

SURFACE TREATMENT

PACK-ALUMINIZATION OF TITANIUM

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Introduction

Numerous studies have been devoted to the problem of titanium or titanium alloys embrittlement by external or internal hydrogen, but very few of them are concerned with the influence of the surface state on it or with protecting coatings against hydrogen penetration. The results presented here concern an aluminum base coating. Aluminum itself, as bulk material, is known to be almost insensitive and impervious to hydrogen; on the other hand it is present as alloying element in most of the industrial titanium alloys.

The pack aluminization conditions and the coating structure are first presented. Then the influence of the coating on the mechanical properties and his efficiency against hydrogen penetration are pointed out. At least special attention is turned to a new $TiAl_2$ phase.

1. - Starting materials and aluminization treatment

The titanium used (T 40 from Ugine-Aciers) was a 1 mm diameter wire, with an equiaxed structure and a 30 μm average grain size. The cement, similar to those used for nickel or nickel-base alloys pack-aluminization (1 - 2) consisted of 99,5 % pure Al, AlF_3 and Al_2O_3 powders. The samples were degreased by ultrasonic treatment in alcohol and dried. The treatments were carried out in alumina crucibles, heated in a resistance furnace. In order to compensate the activator loss by saturating the atmosphere with AlF_3 , a crucible containing only the cement was disposed before the one containing the samples. All treatments were performed under purified argon flow. After treatment, samples were allowed to cool slowly except for the study of the $TiAl_2$ phase.

A preliminary study (3) allowed to specify the influence of the main parameters (cement composition, duration, temperature) on the specific weight gain. The results obtained (some of them are presented in Fig. 1) led to the choice of the following optimal conditions : cement composition 88 w/o Al_2O_3 , 4 w/o AlF_3 , 8 w/o Al; temperature 1083 K.

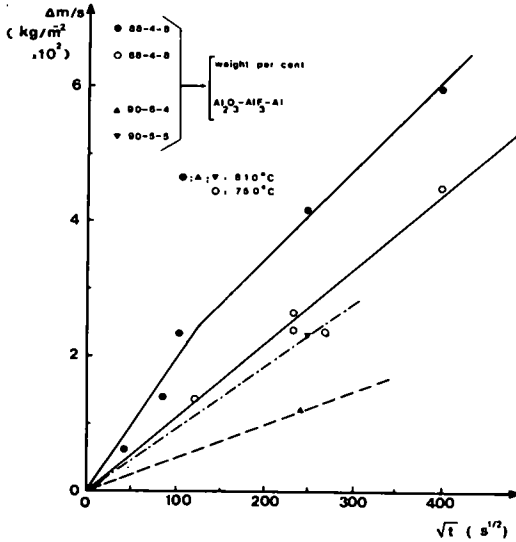


Fig. 1: Specific weight gain versus time square root for various cement compositions

2. - Coating analysis

Microprobe analysis, X-ray diffraction and conventional metallographic examination were used in order to identify the phases present in the coating and the layers thicknesses.

2.1. - Phase identification

Fig. 2 shows the titanium concentration profile obtained after a 44 hours long treatment, and the formulas of the phases obtained from quantitative analysis of the two components. It proves that at 1083 K, in the Ti-Al phase diagram, the following phases must exist :

$Ti-\alpha Ti / Ti_6Al / \gamma(TiAl) / TiAl_2 / TiAl_3 / Al$ liquid.

If the Ti_6Al phase is known (4), no mention was found in the literature of the $TiAl_2$ phase.

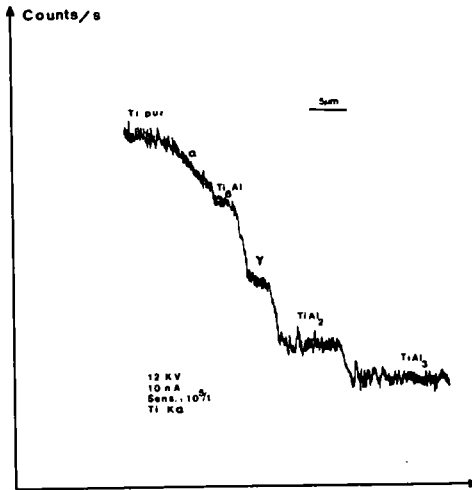


Fig. 2: Titanium concentration profile
(44 hours treatment)

