Preparation of tantalum carbide films by reaction of electrolytic carbon coating with the tantalum substrate

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Abstract

This article demonstrates that coatings of tantalum carbide can be obtained by electrodeposition of carbon in molten fluorides on a tantalum substrate as an alternative to the CVD process. The structural characteristics of the carbon deposited by the electrolytic route lead to a high reactivity of this element towards a tantalum cathode to produce tantalum carbide. Mutual reactivity was shown to be enhanced if tantalum plate is replaced by an electrodeposited layer of tantalum, where the fine microstructure provides a catalytic effect.

Keywords

Electrodeposition, carbon, tantalum carbide, molten fluorides, solid state diffusion.

1. Introduction

Up to now, layers of tantalum carbide have been synthesised by chemical vapour deposition of carbon on a tantalum substrate in a 1300-1500°C temperature range. The carbon prepared in this way is very reactive towards the substrate and the interdiffusion of tantalum and carbon produces 10-20 μm layers of TaC and Ta_2C on the surface of tantalum plate after 50 hours of treatment [1].

A similar process using reactive electrodeposition of carbon as an alternative to CVD process was examined here. In this way, the overall process consists of

electrodeposition of carbon on a tantalum substrate with diffusion of the carbon produced leading to the formation of tantalum carbide.

The success of this operation, based on a solid state reaction, is obviously affected by the state of division of each reactant:

- we demonstrated [2] that carbon can be electrodeposited in fluoride media, and in further work [3], focused on the electrocrystallisation process, that the nucleation of carbon is progressive and provides a constant source of small amorphous grains at the cathode surface,
- in a recent article [in press] concerning the electrocrystallisation of tantalum in molten fluorides, we optimized the electrolysis current to obtain a regular and microstructured layer of tantalum over a stainless steel substrate.

In the present work, we used instead of solid tantalum plate an electrodeposited layer in which the small grain size enhances the contact area of the cathode and thus acts as a catalyst.

Following optimisation of the operating conditions for the tantalum coating structure and optimisation of the operating conditions for the carbon coating morphology, we observe the reaction between the electrodeposited carbon and a cathodic substrate made successively of tantalum plate and of a thin tantalum coating.

2. Experimental Details

2.1 The electrochemical cell

All the experimental systems have already been detailed in previous works [2,4].

2.2 Experimental techniques

All the electrolyses were carried out with a PGSTAT 30 galvanostat/potentiostat with autolab software.

The deposits of carbon, tantalum and carbides are characterised using physical techniques:

(i) XRD (SEIFERT) to analyse the crystallised compounds with the following operating conditions : $20° < 2\theta < 90°$ with a sweep rate of 0.05°/20s,

(ii) scanning electron microscopy (LEO 435 VP) and an EDS probe for the observation and the chemical analysis of the deposits respectively.

3. Results and Discussion

The overall process consisted in making a tantalum coating on a usual substrate (stainless steel, copper, etc) then followed by carbon coating of the tantalum layer.

Each coating was optimised in order to enhance the microstructure of the two reactive elements. Indeed, the intermetallic diffusion between tantalum and carbon is facilitated if both coatings are microstructured instead of containing big crystals.

3.1 Optimisation of operating conditions on tantalum coatings morphology

The preparation of tantalum coatings is well controlled by our team [4-6]. We first recall the operating conditions and the previous results: (i) electrolyte: LiF-NaF + K_2TaF_7, (ii) temperature range: 750 – 900°C, (iii) the electrode process: direct electroreduction of TaF_7^{2-} ions into tantalum exchanging five electrons, and (iv) the coatings are adherent and smooth at moderate current densities.

The oxide content is to be controlled for successful electrodeposition as we reported in a recent article [6], where we demonstrated that the contamination of the bath by these ions hinders the success of the coating.

The optimization of the experimental conditions in terms of microstructure was missing up to now and thus was examined here.

