# OBTENTION OF SILICIDE COATINGS ON TITANIUM BY PACK-CEMENTATION

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## Introduction

Metallic silicides exhibit very often a good oxidation resistance at high temperature, due to the formation of a silicon oxide scale impervious to oxygen. Among the binary silicides ($MSi_2$ or $M_5Si_3$ type) $TiSi_2$ and $Ti_5Si_3$ have a very good oxidation resistance (1). On the other hand high temperature applications of titanium may be limited by the poor oxidation resistance of the metal itself.

In spite of these facts very few studies concerning the protection of titanium by tinanium silicides coatings have been done (2 - 3). It seemed then interesting to try to obtain such coatings by means of the simple pack-cementation technique.

## 1. - Experimental procedures

Pack siliconizing was carried out in an alumina crucible, filled with a mixture of alumina as inert filler, silicon as reagent, and aluminium fluoride or chloride as activator. The samples were titanium plates (10 X 10 X 0,5 mm). Before treatment they were etched in an mixture of $HNO_3$ and HF, cleaned and dried. All treatments were performed under purified argon flow. After the treatment samples were cleaned by ultrasonic treatment in alcool, and weight gains were measured. The nature and the amounts of the different phases present in the coating were determinated by X-Ray diffraction, metallographic examination and microprobe analysis.

## 2. - Results

The main parameters of the coating treatment were investigated : nature and amount of the activator, silicon amount, duration and temperature.

### 2.1. - Nature and amount of the activator

Fluorides were chosen because they are known to be the most efficient activators in pack cementation (4). First experiments were performed with $AlF_3$. Then, because it condenses at the coating surface, NaF was tested. The tests were performed in the following standard conditions :
temperature 1223 K , duration 57,6 $10^3$s, silicon content of the pack 15 w/o. Results are summarized on Fig. 1.

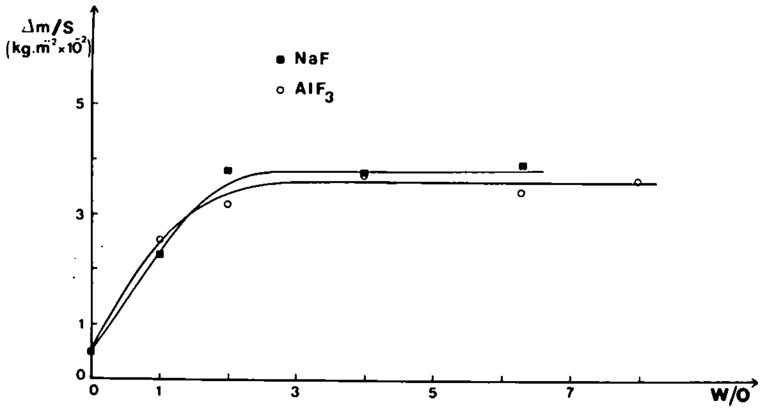


Fig. 1: Influence of the amount (weight per cent) and the nature of the activator

In both cases the specific weight gain sharply increases until an approximative value of 2w/o is reached. Then it holds a constant value which is almost the same for the two activators. Accounting the higher fluor content of $AlF_3$, NaF seems to be lightly more efficient. But coatings obtained with NaF are poorely adherent and their external appearance suggest the presence of a liquid phase during the process. Consequently $AlF_3$ was retained for all subsequent experiments in the proportion of 4w/o.

2.2. - Silicon amount

The influence of the silicon amount was investigated in the range 0 to 15 w/o for 57,6 $10^3$S long treatments and at 1223 K. Specific weight gain is plotted on Fig. 2 versus silicon content.

It varies sharply for low silicon contents, lesser thereafter.

