

# Sintering of (alumina + titanium) powder mixtures and elaboration of the corresponding cermets

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We considered the possible formation of a bond between a ceramic ( $\text{Al}_2\text{O}_3$ ) and a metal (titanium). We first concluded that a direct bonding of these two materials would be very unsatisfactory. We managed to obtain good bonding through an  $(\text{Al}_2\text{O}_3 + x\text{Ti})$  cermet placed between the two initial materials. Diffusion tests with  $\text{Al}_2\text{O}_3/\text{Ti}$  or  $(\text{Al}_2\text{O}_3 + x\text{Ti})/\text{Ti}$  couples have shown the appearance of densified layers in the diffusion zone. The study of the influence of the titanium content in the cermet permitted values of  $x$  to be determined which give an appropriate continuity ( $10 \leq x \leq 25$  wt%) across the interface. Measurements by microprobe have shown that the mobility of the  $\text{Al}^{3+}$  ion has a predominant influence in the process leading to the bonding. The nature of the sintering atmosphere plays an important role in the sintering capacity of  $(\text{Al}_2\text{O}_3 + x\text{Ti})$  cermet as well as the densification of the samples.

## 1. Sintering of (alumina + titanium) powder mixtures

In the case of a ceramic-metal bond, the metal must be chosen according to the following requirements:

- (i) its thermal expansion coefficient must be close to that of the ceramic;
- (ii) the interdiffusion between the elements of the two materials must be significant; and
- (iii) the formation of definite brittle compounds must be avoided.

For practical reasons, it is very often difficult to have 100% compatible expansion coefficients; then the metal has to be sufficiently ductile and the bonding has to be achieved in such a way as to minimize stresses near the initial interface. If we bear this in mind and choose pure alumina (or an alumina-rich material) as the ceramic, various metals such as copper, nickel, titanium or alloys such as Kovar, iron-nickel, iron-chromium, can be considered to obtain a ceramic-metal bond.

However, it appears it is quite difficult, or even impossible, to obtain a satisfactory bonding directly between ceramic and metal. A composite material must be introduced in between to achieve a proper bonding. A cermet will be appropriate since it is a combination of the original materials [3-5]. This implies that the metal or the alloy will not reduce the ceramic phase; therefore, it also means that the free enthalpy change associated with the oxide formation constituting the ceramic is somewhat less than that associated with the metal oxide formation [1, 2].

Furthermore, there must be a similar shrinkage when sintering the original materials used for the cermet. If there is not, the material sintered first (most often the metal powder) may form a compact and a discontinuity in the cermet is then observed, which creates an imperfect and heterogeneous densification: obviously it means a defective bond.

This research was meant to find whether it was possible to obtain a bonding between titanium and sintered pure alumina by means of an alumina-titanium cermet. The possibility of chemical diffusion was first considered for  $\text{Al}_2\text{O}_3/\text{Ti}$  or  $\text{Ti}/\text{cermet}$  ( $\text{Al}_2\text{O}_3 + \text{Ti}$ ). The best conditions for the elaboration of such cermets were then determined; some properties of these cermets were also studied briefly. These two materials were chosen for the following reasons:

(i) This type of bonding can be used at high temperatures (1200 to 1300°C) whereas a more traditional one with a powder mixture of manganese and molybdenum (with a silica-type addition) can only be used up to about 800°C [6-8].

(ii) Alumina can be combined with molybdenum or manganese only through the formation of a vitreous phase coating the metal particles and to achieve bonding with the ceramic [9, 10]. However, for  $\text{Ta}/\text{Al}_2\text{O}_3$  cermets a liquid phase appears *in situ* [11], which gives too much migration of metal within the ceramic. In this work we tried to prevent the formation of both the vitreous phase and the liquid phase to obtain a ceramic metal bond with essentially solid solutions linking the materials.

TABLE I Properties of powders

Property	Material	
	Al <sub>2</sub> O <sub>3</sub>	Titanium
Origin	Baikowski	Baudier
Type	CR 1	85 CX 300 TV
Purity (%)	99.98	99.2
Crystal structure	Trigonal (D 51)	cph (A 3) bcc (A 2)
Particle size ( $\mu\text{m}$ )	1.5	1 to 5
Specific area ( $\text{m}^2 \text{g}^{-1}$ )	1	1
Main impurity (p.p.m.)	Fe: 25 Si: 40 Mg: 5 Ti: 5	C: 300 O <sub>2</sub> : 5000 N <sub>2</sub> : 200 Substitutional impurity (sum total): 2000

(iii) The bond should resist oxidation in a way which preserves its initial properties under working conditions. This was not the case for a metal such as zirconium associated with alumina, as preliminary experiments have shown: indeed, a gradual oxidation creates excessive porosity, to such an extent that the bond is rapidly wrecked. Conversely, these preliminary experiments gave promising results for alumina combined with niobium or with titanium [12]. We chose to work with the latter metal, because of its more common industrial use [13–15].

(iv) Finally, as in a ceramic–metal bond diffusion phenomena must necessarily exist and lead to the formation of different phases, it is relevant to consider that equilibrium diagrams for titanium–oxygen and alumina–titanium oxide [16] were already relatively well known, which was likely to facilitate the interpretation of the results.

## 2. Experimental procedure

### 2.1. Materials used

The powders used for this study are given in Table I.

### 2.2. Diffusion couples

The phases appearing at the oxide/metal or oxide/cermet/metal interfaces were studied on samples prepared using a technique similar to that of multi-layer pressed powders. Different combinations (Mi)<sub>c</sub> (with increasing metal content) were first pressed ( $50 \text{ N mm}^{-2}$ ) into cylinders of diameter 10 mm and height 5 mm in a floating die; each sample was then inserted into the alumina powder; finally, these various (Mi)<sub>c</sub> + Al<sub>2</sub>O<sub>3</sub> combinations were pressed into cylindrical agglomerates of diameter 30 mm and height 30 mm under  $200 \text{ N mm}^{-2}$ .

These samples were then sintered at  $1450^\circ \text{C}$  for 12 h in a purified argon atmosphere. The diffusion zones were studied by optical micrography. Vickers microhardness measurements were systematically taken perpendicular to each interface. This gave data for a qualitative characterization of the diffusion zone.

### 2.3. Elaboration of cermets

Various Al<sub>2</sub>O<sub>3</sub>–Ti cermets were prepared from mixtures of the basic powders and pressed into  $5 \text{ mm} \times 5 \text{ mm} \times 20 \text{ mm}$  agglomerates under  $200 \text{ N mm}^{-2}$ . Dimensional changes due to densification were recorded by anisothermal dilatometry. Shrinkages were measured at different temperatures with the curve of the densified material as a reference in each case. For example, the curves in Fig. 1 show the evolution of Al<sub>2</sub>O<sub>3</sub>–50Ti agglomerates pressed without binder (curve a) or with 5% water added during the powder mixing (curve b). In both cases sintering was conducted in argon with a heating rate of  $500^\circ \text{C h}^{-1}$ . The dotted lines (curve a: after  $850^\circ \text{C}$ , curve b: after  $780^\circ \text{C}$ ) give the reference considered for the evaluation of shrinkage.

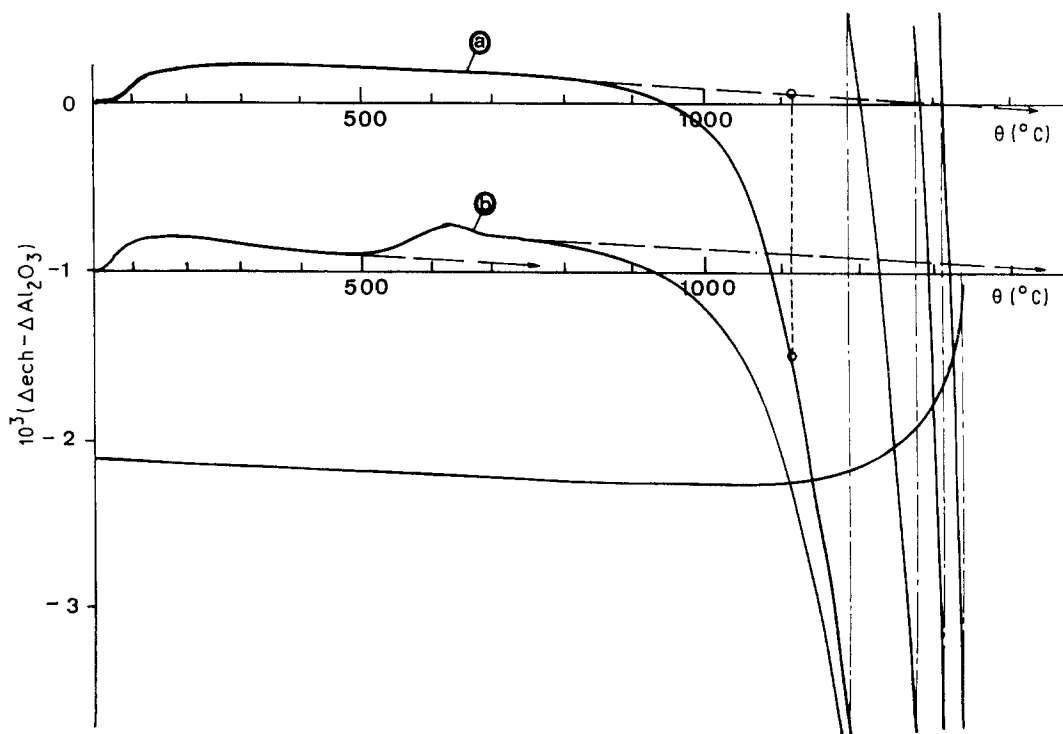


Figure 1 Influence of water addition on the anisothermal sintering of the (50Al<sub>2</sub>O<sub>3</sub>–50Ti) mixture. a, without binder; b, with 5% water added.