For this purpose, we examined the influence of the temperature and the current density on the microstructure of the coating through a two-dimensional experimental design: two values of the variables temperature (800°C and 900°C) and current density (5 and
100 $mA.cm^{-2}$). The substrate was stainless steel and the thickness of the coatings about 20 µm. The microstructure of the coating was assessed by SEM of cross sections after a treatment to reveal the grain boundaries. Figures 1a, b, c and d represent SEM micrographs of cross sections of tantalum coatings prepared for the four operating conditions.

The main observations are:

- temperature effect: at 800°C, the thickness of the layer was more homogeneous than at the higher temperature (900°C),
- current density effect: small crystals were presents at the Ta / steel interface for the higher current density; otherwise at low current density, the coating was made of coarse crystals. This is explained in a previous work on the electrocrystallisation of tantalum in molten fluorides [3], where it was stated that at low current, the nucleation rate is low, and consequently generating few crystals which become coarse grains in the future layer.

We conclude that the best operating conditions for obtaining microstructured coatings are 800°C and 100 mA/cm². Furthermore, in these conditions, the thickness of the coating is very regular, and this can be considered as a promise of a smooth tantalum carbide layer.

3.2 Optimisation of operating conditions on electrolytic carbon coating morphology

3.2.1 Carbon electrodeposition process

In previous works [2], it was shown that the electrochemical reduction of carbonate ions in molten fluoride melts in the 700-900°C temperature range leads to a one-step process exchanging four electrons to produce amorphous carbon:

$$CO_3^{2-} + 4\ e^- \rightarrow C + 3\ O^{2-}$$

Then, we demonstrated that carbon nucleation is progressive whatever the temperature and carbonate ion concentration.

So, these earlier results suggested a high reactivity of the electrodeposited carbon in molten fluorides: (i) amorphous structure; (ii) progressive nucleation. Accordingly, during electrolysis, small and reactive grains are continuously generated at the surface of the substrate; if the reaction with the tantalum substrate is thermodynamically spontaneous, a catalytic effect can be expected from the small size of the carbon particles obtained.

3.2.2 Optimisation of the current density and the temperature with respect to coating morphology

As in the case of tantalum coatings, we used an experimental design with temperature and current density as variables and the morphology of the electrodeposited carbon as endpoint. A series of carbon coatings were obtained on copper electrodes for two temperatures (700°C and 800°C) and for two current densities (60 and 130 $mA.cm^{-2}$). Figures 2a, 2b, 2c and 2d represent SEM micrographs of the carbon coatings prepared for the four operating conditions: 700°C, 60 mA/cm^2; 700°C, 130 mA/cm^2; 800°C, 60 mA/cm^2 and 800°C, 130 mA/cm^2 respectively.

The role of the current density seems to be particularly important on the structure and the morphology of the carbon coatings obtained by carbonate reduction. At the lower temperature (700 °C) and lower current density (60 mA/cm^2), in figure 2a, a fibrous texture with whiskers of electrodeposited carbon is observed. The real surface area of the deposit is very high. While at higher current density (130 mA/cm^2), on figure 2b, the shape of the coating is smoother and more compact.

The temperature has a strong influence on the growth rate: the growth of carbon nuclei is fast, so the deposit is made of big spherical grains regularly distributed over the surface of the cathode. Figure 2d, showing the coating prepared in these conditions (high temperature and current density), also confirms that the carbon grains are not of the same size, which is coherent with the notion of progressive nucleation. This type of coating seemed, to us, to be the most propitious for further reaction of the carbon with tantalum substrate; therefore, the operating conditions of figure 2d were chosen carbon electrodeposition on tantalum.

