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Synthesis reaction of metatitanate $BaTiO_3$

Part 2 *Study of solid–solid reaction interfaces*

A. BEAUGER, J. C. MUTIN, J. C. NIEPCE
*Laboratoire de Recherches sur la Réactivité des Solides, Associé au CNRS, BP 138,
21004 Dijon Cédex, France*

The macroscopic reproduction of the various solid–solid interfaces expected in the synthesis of $BaTiO_3$ from $BaCO_3$ and TiO_2 enabled us to describe the reaction stages in visualizing the diffusion of the entities concerned as well as the domains undergoing transformation. The following results were established or confirmed. (a) Firstly, metatitanate $BaTiO_3$ forms at the expense of TiO_2 by diffusion of barium from $BaCO_3$. (b) Secondly, orthotitanate Ba_2TiO_4 forms at the expense of the $BaTiO_3$ layer by diffusion of barium from $BaCO_3$. (c) Finally, the orthotitanate is converted into $BaTiO_3$ releasing an unidentified species of BaO stoichiometry which diffuses towards TiO_2 through $BaTiO_3$ to form $BaTiO_3$.

1. Introduction

An earlier paper has shown [1] that the synthesis reaction of barium metatitanate $BaTiO_3$ from a powder mixture of barium carbonate $BaCO_3$ and of titanium oxide TiO_2 results from a more or less complex sequence of chemical solid-state reactions. According to this paper and the work of Kubo *et al.* [2], Templeton and Pask [3], Nakayama and Sasaki [4] and Suyama *et al.* [5] the reaction, when it occurs in air, may be broken down into three basic stages.

1. Firstly, formation of $BaTiO_3$ by reaction between $BaCO_3$ and TiO_2 at the expense of TiO_2.
2. Secondly, formation of Ba_2TiO_4 by reaction $BaCO_3$ with the prior-formed metatitanate and at its expense.
3. Finally, destruction of Ba_2TiO_4 leading back to $BaTiO_3$.

This process implies the occurrence of several solid–solid interfaces between both precursor grains whose relative positions might be those proposed in Fig. 1. Experimentally, to our knowledge, only the formation of $BaTiO_3$ at the expense of TiO_2 has been put forward [4, 5]. The formation of Ba_2TiO_4 at the expense of $BaTiO_3$ is proposed and its destruction has not been considered. To verify this assumption the location of the various phases in microstructures during reaction should be shown. As the investigation cannot be carried out on monocrystals, the various interfaces were macroscopically reproduced by superposing the pellets from the four solid phases considered during the calcining, $BaCO_3$, TiO_2, $BaTiO_3$ or Ba_2TiO_4.

2. Experimental details

2.1. Samples

Three types of samples designated A, B or C, in which the main solid–solid interfaces are reproduced were prepared from the four above phases. The first three ($BaCO_3$, TiO_2 and $BaTiO_3$) were marketed materials. The orthotitanate was prepared according to the following reaction $BaCO_3 + BaTiO_3 \rightarrow Ba_2TiO_4 + CO_2$ the mixture of barium carbonate and titanate was heated to about 1100° C under argon flow to obviate carbon dioxide.

The powders from these four phases to which a binder was added were pelleted to the required size. The $BaTiO_3$ pellets were sintered at 1400° C, those of titanium oxide and of orthotitanate at 1100° C. It should be noted that in the case of the orthotitanate sintering must also be performed under argon flow. In the case of $BaCO_3$, pellets were not heated above 900° C to obviate fusion.