2.2. - Aluminization rate

Fig. 3, where the total thickness of the coating and those of the various layers are plotted versus time square root, summarizes the results obtained. It suggests the following remarks:

- The coating only consists of $TiAl_3$ for short-time treatments ($t < 30$ mn).
- Between 30 mn and 2 hours appear the $\alpha + Ti_6Al$ and $\gamma(TiAl)$ layers.
- Then appears $TiAl_2$ ($t > 6$ hours). Its appearance coincides with the perturbations observed on the total and $TiAl_3$ thickness curves.
- When the treatment duration exceeds 50 hours, the total and $TiAl_3$ thicknesses fall abruptly. The external layer becomes porous, poorly adherent and measurements are out of significance.

In short, all treatments with durations shorter than 40 hours produce an adherent grey coating, when for longer treatments, the cement activity becomes to low and the intermediate layers grow at the expense of the external $TiAl_3$ layer. This is confirmed by the bending of the total and $TiAl_3$ thickness curves, and by the thinning of the $TiAl_3$ layer during subsequent annealing.

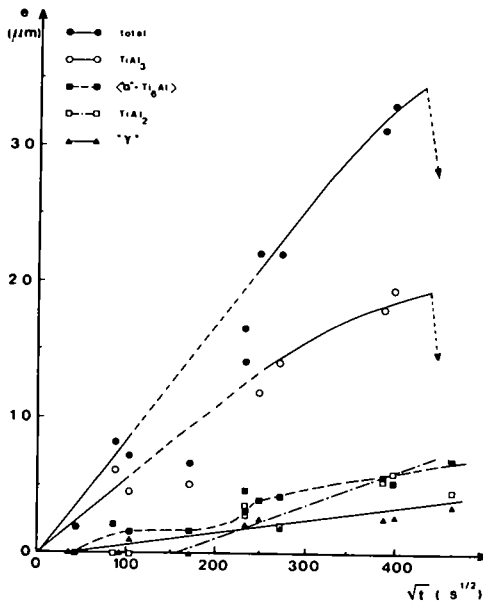


Fig. 3: Evolution of the layers thickness versus time square root

2.3. - Influence of a subsequent annealing treatment

Fig. 4 shows the titanium concentration profiles of a cemented sample as treated (7 hours) and after a 60 hours vacuum annealing at 1073 K. The effect of the thermal treatment can be described as follow :

- The γ solid solution has been partially homogenized.
- A new layer appears which corresponds to the formula Ti_5Al_2 , but consists of Ti_2Al and Ti_3Al .
- The Ti_2Al layer is no more present.
- The Ti_3Al layer has been consumed partly by the growth of $TiAl_2$, partly by sublimation.
- $TiAl_2$ is less affected by the vacuum annealing and acts as a barrier against inner layers volatilisation, as confirmed by vacuum annealing of samples in which this phase is not present.

3. - Effect of coating thickness on the mechanical behaviour

The mechanical (tensile) properties are listed in Table 1 in dependence of the coating thickness. These results lead to the following remarks :

- as long as the coating remains thin ($< 2 \mu m$), a good cohesion at the Ti/ $TiAl_3$ interface is achieved : therefore, the cemented layer is involved in the plastic flow. The little

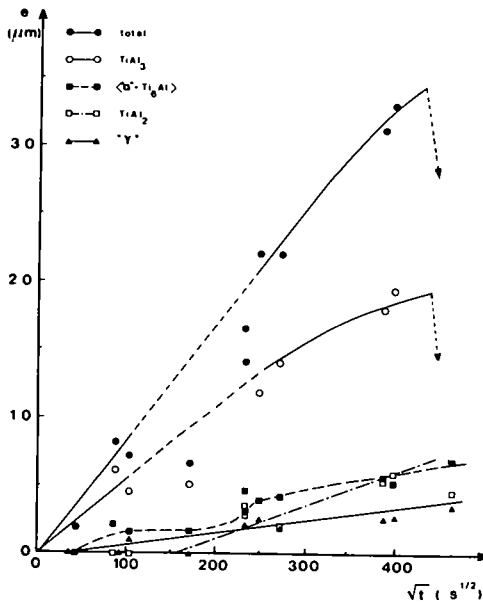


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It can be concluded that the brittle $TiAl_3$ phase largely decreases the ductility of titanium wires as soon as the layer thickness exceeds $2\mu m$.