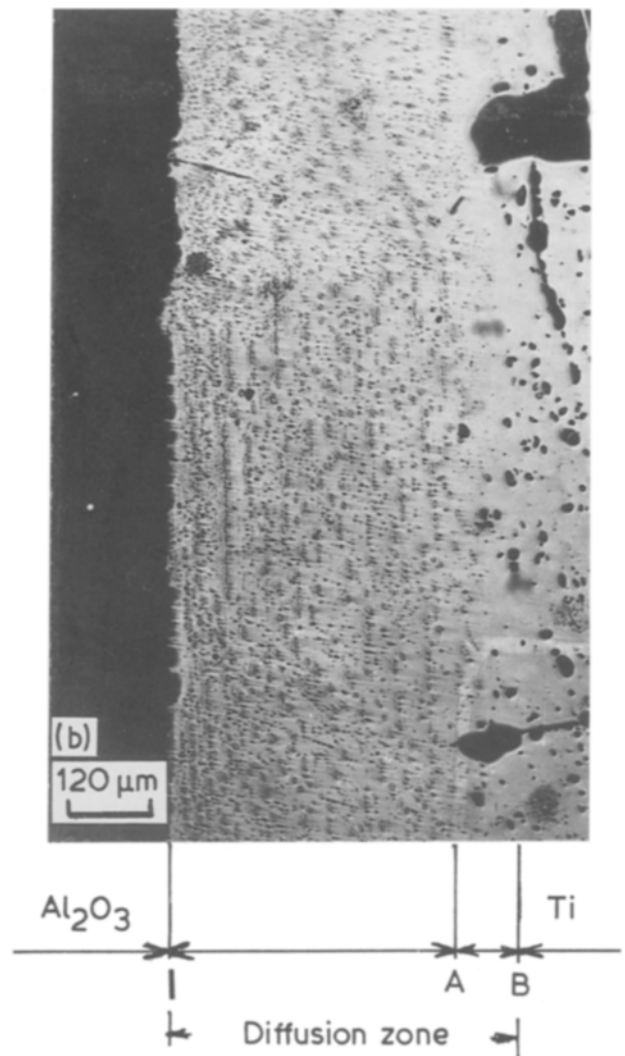
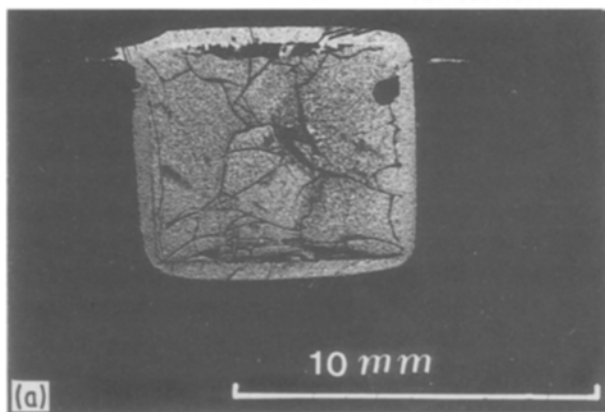


Figure 2 (a) Dense titanium inserted in alumina and treated for 12 h at 1450° C in argon; (b) magnification of the Ti/Al<sub>2</sub>O<sub>3</sub> interface ( $\times 100$ ).

### 3. Experimental results

#### 3.1. Al<sub>2</sub>O<sub>3</sub>/titanium diffusion couple

We used either solid titanium or an agglomerate from the above-mentioned powder pressed under 50 N mm<sup>-2</sup>. Fig. 2a shows the macrography of a sample prepared with solid titanium and treated for 12 h at 1450° C: a diffusion zone appears around the metal core. It should also be noticed that significant porosity and a few cracks developed in the titanium during the thermal treatment. Fig. 2b shows the structure of this diffusion zone. There is a slight stratification and a much lower porosity than in the metal core; furthermore, this porosity is much more evenly distributed. Porosity and cracks in the metal part are likely to be caused by diffusion phenomena, more specifically oxygen diffusion which weakens metal [17–20]. Fig. 3 shows that in the sintered alumina zone the microhardness (measured under a 10 g load) keeps a high and constant value of 1200 VPH; in the intermediate zone (with a higher porosity and cracks), the microhardness is only 300 VPH. Near the metal core its value is rather constant and equal to 1000 VPH. Indeed the two components are far from being combined and a moderate effort can bring out the

metal core. There is a very limited adherence to alumina.

When a titanium agglomerate is initially inserted in alumina powder similar, though less pronounced results are obtained (Fig. 4). In this case, however, there are no cracks at all in the metal core, and a clear lack of adherence between alumina and the intermediate layer has appeared, probably due to a greater sintering of the metal core.

These first experiments show that

- (i) Diffusion exists between the components of the Al<sub>2</sub>O<sub>3</sub>/Ti couple and a notable diffusion zone appears.
- (ii) Cracking develops in the metal core, because of the oxygen increase which weakens it.
- (iii) A lack of adherence appears between alumina and the sintered titanium core.

These results prove that a bond between metal and oxide cannot be obtained simply by joining these materials by thermal treatment. Consequently, a cermet (Al<sub>2</sub>O<sub>3</sub>-Ti) becomes necessary between alumina and titanium. Ideally this cermet would have a progressive titanium content from one interface (pure titanium) to the other (pure alumina). Obviously

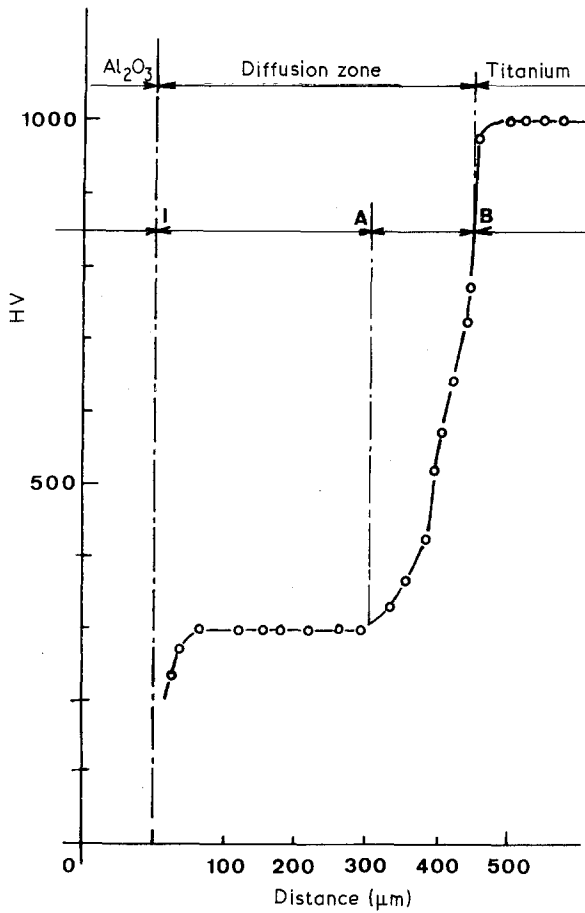


Figure 3 Microhardness change near the Ti/Al<sub>2</sub>O<sub>3</sub> interface.

this cannot be done in practice, and a multilayer sample was prepared.

### 3.2. Alumina/cermet/titanium diffusion couples

As mentioned above, a composite sample was made, with several layers of varying titanium content, as follows:

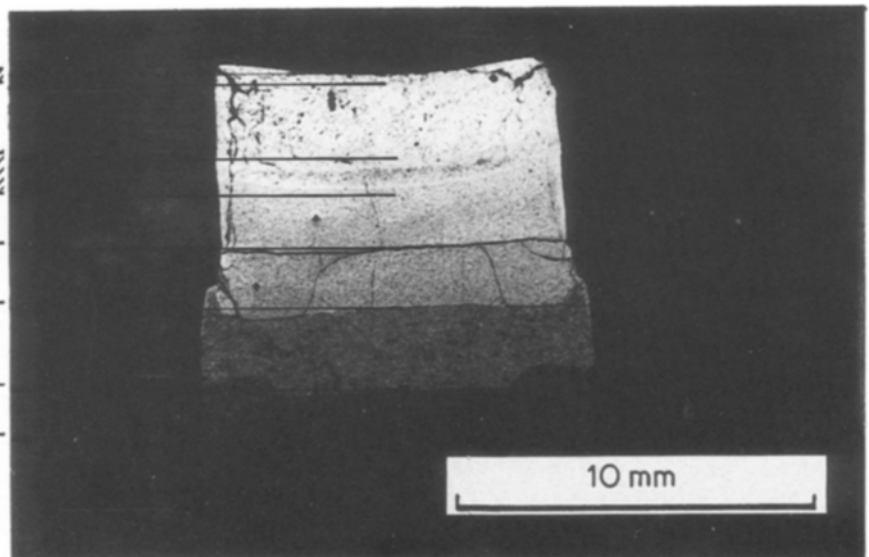
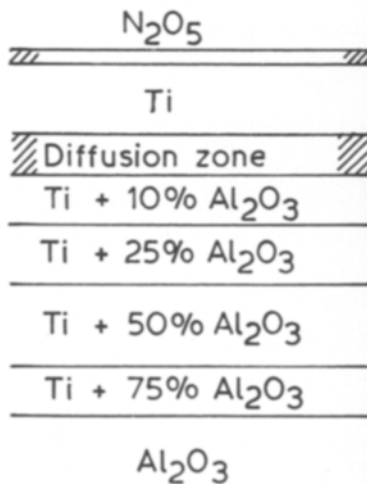
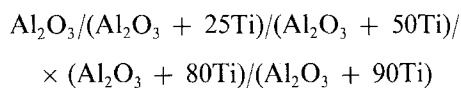


Figure 5 Multilayer sample with a significant gradient of titanium.