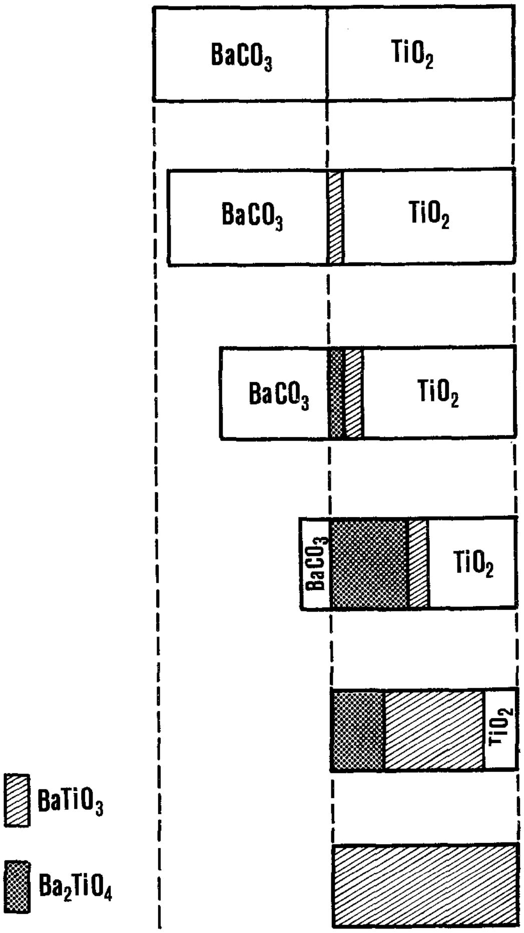

Figure 1 Diagrammatic representation of the composition of $BaCO_3$ and TiO_2 grains at various stages of calcination. The areas are proportional to the respective amount of the four phases present.

Samples A, B and C were obtained by making piles of those various pellets (Fig. 2). The different pellets making up a single sample were always of different diameter to facilitate the detection of the changes due to interface reactions.

2.2. Sample treatment

The various samples were placed into a tubular furnace heated to the appropriate temperature. The treatment was carried out in the air, a condition of industrial calcining, for times between a few hours and a few days.

Samples A and B contained $BaCO_3$; they were not heated to above 900° C to obviate fusion of the pellet of $BaCO_3$, which would have complicated further investigations. It has been shown [1] that treatment time does not seem to change the reaction process, and only affects the reaction rate.

2.3. Characterization of samples after treatment

After treatment the pellets were readily separated, which allowed X-ray diffraction analysis of contact surfaces.

The observation of the various samples by optical and scanning electron microscopy was made both at the surface of the ceramics and along cross-sections. The sections were obtained by cutting samples A, B or C mounted in a resin which will often appear in the micrographs as a rather homogeneous layer between the two ceramic surfaces initially in contact.

After polishing the sections, it was possible to perform the qualitative and quantitative elementary analysis of barium and titanium by electron probe microanalysis (EPMA).

This study allowed, in addition to following the migration of the diffusing elements, the phases $BaTiO_3$ and Ba_2TiO_4 to be distinguished. This distinction was made possible by titanium spectra; indeed, in $BaTiO_3$, the volume concentration in titanium is twice that in Ba_2TiO_4.

3. Results

Three solid–solid interfaces retained our attention: $BaCO_3$–TiO_2, $BaCO_3$–$BaTiO_3$ and Ba_2TiO_4–$BaTiO_3$. The transformation observed in these cases will be reported below. According to Fig. 1 two other solid–solid interfaces are present

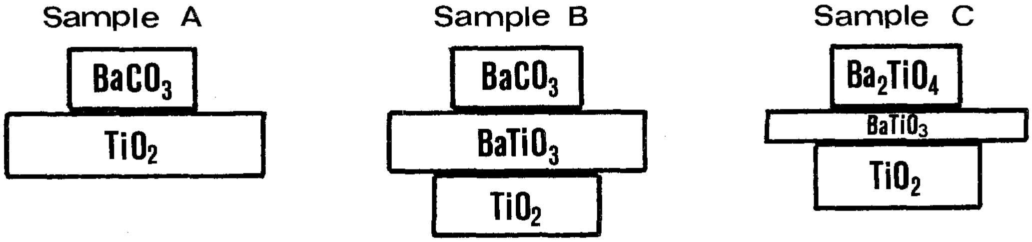

Figure 2 Diagrammatic representation of the stacking of the various reaction couples constituting samples A, B and C.

during the reaction, $BaCO_3$–Ba_2TiO_4 for which no particular investigation was performed, and $BaTiO_3$–TiO_2 for which the results will be reported in the discussion.

3.1. Study of the $BaCO_3$–TiO_2 interface (samples A)

In sections of sample A which has been heated at 750° C for short times (less than one hour), a layer is observed within the TiO_2 pellet near the interface (Fig. 3). The layer is made up of metatitanate $BaTiO_3$.

With longer treatment times at the same temperature, two layers are observed within the ceramics of TiO_2 (Fig. 4). The inner layer, in contact with TiO_2, consists of metatitanate $BaTiO_3$, the outer layer consists of orthotitanate Ba_2TiO_4.

With samples treated at higher temperatures (e.g. 900° C) a single, homogeneous layer occurs, which, by X-ray diffraction, proves to be a mixture of both titanates. This layer is always located inside the original TiO_2 ceramic.