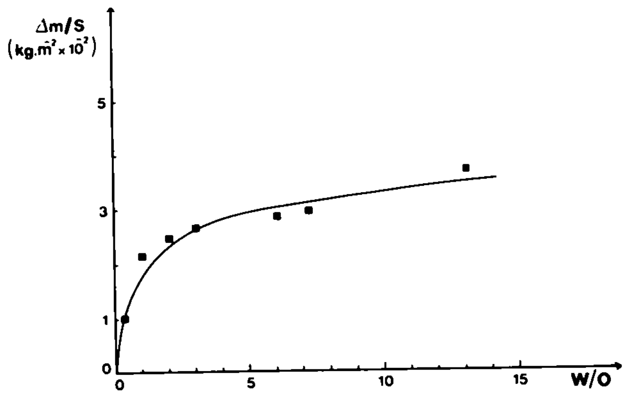


Fig. 2: Influence of the silicon amount (weight per cent)

2.3. - Kinetics

All the experiments performed in order to determine the rate of coating formation and the influence of temperature on it were carried out in the following standard cement :

$Al_2O_3$ 81 w/o Si 15 w/o $AlF_3$ 4 w/o.

Results are summarized on Fig. 3, where the specific weight gain is plotted versus time square root.

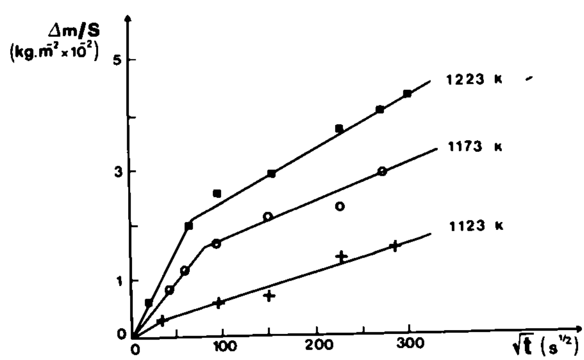


Fig. 3: Specific weight-gain versus time square root for various temperatures

It can be seen that the weight gain does not follow a simple parabolic law, or that the same law can not account for short-time and long-time treatments. Although a satisfactory explanation for that fact was not found, it could result from two phenomenons : the formation of a porous activator scale on the sample surface, and the cement activity lowering due to the loss of activator by sublimation. Both of them are linked to the $AlF_3$ evaporation rate, then more marked for high temperatures.

2.4. - Nature of the coating

Metallographic examination showed the presence of four layers in the coating. X-Ray diffraction patterns proved the existence of $TiSi_2$, TiSi and $Ti_5Si_3$, which was confirmed from microprobe analysis for the two outer layers ($TiSi_2$ and TiSi), when the two inner layers were too thin to allow quantitative analysis. Thicknesses of the three outer layers are plotted versus time square root on Fig. 4, the fourth one being too thin to allow accurate measurements (coating temperature 1223 K).

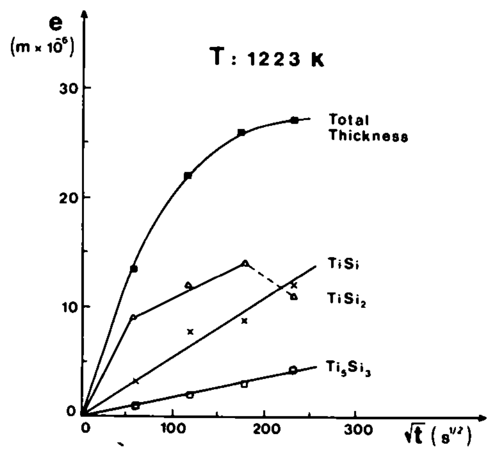


Fig. 4: Layers thickness versus time square root

It can be seen that the TiSi and $Ti_5Si_3$ layers growth obeys a parabolic law, but not that of the $TiSi_2$ layer. The fourth layer is probably due to the presence of the eutectoid at 1133 K for 1 Si per cent in the Ti-Si phase diagram (5).

Conclusion

This study proves the possibility of elaborating silicides coatings on titanium by pack-cementation, and preliminary tests proved the oxidation resistance of these coatings to be good ($0{,}5\ 10^{-2}$ $kg.m^{-2}$ for 50 hours air exposure at 1123 K). However the mechanical behaviour of such composite coatings must be investigated since the brittleness of one of the intermediate layers could lead to catastrophic failure of the entire coating.

References

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