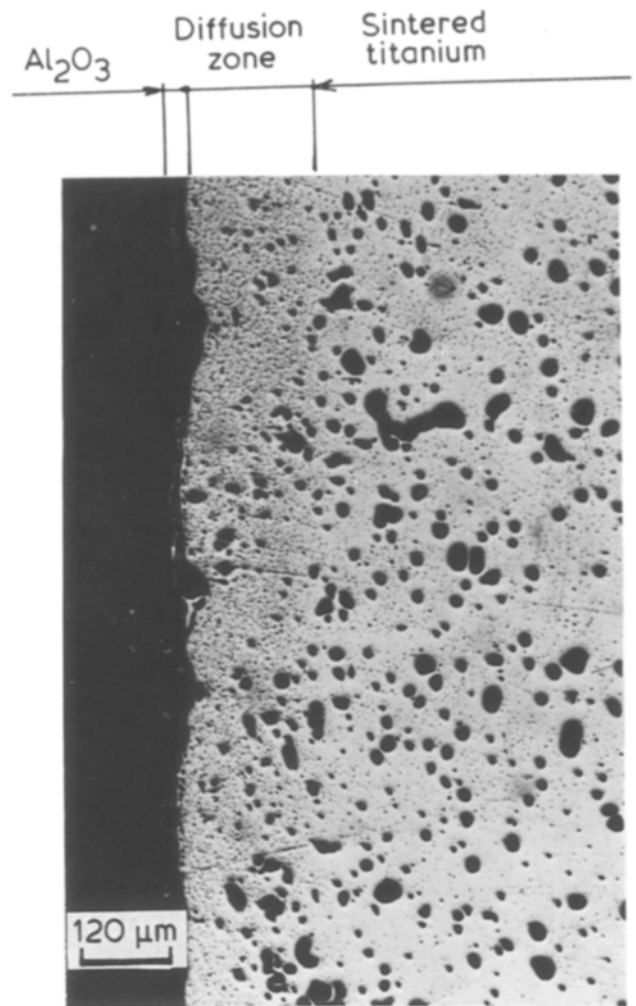


Figure 4 Ti/Al<sub>2</sub>O<sub>3</sub> interface after sintering (×100).

Fig. 5 gives the structure of the cross-section of such a sample treated for 12 h at 1450° C in argon. It mainly shows that adequate continuity in structure has been achieved through the various layers. However, in the middle section, compression stresses may not have been satisfactorily transmitted, thereby causing a lack of cohesion. The greater the local titanium content,

Figure 6 ( $\text{Al}_2\text{O}_3 + 25\% \text{Ti}$ )/Ti interface ( $\times 100$ ).

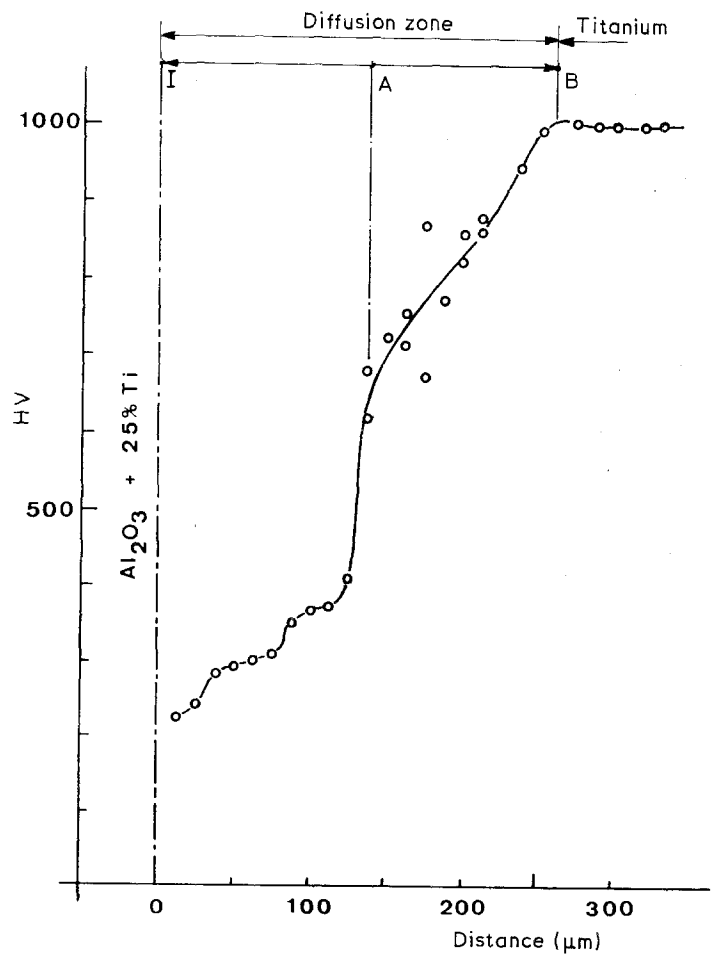
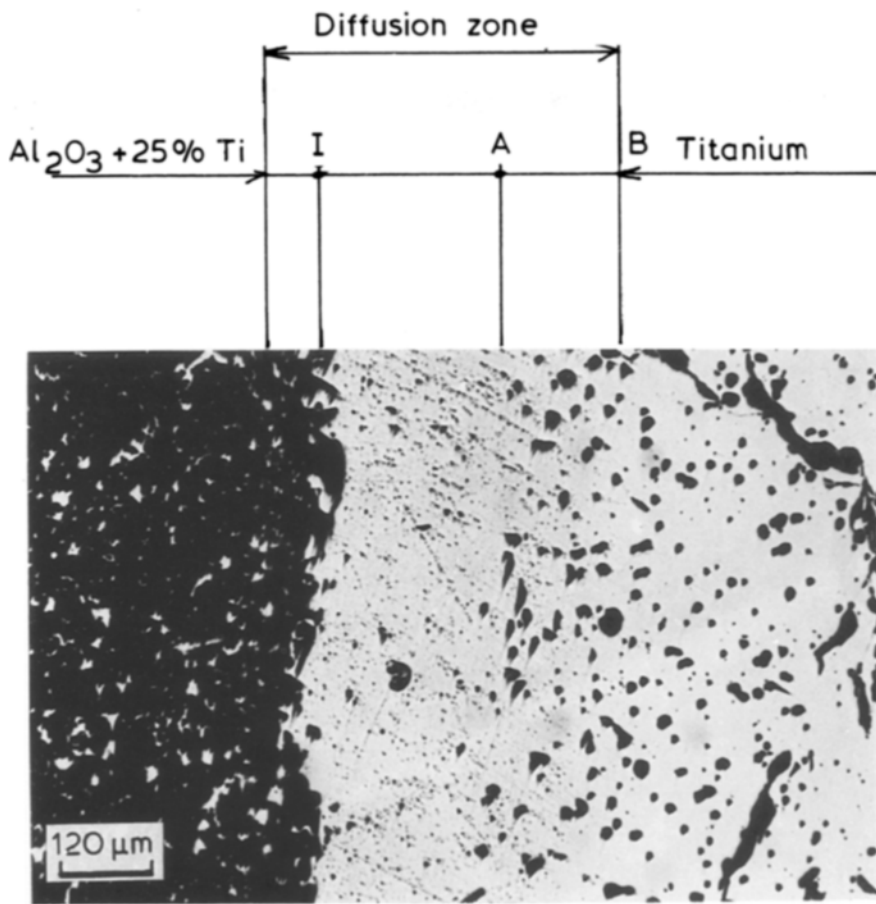


Figure 7 Microhardness change near the ( $\text{Al}_2\text{O}_3 + 25\% \text{Ti}$ )/Ti interface.