3.3 Reactive Electrodeposition of Carbon on Tantalum

3.3.1 Thermodynamic and kinetic aspects

Gibbs energy at 1000K of both TaC ($\Delta_f G° = -140.9$ kJ/mol) and Ta_2C ($\Delta_f G° = -209.6$ kJ/mol) prove that these compounds are thermodynamically stable [7], and that the reaction between tantalum and carbon should be spontaneous; nevertheless, we know that a reaction proceeding between two solid phases put into contact needs special conditions to be activated. As mentioned, a strong catalytic effect can be expected from the permanent supply at the tantalum cathode surface of small grains of carbon during the electrolysis of carbonate ions in fluorides; likewise the reactivity of tantalum must be improved by the small grain size at the surface of the cathode since it is well known that the reactivity of tantalum proceeds mainly in the grain boundaries.

3.3.2 Observation of the formation of tantalum carbides

Preliminary carbon electrodeposition runs at 1073 K of on smooth surfaces of tantalum plate yielded only a thin carbide layer (less than 1 μm in 2 hours) on the cathodic surface, as shown in the micrograph in figure 3. So, it was decided to use a tantalum coating on stainless steel as cathode material.

Figure 4 represents an XRD spectrum of the tantalum carbide layer obtained in this way: 20 μm of tantalum and carbon deposition for 2 hours at 130 mA/cm² at 800°C. Normally, at the interface of TaC layer and Ta substrate, a thin layer of Ta_2C should be expected whereas we can notice in this spectrum that the layer is made entirely of TaC. This result proves that the kinetic of formation of Ta_2C is very slow. We can also observe that some tantalum is still visible in the spectrum, indicating that carbon interdiffusion within the tantalum layer is not complete.

As we can see in figure 5a and 5b, thick carbide layers are obtained on electrodeposited Ta (about 7-8 μm). Obviously, this result confirms that the microstructure of the Ta coating and the nucleation mode of the carbon promote a catalytic effect, due to a much more extended area of contact between the two elements. As evidenced in the micrograph in figure 6 and its magnification of figure 7, the penetration of small grains of carbon supplied by the electrodeposition process proceeds within the grain boundaries and the rate of the reaction increases significantly when the contact between the two elements is enhanced. This work confirms the high reactivity of

carbon electrodeposited in molten fluorides in the formation of tantalum carbides as proved by the analysis of the diffusion layer [8]).

Notice that reference [9] mentions a similar approach in molten oxysalts for obtaining layers of borides and silicides of refractory metals (W, Mo) or oxides (Cr_2O_3) by an electrolytic process in two stages: (1) deposition of the refractory metal or of the oxide; (2) reactive electrodeposition of B or Si.

4. Conclusion

This work confirms the high reactivity of electrodeposited carbon in molten fluoride media towards tantalum and the reaction proceeding between the two elements in the grain boundaries of tantalum.

Nevertheless, the XRD pattern of the layer shows that Ta is still present in the coating, meaning that the reaction is not complete and that the diffusion of reactive carbon is too rapid compared with the reaction within the tantalum grains. Further optimisations should lowering the diffusion of carbon in the grain boundaries and increase the reaction rate in the tantalum bulk.

These results lead us to conclude protective coatings of tantalum carbides generated by the electrochemical route over a moderate temperature range (700 – 900°C) can be now expected as an alternative to Chemical Vapour Deposition which proceeds at higher temperatures (1300°C).

This conclusion can be extended to the possible preparation of other refractory metal carbides (Nb, Mo, W…) in this way, so the methodology described here seems to be promising for the electrosynthesis of such compounds.

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Legend of figures

Figure 1: Evolution of the microstructures of tantalum coatings observed by SEM for various operating conditions: (a) T = 800°C, j = 5 mA/cm², (b) T = 800°C, j = 100 mA/cm², (c) T = 900°C, j = 5 mA/cm², (d) T = 900°C, j = 100 mA/cm².

Figure 2: SEM observation of carbon coatings on steel at various current densities and temperature: (a) T = 700°C, j = 60 mA/cm², (b) T = 700°C, j = 130 mA/cm², (c) T = 800°C, j = 60 mA/cm², (d) T = 800°C, j = 130 mA/cm².

