity plateau. It decreases from higher temperatures. For temperatures below  $675^\circ\text{C}$ , eutectoid temperature (5) (6), the  $R_{He}$  values are scattered. This is may be assumed to represent the presence more or less important of  $\text{TiCr}_2$  in the samples.

For higher contents alloys (4000 and 5000  $\mu\text{g/g}$ ), there is no plateau of resistivity; the ratio  $R_{He}$  grows till an evaluated temperature of  $720^\circ\text{C}$  and

decrease after. For these two contents, values are grouped on a same curve. All the points of the curve correspond to equilibrium state. For lowest temperatures, about 600°C, the anneals lastings are 200 hours. We notice that the times necessaries for attain equilibrium state in Ti-Cr diagram, are much more importants than for Ti-Fe diagram. This indicate the quite particular iron behaviour in titanium.

From the different plateau values of  $R_{He}$ , we can draw the curve  $R_{He} = f(c \text{ in } \mu\text{g/g})$  (figure 2).

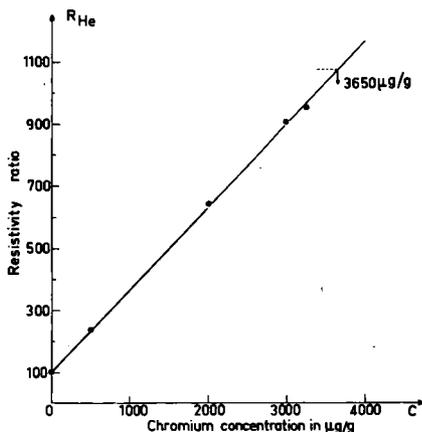


Fig. 2: Determination of the influence chromium coefficient on the  $\alpha$  titanium electrical resistivity ratio.

The experimentals points follow a line (5) which equation is :

$$R_{He} = (0.27c + 100)10^{-4}$$

If  $c$  is the concentration in  $\mu\text{g/g}$ , the levitated started titanium resistivity ratio being 100.

If we use the electrical resistivity value at 273K of a relatively pure titanium ( $R_{H_2} = 309.10^{-4}$ ) given by Wassilewski (7) :

$$\rho_{273} = 42.67 \pm 0.05 \mu\Omega\text{cm}$$

Electrical resistivity of titanium-chromium alloys at liquid helium temperature may be given in relation with content, given in at %, according to the relation :

$$\rho_{4,2K}(\mu\Omega\text{cm}) = 12.48c' + 0.4267$$

We see that the influence coefficient of chromium in titanium at liquid helium temperature is 12.48  $\mu\Omega\text{cm/at } \%$ . It is lower than iron's :

33.4  $\mu\Omega\text{cm/at } \%$  (8), but much higher than aluminium's : 0.3  $\mu\Omega\text{cm/at } \%$  (9).

It is about the same that oxygen's (10).

The use of results obtained on figure 1 and 2 enables to draw the chromium solubility into  $\alpha$  titanium curve (figure 3).

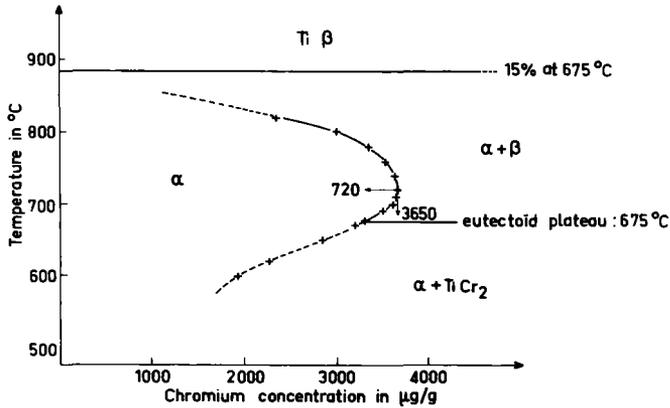


Fig. 3: Phase chromium-titanium diagram for low chromium content values.

There is a maximum solubility of 3650  $\mu\text{g/g}$  at 720°C; at the eutectoid temperature, the solubility is 3300  $\mu\text{g/g}$ . The chromium solubility in titanium is, consequently, retrograde like iron's (8).

If we consider the distribution coefficient

$$K = \frac{X_{\text{Cr}}^{\alpha}}{X_{\text{Cr}}^{\beta}}$$

$X_{\text{Cr}}^{\alpha}$  is the partial molar chromium concentration in  $\alpha$  titanium

$X_{\text{Cr}}^{\beta}$  is the partial molar chromium concentration in  $\beta$  titanium

$X_{\text{Cr}}^{\alpha}$  can be evaluated from our experimental values

$X_{\text{Cr}}^{\beta}$  being evaluated from phase diagram values of Floe and Hansen (5) (6).

Then we can draw the curve  $\ln K = f\left(\frac{1}{T}\right)$ . According to the thermodynamics provisions of Thurmond and Struthers (11) we have a line which equation is:

$$\ln \frac{X_{\text{Cr}}^{\alpha}}{X_{\text{Cr}}^{\beta}} = 5.4 - \frac{8400}{T}$$

in the form of  $B - \frac{A}{T}$ . The A and B coefficients may appreciably vary according to the  $X_{\text{Cr}}^{\beta}$  values read on the phase diagram.

If we try evaluating the solidus  $\alpha$  according to the solidus  $\beta$  phase diagram of Floe and Hansen (5) (6) and the Thurmond and Struthers (11) and Swalin (12) calculations, that we had made before for iron (4) (13). We find the following distribution coefficient equation:

$$\ln K = \ln \frac{X_{\text{Cr}}^{\alpha}}{X_{\text{Cr}}^{\beta}} = 9.89 - \frac{12532}{T}$$

This expression is quite different of our previous equation established from this experimental data work. It will show that solubility is retrograde but the maximum coordinates are different. This result from the differences of solubility values at the eutectoid temperature (5000  $\mu\text{g/g}$  instead of 3300  $\mu\text{g/g}$ ) and from the fact that when we calculate we supposed, on the one hand, an equivalence between the liquidus line corresponding to the  $\alpha - \beta$  transformation which was entirely in the solid phase, and the liquidus line corresponding to the liquid-solid solution equilibrium, and on the other hand, we supposed that the solution is regular, and in equilibrium with an ideal liquid one.

### Conclusions

This work shows the chromium solubility in  $\alpha$  titanium is retrograde. At eutectoid temperature (675°C) the solubility value is 3300  $\mu\text{g/g}$  whereas at 720°C it is 3650  $\mu\text{g/g}$ . The experimental curve of the chromium solubility variation in  $\alpha$  titanium is appreciably different of the calculated one from the previous data and the thermodynamic calculations of Thurmond and Struthers.

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