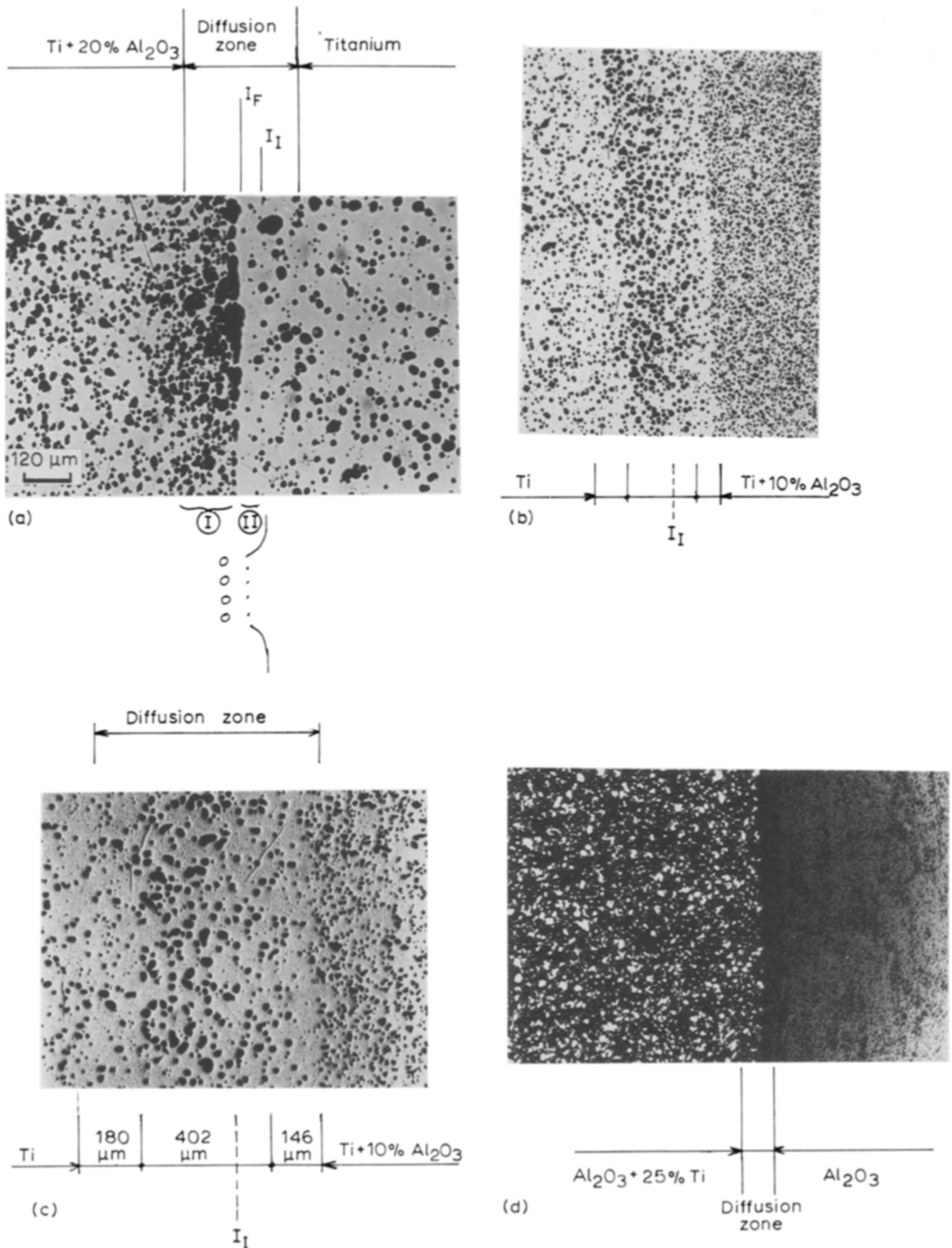


Figure 8 Structural aspect of diffusion zones in various couples: (a) (Ti + 20Al<sub>2</sub>O<sub>3</sub>)/Ti ( $\times 35$ ), (b) (Ti + 10Al<sub>2</sub>O<sub>3</sub>)/Ti ( $\times 35$ ), (c) (Ti + 10Al<sub>2</sub>O<sub>3</sub>)/Ti ( $\times 70$ ), (d) (Al<sub>2</sub>O<sub>3</sub> + 25Ti)/Al<sub>2</sub>O<sub>3</sub> ( $\times 50$ ).

the better the densification; no sign of lack of cohesion was observed. It is also likely that the initial interface between the cermet with the highest titanium content and alumina has shifted during the thermal treatment (this will be discussed later).

We then analysed on a finer scale various titanium/(Al<sub>2</sub>O<sub>3</sub> + xTi) interfaces. Fig. 6 corresponds to a sample in which  $x = 25\%$  Ti. There is a definite

change of porosity beyond the linking zone between the two components: high porosity in the sintered titanium zone, very low porosity in the central zone (which suggests a Kirkendall effect), while there is an intermediate porosity in the cermet region. There seems to be already a continuous structure for this relatively limited titanium content in the cermet.

The microhardness curve with measurements taken

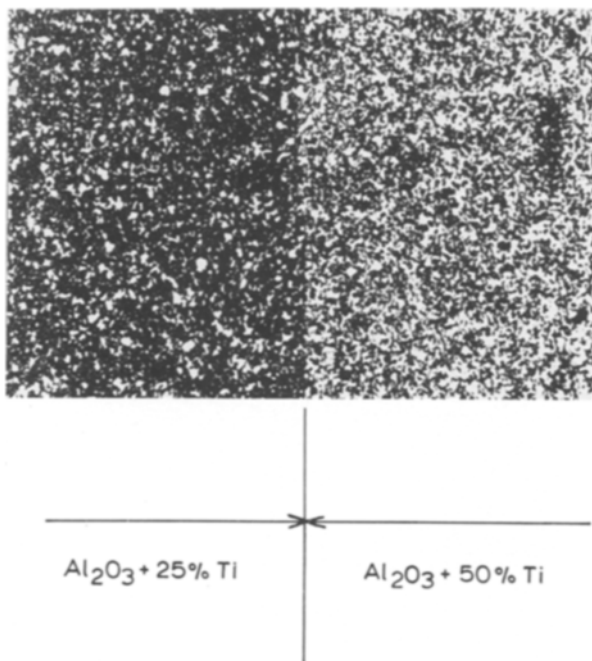


Figure 9  $(\text{Al}_2\text{O}_3 + 25\text{Ti})/(\text{Al}_2\text{O}_3 + 50\text{Ti})$  interface ( $\times 35$ ).

from the area corresponding to the cermet (Fig. 7) is slightly different from that corresponding to  $\text{Ti}/\text{Al}_2\text{O}_3$  (Fig. 3). Indeed there is a regular increase as far as about  $150\ \mu\text{m}$  from the initial interface; beyond, the change in hardness becomes meaningful, between  $150$  and  $250\ \mu\text{m}$ :  $1000\ \text{HV}$  is reached at  $250\ \mu\text{m}$  which characterizes the metal part of the couple. This change in hardness suggests that solid solutions of variable compositions may have formed, or even compounds.

Further examination of the structure of the diffusion zones between titanium and relatively titanium rich mixtures gave further data. In Fig. 8a, where  $x = 80\%$  Ti, the porosity is slightly higher for the  $(\text{Al}_2\text{O}_3 + \text{Ti})$  portion and definitely higher very near the diffusion zone (Zone I); however, it comes close to zero in the next thin layer (Zone II). This is again obviously linked to a Kirkendall effect which will be examined below.

For  $x = 90\%$  Ti (Figs 8b and c) there is a continuity between the two layers. However, this continuity seems to come from an intermediary diffusion zone of about  $400\ \mu\text{m}$  with a marked porosity (greater than on the titanium side). This central zone is bordered by two quasi-pore-free bands of about  $150\ \mu\text{m}$ .

We also examined some  $\text{Al}_2\text{O}_3/(\text{Al}_2\text{O}_3 + x\text{Ti})$  interfaces. For example, in Fig. 8d  $x = 25\%$  Ti; the bond shows a good continuity and a homogeneous porosity in the combined materials zone (the lighter phase is for titanium). When  $x = 50\%$  Ti the results are similar, with a greater proportion of lighter phase. When two mixed combinations are chosen, continuity between the two components is also easily achieved. Fig. 9 shows an  $(\text{Al}_2\text{O}_3 + 25\text{Ti})/(\text{Al}_2\text{O}_3 + 50\text{Ti})$  couple.

Finally, these various experiments show that a good continuity of structure can be obtained, on the one hand between  $(\text{Al}_2\text{O}_3 + x\text{Ti})$  and titanium or alumina, and on the other hand between cermets of various titanium content. To simplify the procedure, we then verified that only one cermet (for example  $\text{Al}_2\text{O}_3 + 25\text{Ti}$ ) was necessary between the two initial components (as in Fig. 10). If we then consider the elaboration conditions of these cermets, we are led to study in detail the sintering behaviour of agglomerates initially constituted of a mixture of alumina and titanium powders, the metal content remaining below  $60\ \text{wt}\ \%$ .