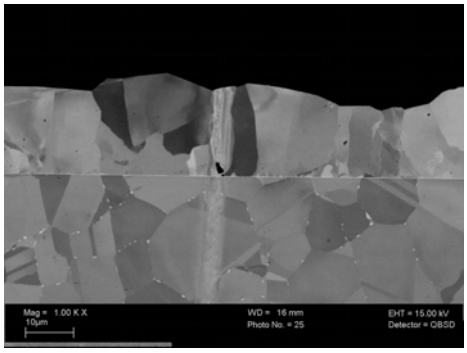
Figure 3: Optical observation of the cross section tantalum plate after electrolysis in carbon deposition optimized conditions.

Figure 4: XRD spectrum of tantalum coating after 2 hours of carbon coating at 130 mA/cm² and T = 800°C.

Figure 5a and 5b: Optical observations of tantalum carbide layer obtained with tantalum coating made at T = 800°C and j = 5 mA/cm² and carbon coating made during 2 hours at 130 mA/cm² and 800°C.

Figure 6: Optical observation of the interface between the tantalum carbide layer and the stainless steel substrate.

Figure 7: SEM micrograph (×2000) of the tantalum carbide layer.



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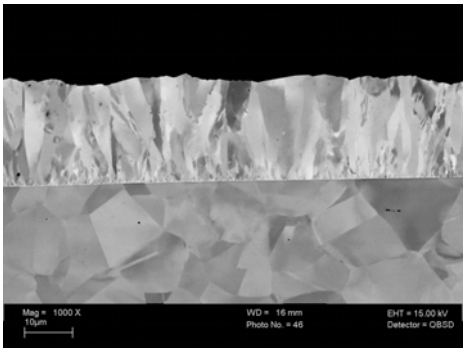

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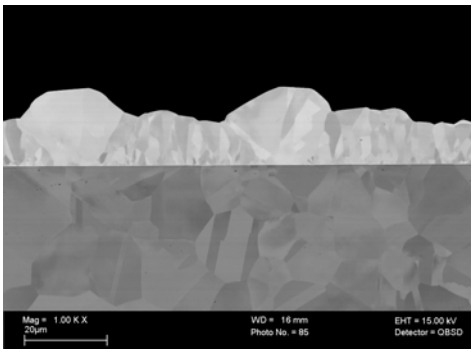

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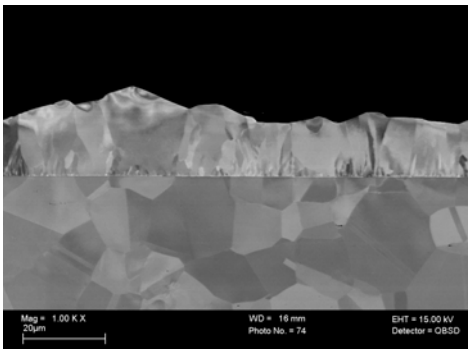
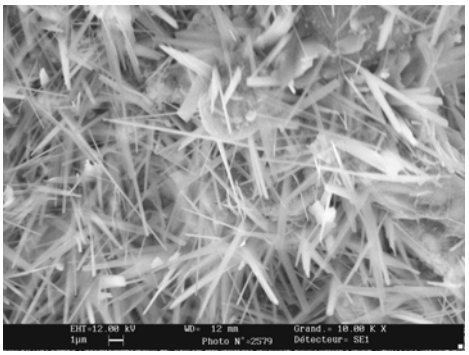


(d)

Figure 1



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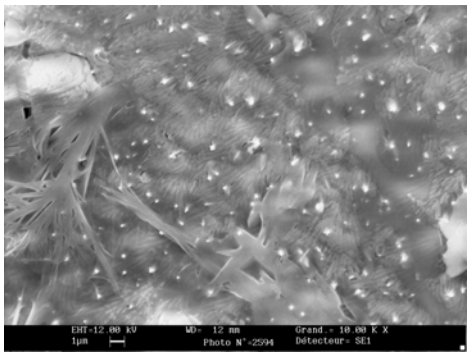