3.2. Study of the $BaCO_3$–$BaTiO_3$ interface (samples B)

Near the interface, within the $BaTiO_3$ pellet, a layer of orthotitanate forms during heat treatment (Fig. 5). It is observed as a distinct layer whatever the treatment temperature up to 900° C for the above reasons and this is contrary to what happens with A samples in which metatitanate occurs during heat treatment.

3.3. Study of the Ba_2TiO_4–$BaTiO_3$ interface (samples C)

On the sample sections, after treatment, transformations are observed on both sides of the interface and near it. In the Ba_2TiO_4 pellet, the orthotitanate transformed into metatitanate. In the $BaTiO_3$ pellet, the changes are more distinct (Fig. 6). The $BaTiO_3$ grain boundaries are disrupted and, between the grains, a barium-rich substance, containg no titanium, has penetrated.

4. Discussion and further results

Three main points become apparent from the experimental results.

4.1. Metatitanate $BaTiO_3$ occurs by diffusion of barium through titanium oxide

This result is validated by studying A samples after treatment and agrees with what has been shown by Nakayama and Sasaki [4] on rutile monocrystal.

With the B and C samples we also expected to observe a reaction interface inside the TiO_2 ceramic. It has actually been shown that barium

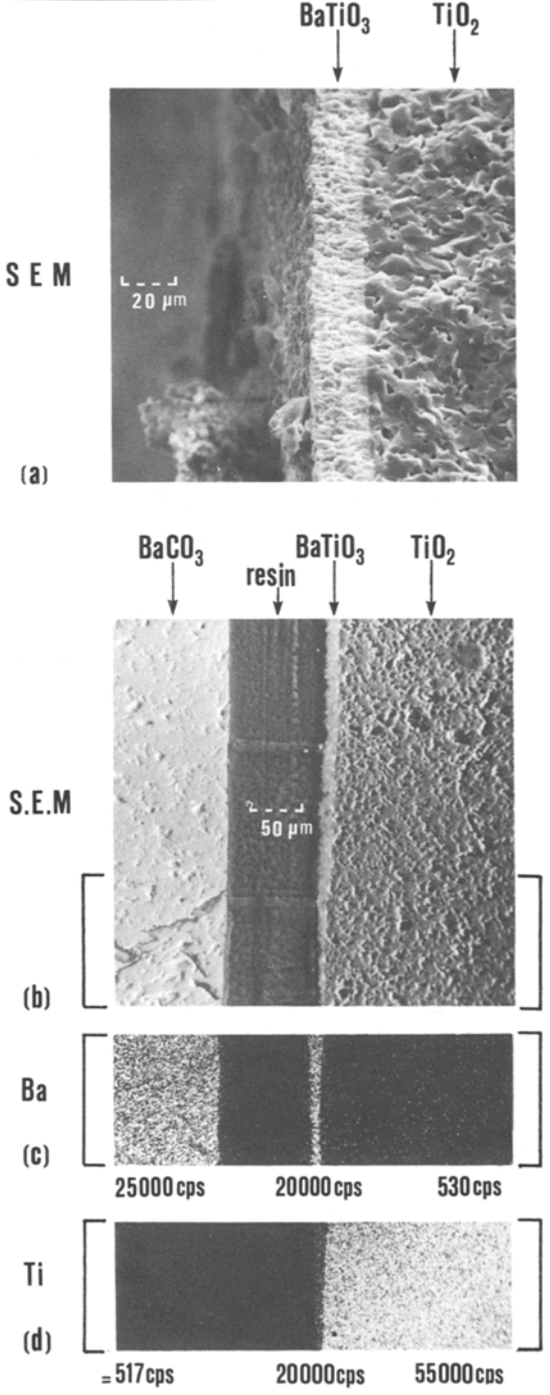

Figure 3 $BaCO_3$–TiO_2 Interface after treatment (sample A, $T = 750°$ C, $P = 1$ atm air, $t = 45$ mn). Result: $BaTiO_3$ forms at the expense of TiO_2.