#### 4. Sintering behaviour of alumina-titanium cermets

Experiments were made by anisothermal dilatometry, with agglomerates which were uniaxially pressed from various mixtures. These mixtures were either prepared dry or with a  $5\%$  water content for easier pressing. They were sintered in a static argon atmosphere. The actual treatment atmosphere remained dry for agglomerates without addition, whereas it was obviously wet argon in the latter case. With the results of the comparison between these two processes we were able

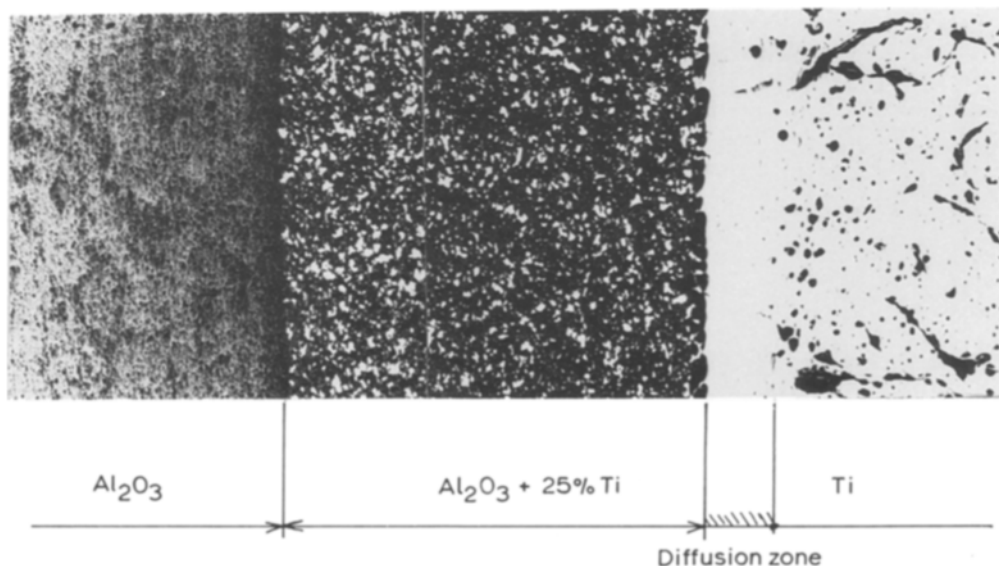


Figure 10 Bonding between  $\text{Al}_2\text{O}_3$  and titanium through an intermediate cermet  $(\text{Al}_2\text{O}_3 + 25\text{Ti})$ .

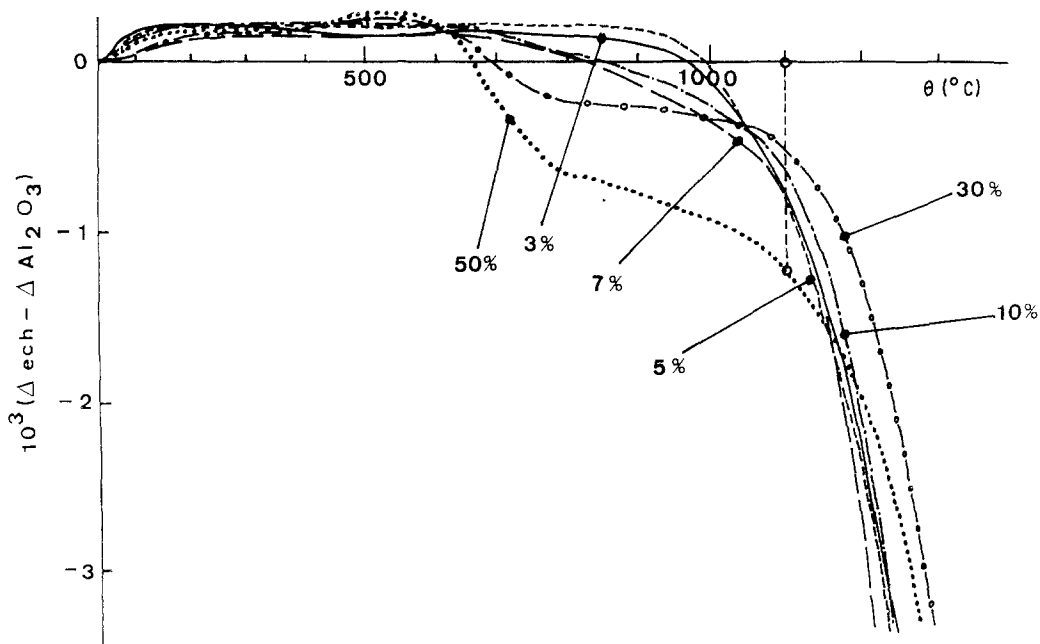


Figure 11 Dilatometric curves recorded from mixtures with different amounts of titanium (in dry argon).

to determine whether water vapour was or was not likely to have a noticeable influence on sintering.

#### 4.1. Sintering in dry argon

Fig. 11 corresponds to cermet with titanium contents ranging from 3 to 50 wt %. Anisothermal shrinkage curves show that for a titanium content of a maximum of 10 wt %, only the initial sintering temperature change is to be noticed. However, for a greater metal content there is a first (relatively limited) contraction between 650 and 950°C, while most of the shrinkage takes place above 1100°C: the first contraction must obviously be linked to an early sintering of the metallic particles. Fig. 12 shows the variations of shrinkage at 1100 and 1350°C: it can be seen that at 1100°C shrinkage is not linked to titanium content, whereas at 1350°C it tends to decrease as the metal content increases.

#### 4.2. Sintering in wet argon

Fig. 13 is for cermets with a titanium content of 3, 6, 9, 30 and 50 wt %. The continuous line corresponds to the alumina base. For this type of atmosphere the initial sintering temperature of the cermet always depends, to some extent, on the titanium content: the higher the content, the lower the temperature.

The shrinkage variation curves for 1100 and 1350°C (Fig. 14) show that the influence of titanium remains small at the lower temperature, at least for a titanium content of 9% maximum. However, this influence is noticeable at 1350°C: on the one hand, the shrinkage varies between 3 and 6% titanium contents, and on the other hand it increases when the titanium content is higher than 10%. In addition, the shrinkage for samples sintered in wet argon is definitely more important than in dry argon.

In addition, the shrinkage curves of Fig. 13 show,

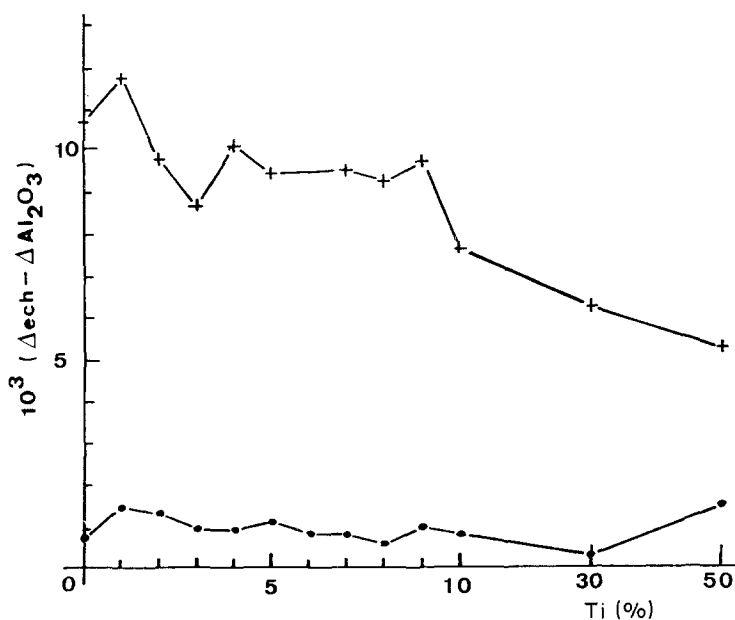


Figure 12 Shrinkage change at (●) 1100 and (+) 1350°C from  $(Al_2O_3 + 25Ti)$  agglomerates sintered in dry argon.



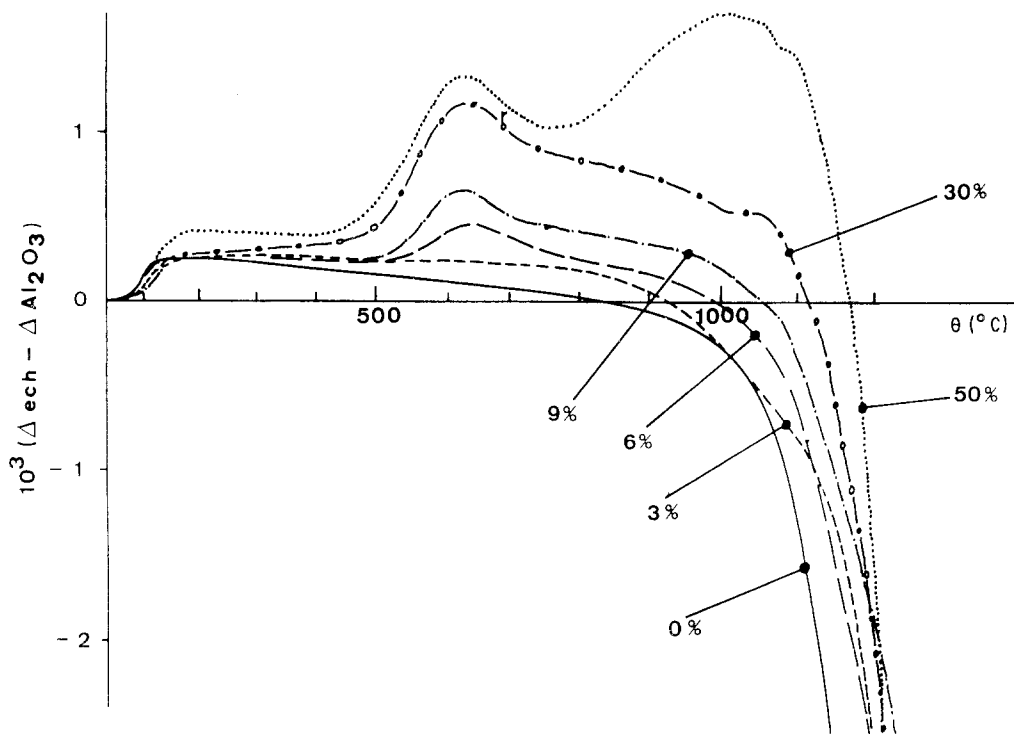


Figure 13 Dilatometric curves relative to agglomerate with different titanium content, sintered in wet argon.