4.- Aluminide coatings as hydrogen permeation barrier

The hydrogen contamination tests were carried out in a Sieverts apparatus. The hydrogenation conditions are given in Table 2.

Cementation at 1083 K during :	Hydrogenation 3 hours-773K Hydrogen pressure :	C_H (% at.)	C_H (ppm)
0,5 hour	1333 Pa	0,31	65
	6665 Pa	0,38	80
8 hours	1333 Pa	0,26	55
	6665 Pa	0,55	115
20 hours	1333 Pa	0,31	65
	6665 Pa	0,33	70
44 hours	1333 Pa	0,69(?)	145(?)
	6665 Pa	0,19	40
as annealed	without hydrogenation	0,09	19
	1333 Pa	1,83	390
	6665 Pa	7,91	1790

Table 2

For a given pressure all the samples were hydrogenated simultaneously. After this treatment, the hydrogen was analysed by vacuum extraction at 1323 K. Internal friction measurements at low frequency were also performed (8).

The results are listed in table 2 which reproduces the hydrogen contents of the various samples. It is to be noted that the H contents of the cemented samples are located at a very low level (55 to 115 ppm) whereas for the uncoated sample under the same hydrogenation conditions, the values lie between 390 and 1790 ppmH. Further it is noteworthy that both the hydrogen pressure and the coating thickness (and therefore the nature of the layers) seem to have only little influence.

The most important feature here is that an aluminide coating, even for low thickness, if obtained in optimal conditions, acts as a very efficient barrier against gaseous hydrogen penetration. It is presumed that $TiAl_3$ plays the relevant part in this behaviour.

5. - On the phases encountered in this study

Surprisingly, the phases observed after cementation at 1083 K were not exactly those expected on the base of the equilibrium diagram given in (5) and completed in (4).

If the Ti_6Al phase was already mentioned by (4), this phase appears in our study after about 10 hours at 1083 K and seems to disappear, giving $Ti_2Al + Ti_3Al$, after long vacuum annealing at 1073 K. These two last phases were observed by (6) who determined their fields of stability as well as the eutectoid plateau ($Ti_3Al \rightleftharpoons Ti\alpha + Ti_2Al$) at 953 K, but made no mention of Ti_6Al . According to our own observations, it seems that Ti_6Al is a metastable phase in our cementation conditions.

The only reference concerning the $TiAl_2$ phase is due to (7). These authors observed a unique phase in the Ti-Al diagram between 45 and 67 % at. Al after annealing during 4 days at 1073 K, water quenching and subsequently annealing during 4-7 hours at 893 K. The structure of this phase was determined to be similar to $TiAl$ with a substructure similar to $HfGa_2$ (trigonal centered, $a = 3,976 \text{ \AA}$ and $c = 24,360 \text{ \AA}$).

In order to confirm this, synthetic alloys of composition $TiAl_2$ were prepared by plasma melting. Microscopic observations and microprobe analysis of them show a unique phase of composition $TiAl_2$. The structure of this very hard phase ($HV = 4200 \text{ MPa}$ with a load of 0,010 Kg) was determined after annealing at 1083 K during 40 hours and subsequently quenching. A hexagonal primary structure with $a = 15,656 \text{ \AA}$ and $c = 23,536 \text{ \AA}$ seems to fit with the obtained X-rays patterns. The examination of other compositions near 67 % at. Al further showed $TiAl_2$ to result from a peritectic transformation.

On the other hand, the cementation temperature was varied between 1013 K and 1083 K for a constant duration of 24 hours and the samples were quenched or allowed to cool slowly. The concomitant observations show that the $TiAl_2$ phase forms only above 1033 K and that without quenching only the $TiAl_3$ and $TiAl$ phases are present.

Summary

An adherent coating can be obtained by pack-aluminization of titanium in easily reached technological conditions. Analysis of the composite coatings yields to the characterization of a new $TiAl_2$ phase. The mechanical behaviour remains almost unaltered for thin ($\approx 2 \mu\text{m}$) coated wires. Such a coating could be a very efficient barrier against gaseous hydrogen penetration and could find industrial application in preventing hydrogen embrittlement of titanium.

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