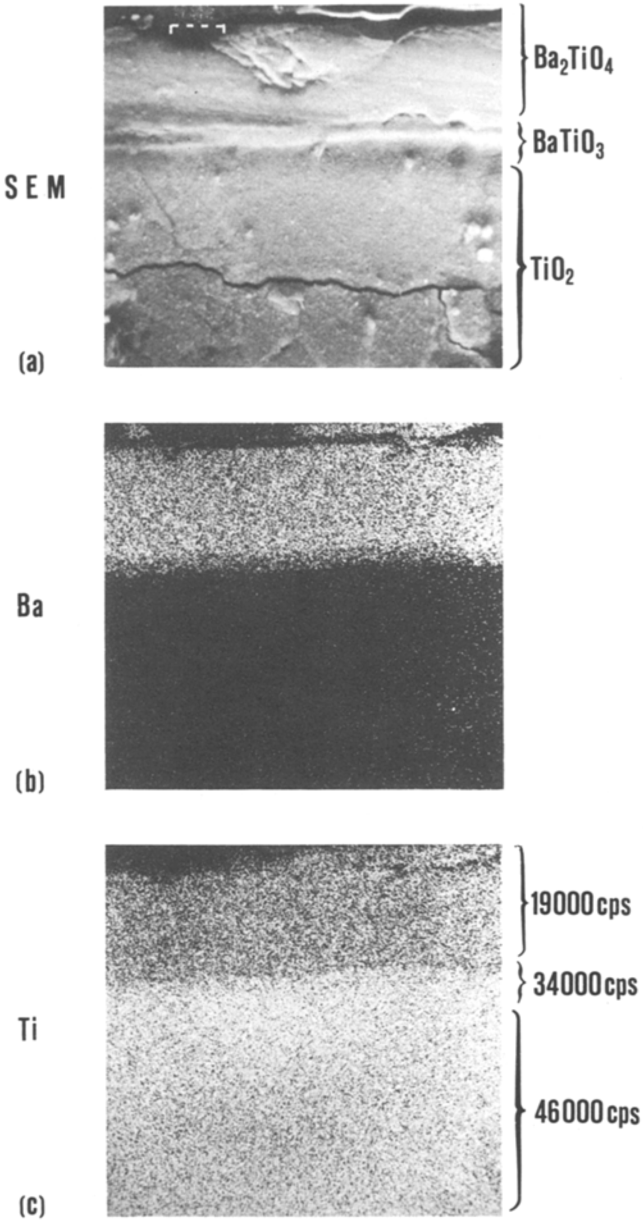

Figure 4 $BaCO_3$–TiO_2 Interface after treatment (sample A, $T = 750°$ C, $P = 1$ atm air, $t = 24$ h). Results: Ba_2TiO_4 forms at the expense of $BaTiO_3$. Distinction between the two titanates by titanium diagrams of electron microprobe.

diffuses through TiO_2 (Fig. 7) however, the phase formed in TiO_2 at the macroscopic interface, $BaTiO_3$–TiO_2 is not metatitanate.

The formation of the phase observed is not attributable to a diffusion of barium from $BaCO_3$ or Ba_2TiO_4. In fact, the same phase has been obtained in a sample only made of the two ceramics, one of $BaTiO_3$ and the other of TiO_2; thus it is certainly a titanate richer in titanium than $BaTiO_3$.

Probably, in the case of B and C samples, the excessive thickness of the $BaTiO_3$ layer is responsible for the formation of this new phase in TiO_2: Moreover, it is not observed in the case of the calcining of micrometric powders intimately mixed together [1].

The formation of $BaTiO_3$ at the expense of TiO_2 is however observed in the case of a reaction couple of Ba_2TiO_4 and TiO_2 ceramic (Fig. 8).