between 500 and 700°C, a clear expansional anomaly in amplitude, which is all the more important as the metal content is high. To confirm the influence of titanium we recorded anisothermal dilatometric curves for pure titanium agglomerates pressed either from

dry powder, or from powders with 10% water content, then dried at 110°C. The results (Fig. 15) clearly show that titanium reacts with water vapour from about 450°C and that there is a swelling of the agglomerate up to about 600°C. The shrinkage variations

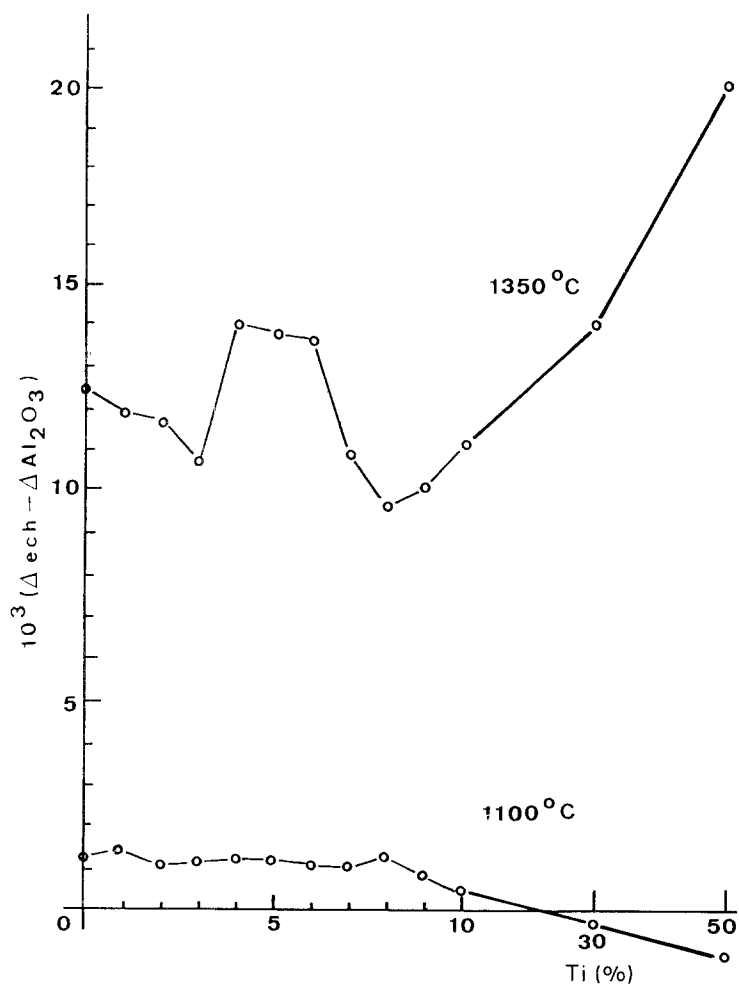


Figure 14 Shrinkage change at (O) 1100 and 1350°C from  $(Al_2O_3 + xTi)$  agglomerates sintered in wet argon.

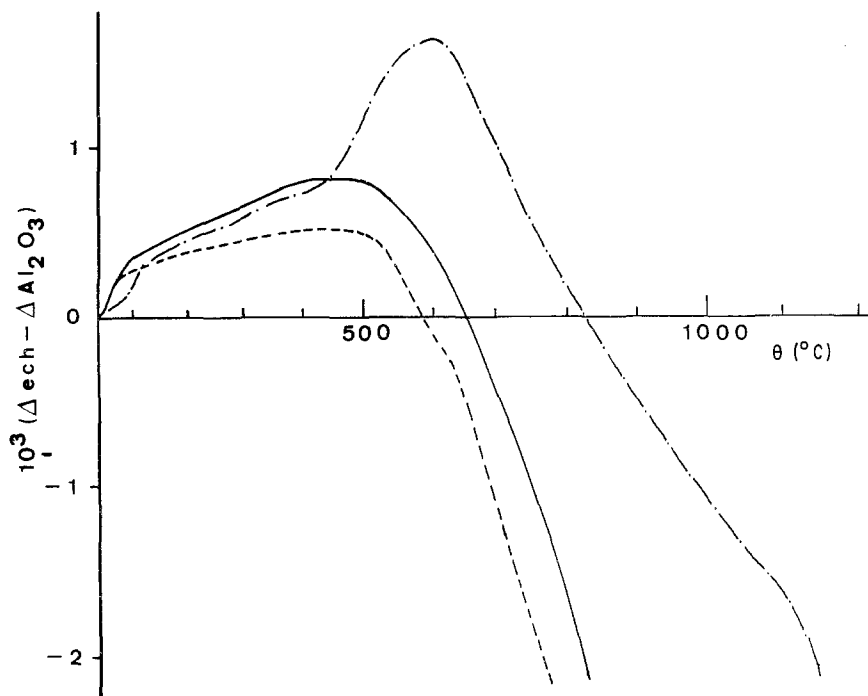


Figure 15 Influence of water vapour on the sintering of titanium in argon: (—) no water; (---) 10% water; (- - -) 10% water, then dried.

above 600°C are similar for agglomerates with no more water. For the wet titanium powder, the densification takes place more gradually.

These experiments lead to the conclusion that titanium does cause the expansional anomaly observed between 450 and 600°C during the sintering of cermets in wet argon. The nature of the phenomena appearing in the above-mentioned conditions must now be determined, as well as their influence on further sintering of the cermets.

#### 4.3. X-ray studies

Various measurements were done on samples treated at 1450°C for 12 h in dry or wet argon. For samples treated in dry argon the patterns (Fig. 16a) show no reaction between alumina and titanium. Conversely, after treatment in wet argon (Fig. 16b), the patterns show lines which are distinct from those of alumina and titanium, and appear for Bragg angles related to the diffraction from  $TiO_2$  and  $Al_2TiO_5$  compounds (Table II).

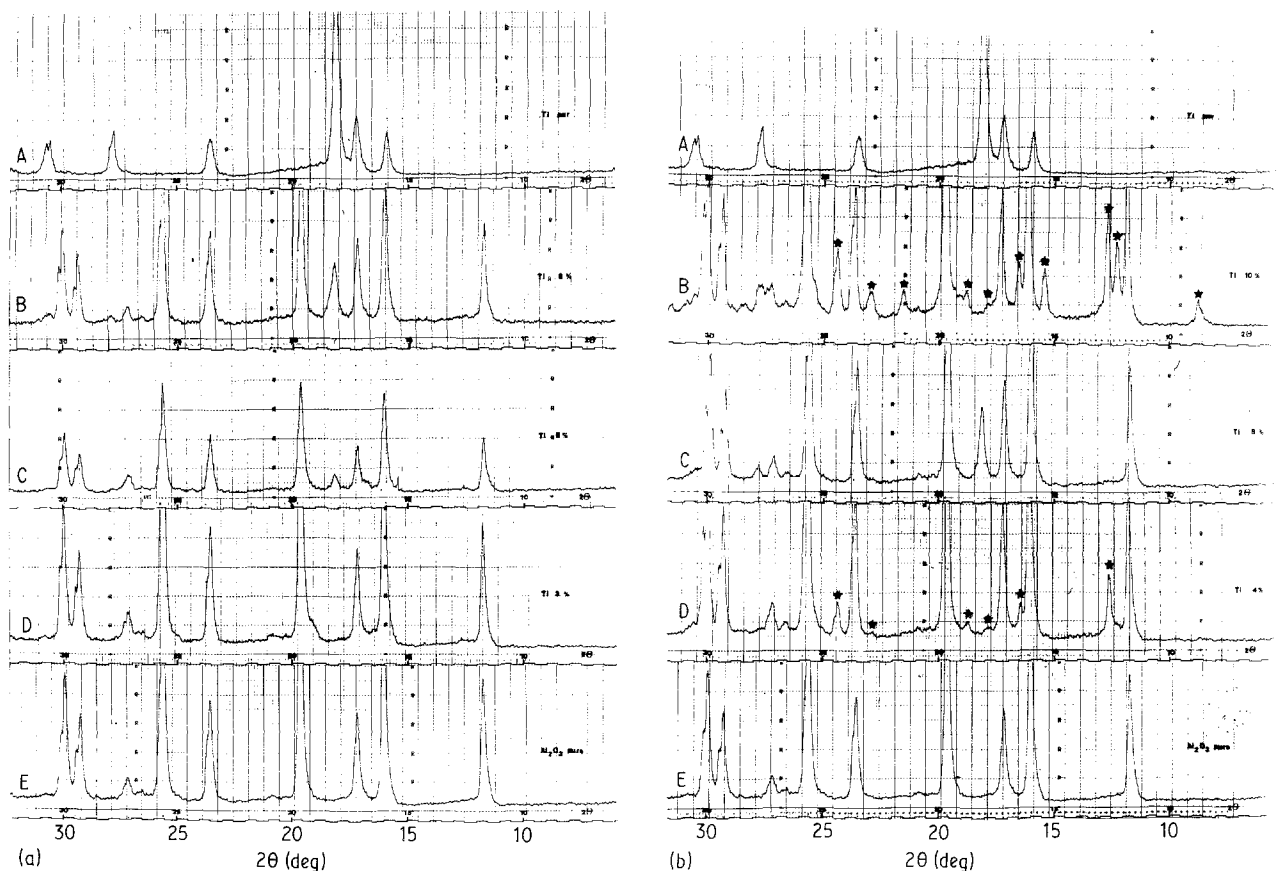


Figure 16 Diffraction patterns recorded from samples with different concentrations in titanium. (a) In dry argon: (A) pure titanium, (B) 9% Ti, (C) 6% Ti, (D) 3% Ti, (E) pure  $Al_2O_3$ . (b) In wet argon: (A) pure titanium, (B) 10% Ti, (C) 8% Ti, (D) 4% Ti, (E) pure  $Al_2O_3$ .