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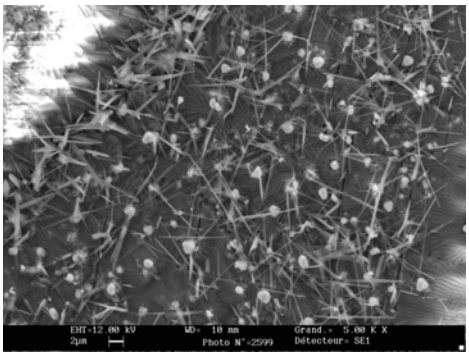

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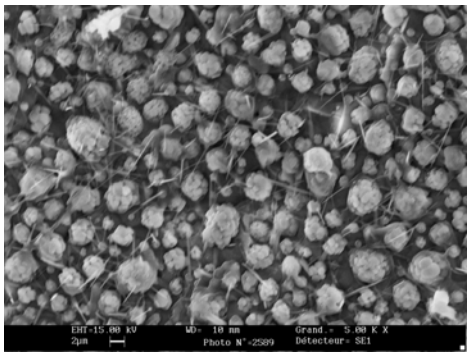

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Figure 2

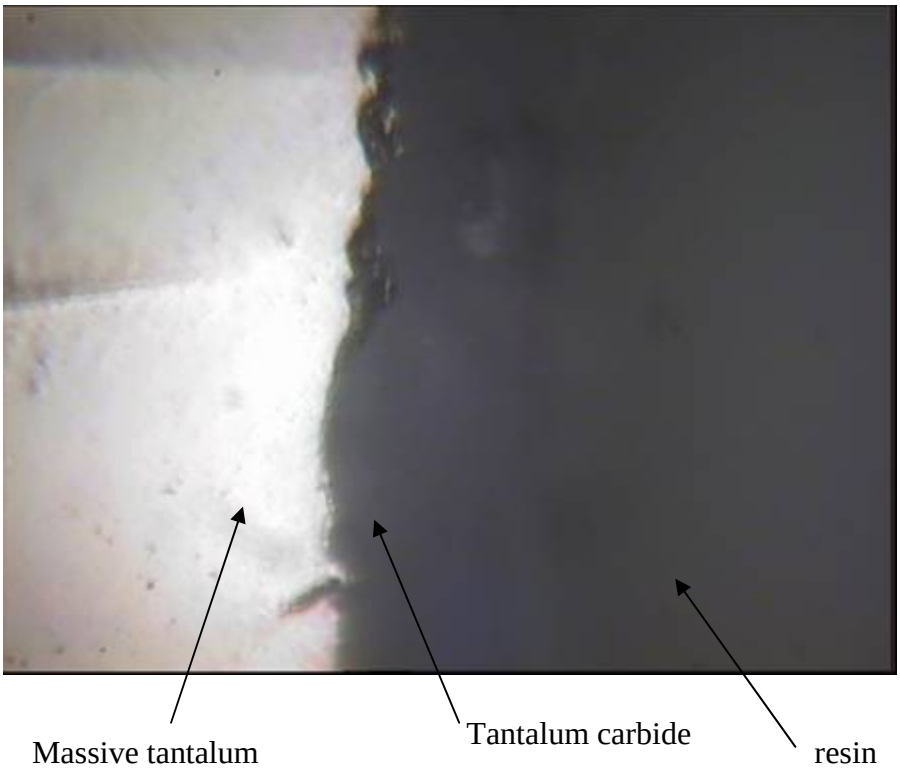

Figure 3

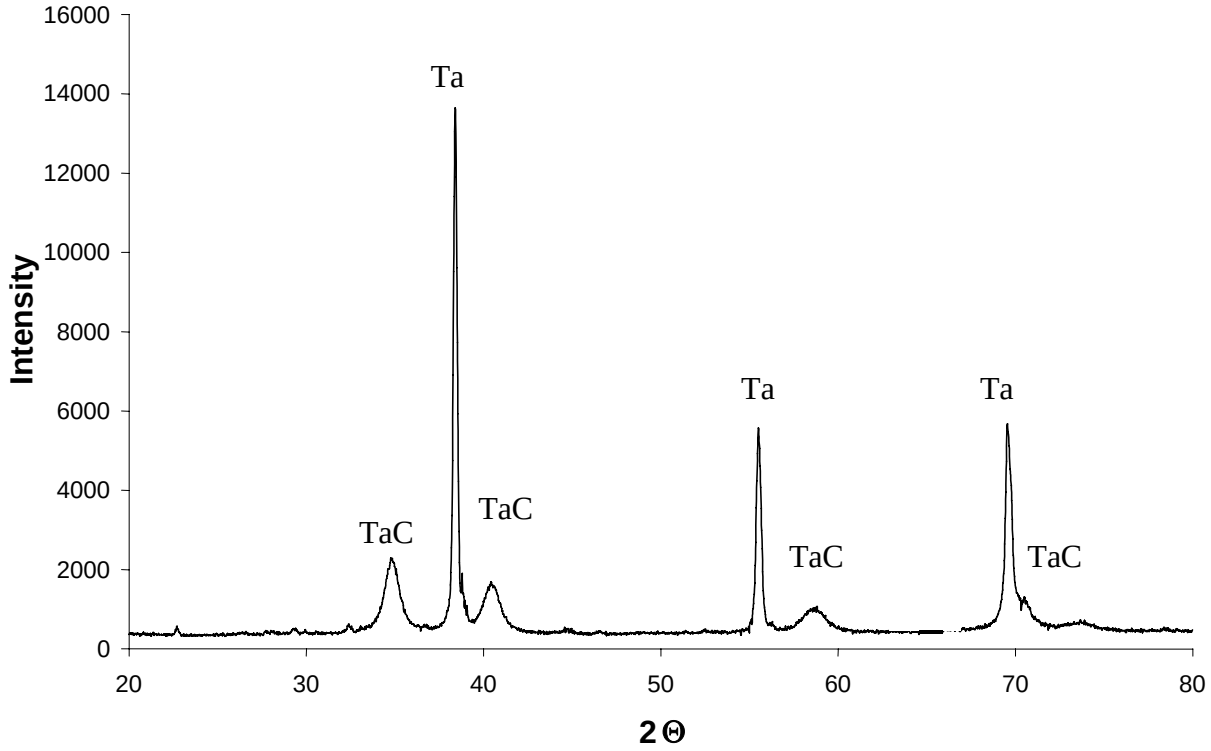
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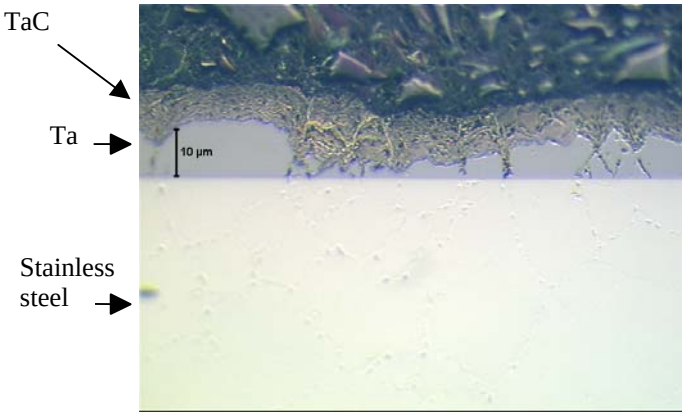
Figure 4