4.2. Orthotitanate Ba_2TiO_4 occurs by diffusion of barium through metatitanate $BaTiO_3$

Studies carried out by Kubo *et al.* [2] and Beauger

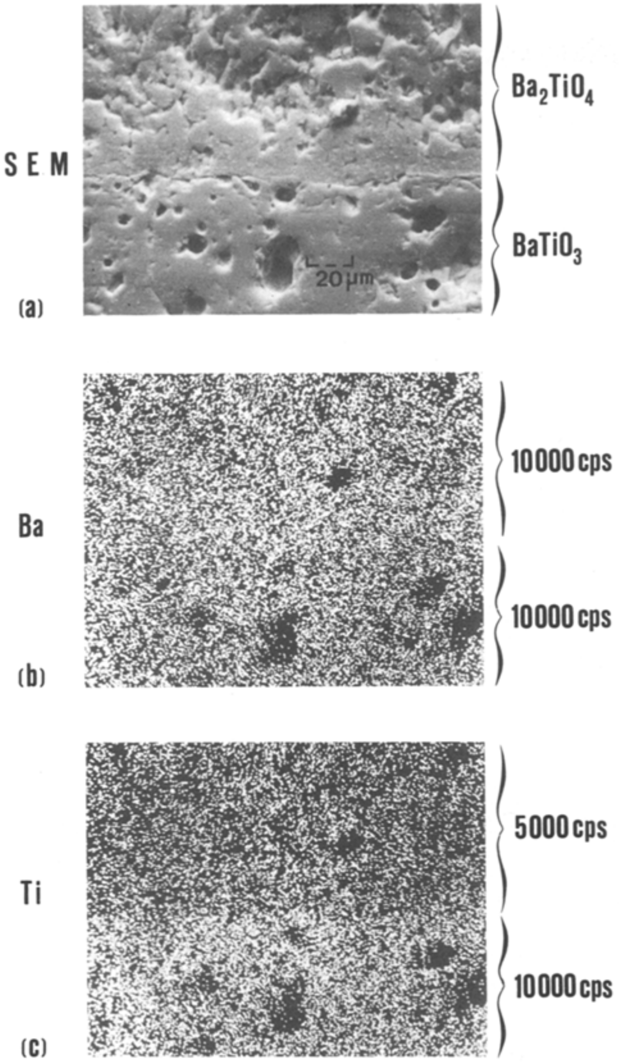

Figure 5 $BaCO_3$–$BaTiO_3$ interface after treatment (sample B, $T = 850°$ C, $P = 1$ atm air, $t = 3$ days). Result: Ba_2TiO_4 forms at the expense of $BaTiO_3$.

et al. [1] favour the formation of the orthotitanate through the reaction

$$BaCO_3 + BaTiO_3 \rightarrow Ba_2TiO_4 + CO_2$$

at the $BaCO_3$–$BaTiO_3$ interface. The occurrence, then the accumulation of metatitanate in this reaction couple, generates favourable conditions for the formation of orthotitanate according to this reaction. The barium from $BaCO_3$ diffusing towards TiO_2 to form $BaTiO_3$ must overcome a layer of $BaTiO_3$. Diffusion is thus slowed down and barium accumulates. The metatitanate in contact with $BaCO_3$ is transformed into Ba_2TiO_4 as shown in Fig. 1.

This interpretation is validated by the results obtained after treating samples A or B.

4.3. The presence of the oxide TiO_2 is essential in the transformation of orthotitanate into metatitanate

Studying the transformation, at 900° C, of mixtures of barium carbonate and TiO_2 oxide showed that the proportion of orthotitanate that occurred in the meantime begins to decrease when all the carbonate has been consumed [1]. At the end of calcination Ba_2TiO_4 disappears totally, with $BaTiO_3$ remaining the only reaction product (Fig. 1).

From the point of view of the chemical balance the disappearance of Ba_2TiO_4 can only be explained by the reaction