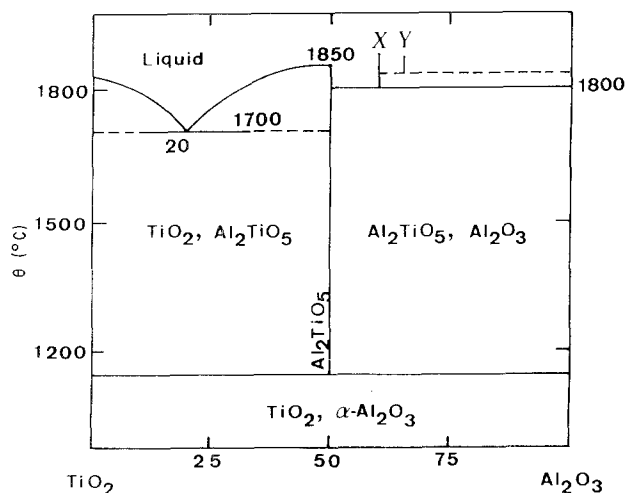


Figure 17  $\text{Al}_2\text{O}_3$ - $\text{TiO}_2$  phase diagram.

These compounds may actually have formed one after the other: indeed  $\text{TiO}_2$  oxide can come from the reaction between titanium and water vapour [21], from 500 to 650°C according to the reaction  $\text{Ti} + 2\text{H}_2\text{O} \rightarrow \text{TiO}_2 + 2\text{H}_2$ . Titanium oxide can then combine with alumina at more than 1100°C, as shown by the equilibrium phase diagram in Fig. 17 [16] to form  $\text{Al}_2\text{TiO}_5$  according to the reaction  $\text{Al}_2\text{O}_3 + \text{TiO}_2 \rightarrow \text{Al}_2\text{TiO}_5$ .

The difference in shrinkage for cermets sintered in dry or wet argon (Figs 12 and 14) clearly shows the influence of the  $\text{Al}_2\text{TiO}_5$  phase formation on their sintering capacity for temperatures of 1350°C or above. Cermets sintered in wet argon seem to have a higher densification capacity, particularly for titanium contents above 10 wt %.

#### 4.4. Discussion

There are several consequences to these results.

(a) First, it should be clear that a good bonding between alumina and titanium cannot be directly achieved. Interdiffusion between these two materials,

TABLE II Bragg spacings of compounds

$\text{Al}_2\text{O}_3 + 9\% \text{Ti}$		$\text{Al}_2\text{TiO}_5$		$\text{TiO}_2$	
$d$ (nm)	$I/I_0$	$d$ (nm)	$I/I_0$	$d$ (nm)	$I/I_0$
0.4673	28	0.4728	80		
0.3336	40	0.3361	80		
0.3230	100			0.3238	100
0.2663	28	0.2654	100		
0.2485	24			0.2484	40
0.2291	20			0.2292	7
0.2170	36	0.2144	60		
0.1909	24	0.1900	50		
0.1786	20	0.1786	30		
0.1684	80	0.1678	30	0.1683	50
0.1622	40	0.1600	100		

when they are directly associated, leads to a local cracking or to some decohesion. For a couple  $\text{Al}_2\text{O}_3$ /(sintered titanium) this phenomenon essentially comes from the different densification rate of the two materials during sintering. To avoid this an  $(\text{Al}_2\text{O}_3 + x\text{Ti})$  cermet seems necessary in between the two materials.

(b) The previous study showed that for a content  $x$  of the metal component between 20 and 50% a satisfactory continuity could be achieved, on the one hand between alumina and cermet, and on the other between cermet and titanium. However, if an  $(\text{Al}_2\text{O}_3 + x\text{Ti})$  cermet is to be placed in between alumina and titanium, the interface zone cermet/titanium should be checked for possible damaging phenomena. We have already mentioned the formation of intermediate zones with a low porosity (always much lower than in the metal core: see Fig. 6 for the  $(\text{Al}_2\text{O}_3 + 25\text{Ti})/\text{Ti}$  couple). Such zones may be lined on the cermet side by zones with a high pore density (see Fig. 8a for the  $(\text{Al}_2\text{O}_3 + 80\text{Ti})/\text{Ti}$  couple).

(c) We suggested before that this behaviour could be linked to a Kirkendall effect. A comparison of Figs 2b, 6 and 8a to c shows that a change in the titanium gradient does not suggest a dominant role for this element. One of the alumina components seems more

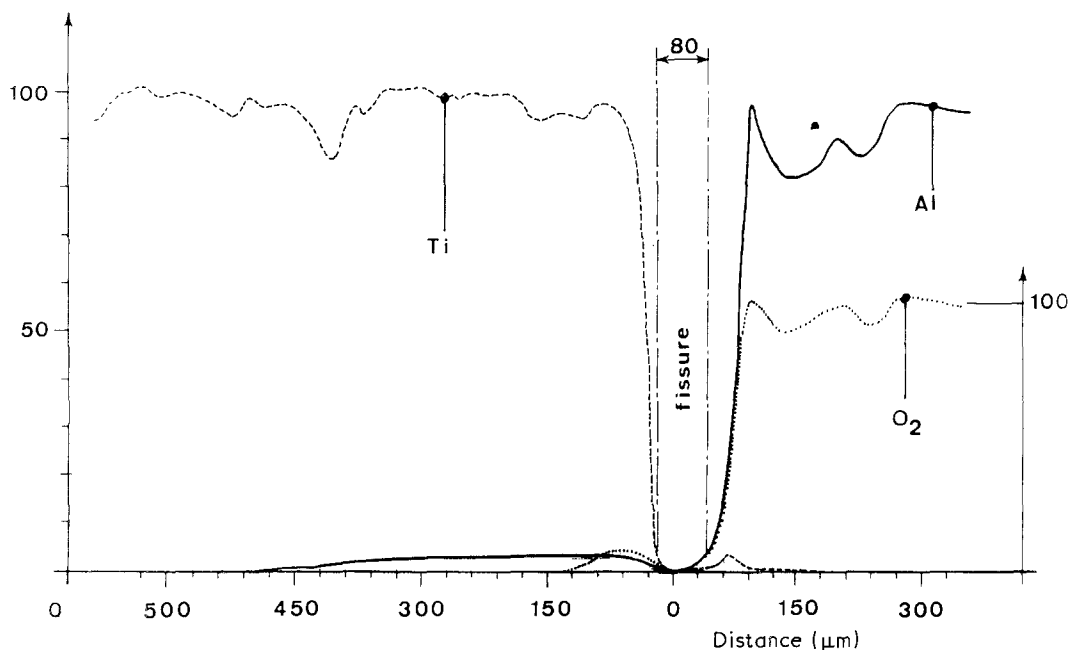


Figure 18 Microanalysis near the  $\text{Ti}/\text{Al}_2\text{O}_3$  interface.

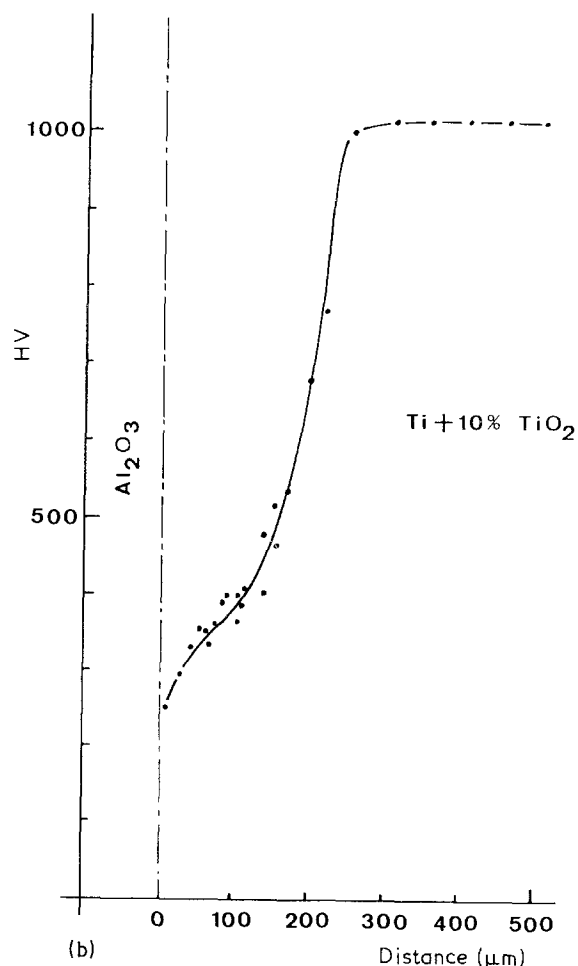
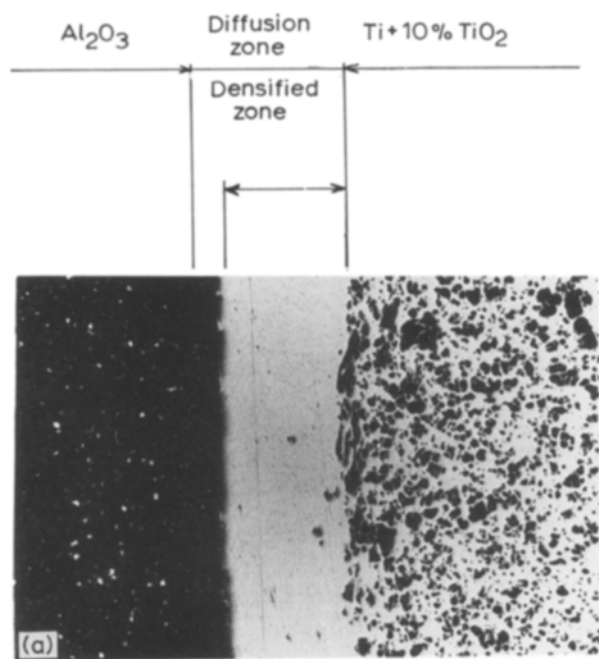