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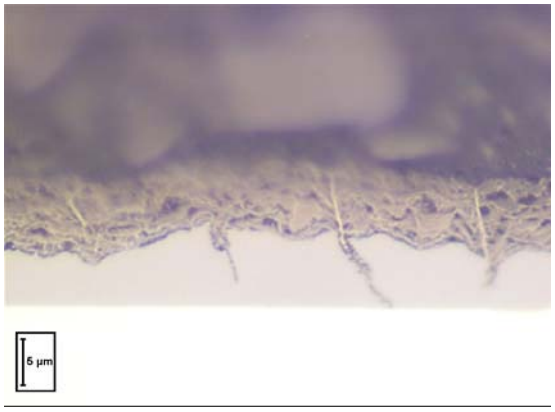

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Figure 5

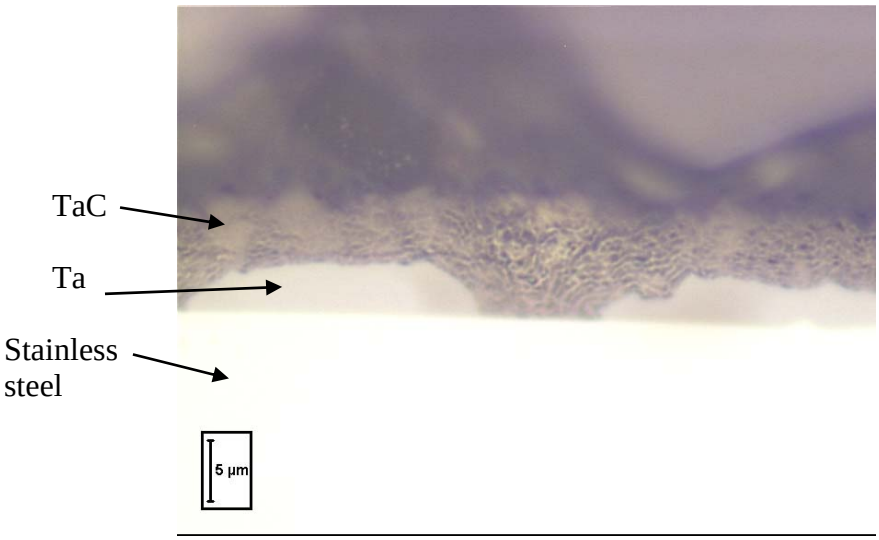

Figure 6

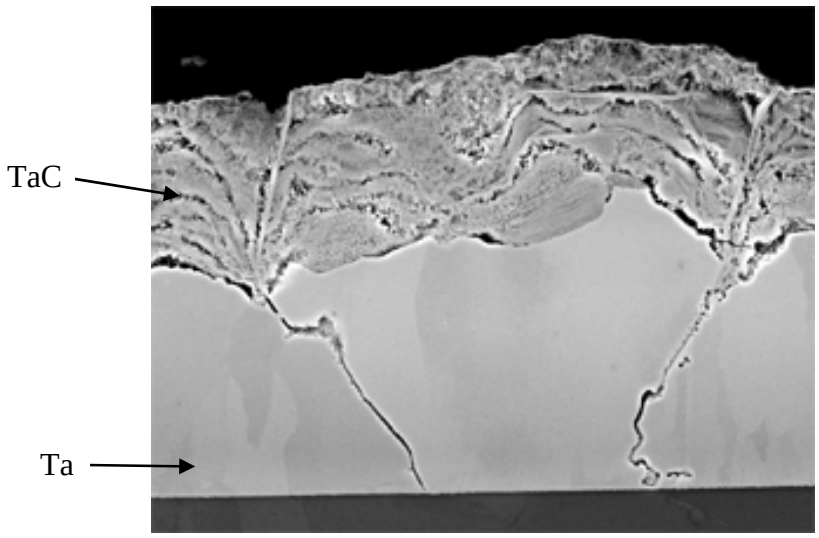

Figure 7