Figure 19 (a)  $\text{Al}_2\text{O}_3/(\text{Ti} + \text{TiO}_2)$  interface ( $\times 35$ ); (b) microhardness change near this interface.

likely to control the process. We can suppose that if titanium atoms come in substitution in the alumina cell, they must increase the number of aluminium vacancies and make for an easier diffusion of this element. At the same time, there would be a decrease of the oxygen vacancies [22] and hence a slower diffusion of this latter element.

(d) To confirm this hypothesis we determined the variations of the titanium, aluminium and oxygen content through a microprobe analysis along a perpendicular to the  $\text{Ti}/\text{Al}_2\text{O}_3$  interface (couple treated at  $1450^\circ\text{C}$  in argon for 12 h); Fig. 18 gives the results. There are three main points:

(i) titanium atoms do replace aluminium ones, diffusion taking place on about  $100\ \mu\text{m}$ ;

(ii) aluminium atoms diffused for about  $450\ \mu\text{m}$  into titanium; however, the aluminium content remains low at around 4%;

(iii) oxygen atoms diffused into titanium for a distance of about  $100\ \mu\text{m}$ , the oxygen content being low (around 2%).

Thus, the previous hypothesis is confirmed. Nevertheless, to be really sure of the nature of the process, we prepared an  $\text{Al}_2\text{O}_3/(\text{Ti} + 10\% \text{TiO}_2)$  diffusion couple (with  $\text{TiO}_2$  in its rutile form) that we treated at  $1450^\circ\text{C}$  for 12 h in argon. Fig. 19a shows that a densified zone of thickness of about  $200\ \mu\text{m}$  forms with, on the alumina side, a thin ( $5\ \mu\text{m}$ ) but porous zone giving decohesion between the two portions. In addition, the

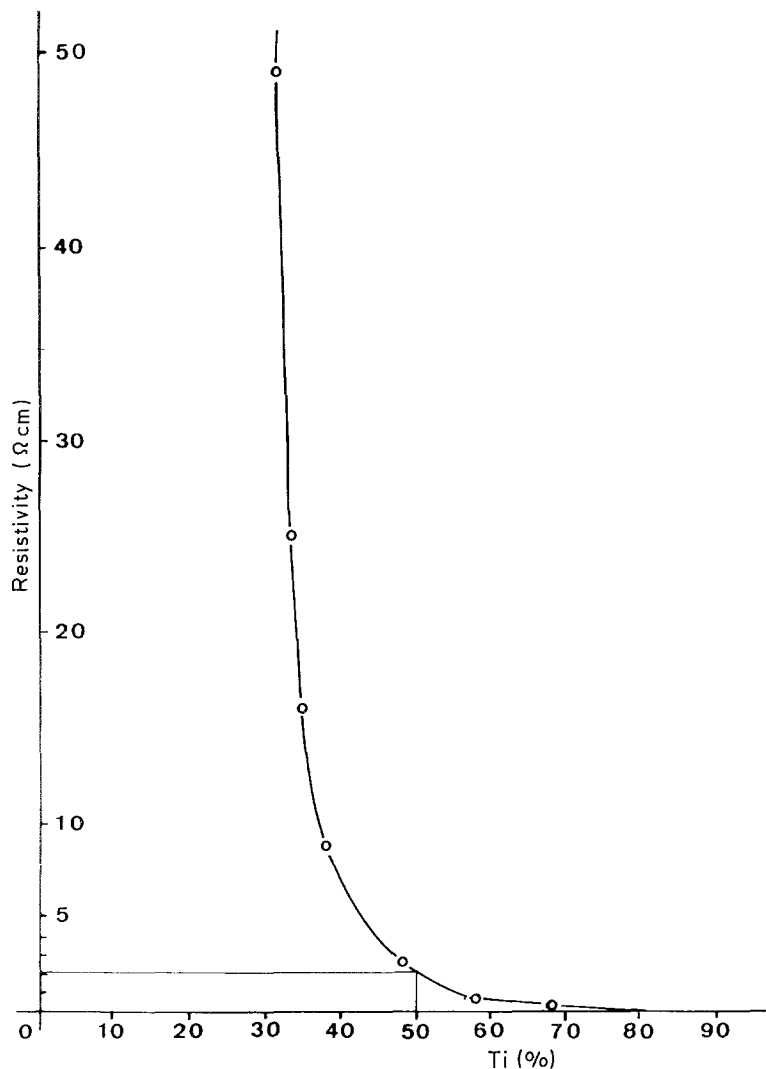
( $\text{Ti} + \text{TiO}_2$ ) part has a high porosity which shows that the sintering of the titanium powder has been incomplete because of the high quantity of oxide added. Measurements in the diffusion zone (Fig. 19b) show that the microhardness changes progressively. We can conclude from these experiments that there is a Kirkendall effect in the alumina/titanium couples, the main cause being the aluminium atom. This effect remains rather limited and has no really severe consequences as to the cohesion of the ceramic metal bond, providing that the influence of the aluminium gradient is minimized through an  $(\text{Al}_2\text{O}_3 + x\text{Ti})$  cermet and that the number of aluminium vacancies does not increase too much (it would facilitate excessively the aluminium diffusion), which means that  $x$  values should not be too high.

(e) The sintering behaviour of  $\text{Al}_2\text{O}_3/\text{Ti}$  cermets has demonstrated the influence of the composition and of the sintering atmosphere; more specifically, the water vapour in argon greatly facilitates densification at high temperatures ( $1350^\circ\text{C}$ ). X-ray studies showed that stable compounds such as  $\text{Al}_5\text{TiO}_5$  and  $\text{TiO}_2$  appear. These phases result from titanium oxidation caused by water vapour, followed by a titanium oxide reaction to alumina giving the  $\text{Al}_5\text{TiO}_5$  compound. Titanium oxide, at least when in limited quantity, notably increases alumina densification [23].

## 5. Conclusions

In this study we considered the possible formation of

Figure 20 Resistivity changes in (Al<sub>2</sub>O<sub>3</sub> + Ti) cermet with different titanium contents.



a bond between a ceramic (Al<sub>2</sub>O<sub>3</sub>) and a metal (titanium) without either a vitreous phase nor a liquid phase on the interface of the two components, at any time during the heat treatment.

1. We first concluded that a direct bonding of these two materials would be very unsatisfactory. We managed to obtain good bonding through an (Al<sub>2</sub>O<sub>3</sub> + xTi) cermet placed between the two initial materials.

2. Diffusion tests with Al<sub>2</sub>O<sub>3</sub>/Ti or (Al<sub>2</sub>O<sub>3</sub> + xTi)/Ti couples have shown the appearance of densified layers in the diffusion zone. They are the result of the three components involved (aluminium, oxygen, titanium) which locally can also form solid solutions or the Al<sub>2</sub>TiO<sub>5</sub> compound. A study of the influence of the titanium content in the cermet between ceramic and metal led us to determine values of the  $x$  range giving an appropriate continuity (10 to 25 wt %).

3. Measurements by microprobe have shown that the mobility of the Al<sup>3+</sup> ion has a predominant influence in the process leading to the bonding.

4. The nature of the sintering atmosphere plays an important role in the sintering capacity of (Al<sub>2</sub>O<sub>3</sub> + xTi) cermets. A slightly wetted argon atmosphere facilitates the formation of TiO<sub>2</sub> oxide and that of the Al<sub>2</sub>TiO<sub>5</sub> compound as well as the densification of the samples.

In a prospective way, we also considered one of the properties of the (Al<sub>2</sub>O<sub>3</sub> + xTi) cermets. To this end

we measured their electrical resistance, one of the properties which is interesting in these materials. The results, according to the added percentage of titanium, are shown in Fig. 20: the resistivity increases from 2.5 to 50 Ω cm when the titanium content varies from 50 to 30 wt %. For a lower amount, the resistivity suddenly becomes very high and could not be measured precisely with the simple method used.

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