$$Ba_2TiO_4 + TiO_2 \rightarrow 2BaTiO_3$$

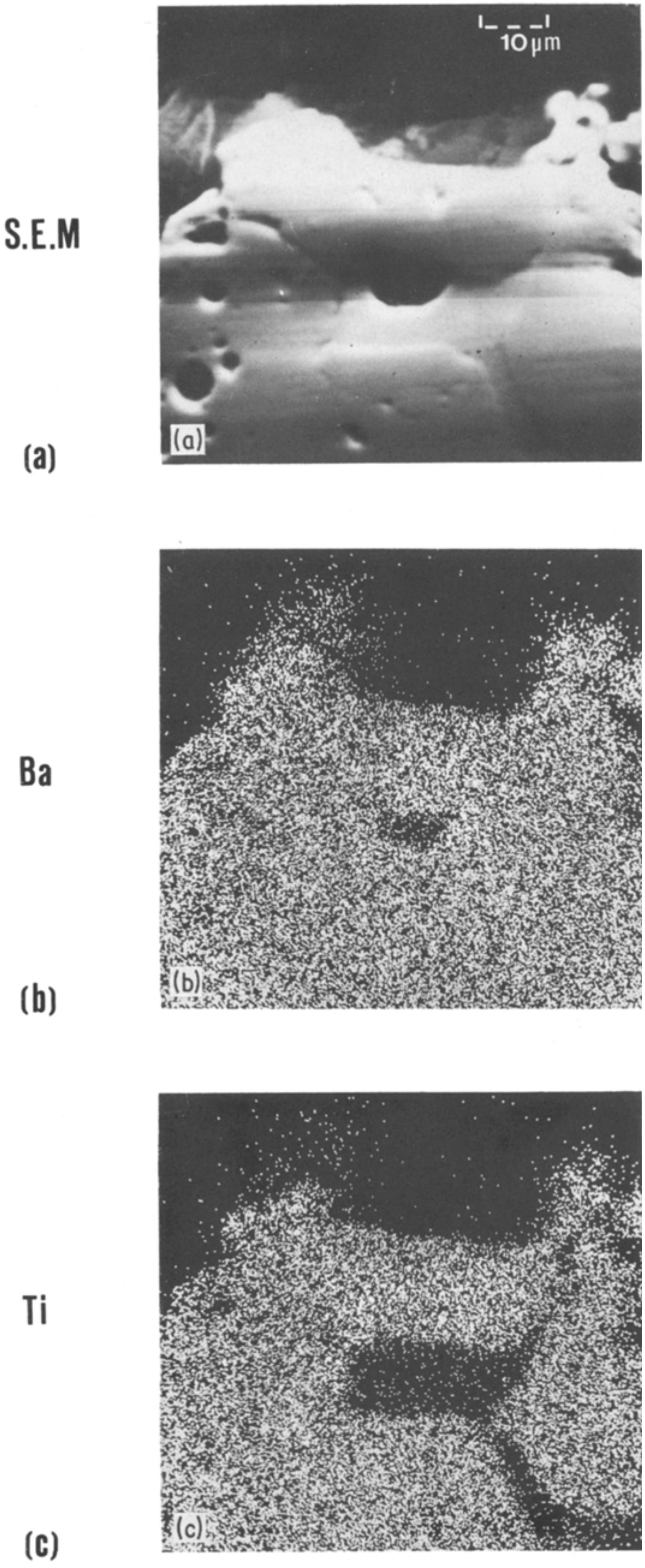

Figure 6 Ba$_2$TiO$_4$–BaTiO$_3$ interface after treatment (sample C, $T = 1300°$ C, $P = 1$ atm air, $t = 92$ h). Result: A barium-rich substance and containing no titanium diffuses between the BaTiO$_3$ grains.

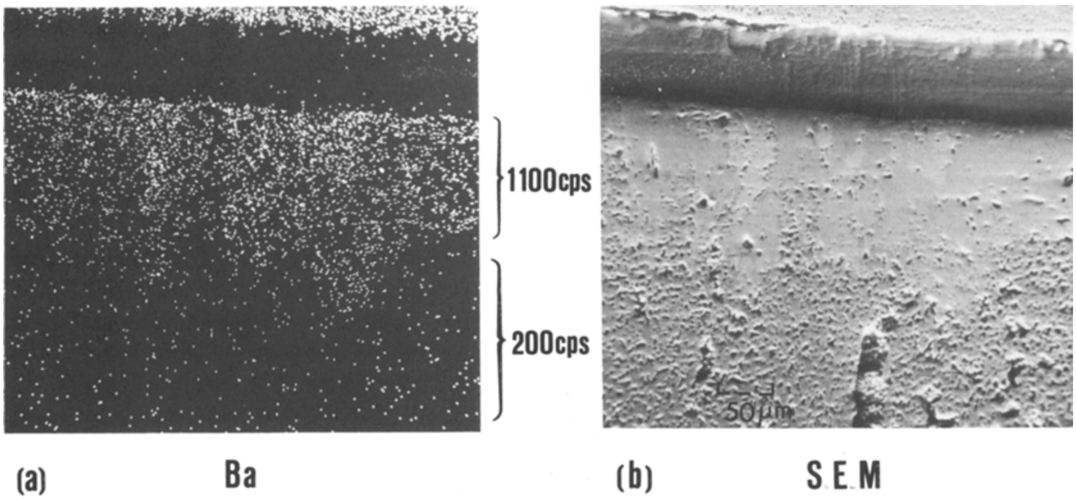

Figure 7 $BaTiO_3$–TiO_2 interface after treatment (sample C, $T = 1100°$ C, $P = 1$ atm air, $t = 15$ days). Result: barium diffuses into the TiO_2 ceramic.

However, according to Fig. 1 and to the above results, the layers of Ba_2TiO_4 and TiO_2 within a sample are always separated by a layer of metatitanate and we may wonder how the conversion of Ba_2TiO_4 into $BaTiO_3$ occurs: studying the Ba_2TiO_4–$BaTiO_3$ interface after treating samples C shows that the part of the Ba_2TiO_4 ceramic which is in contact with the $BaTiO_3$ ceramic is

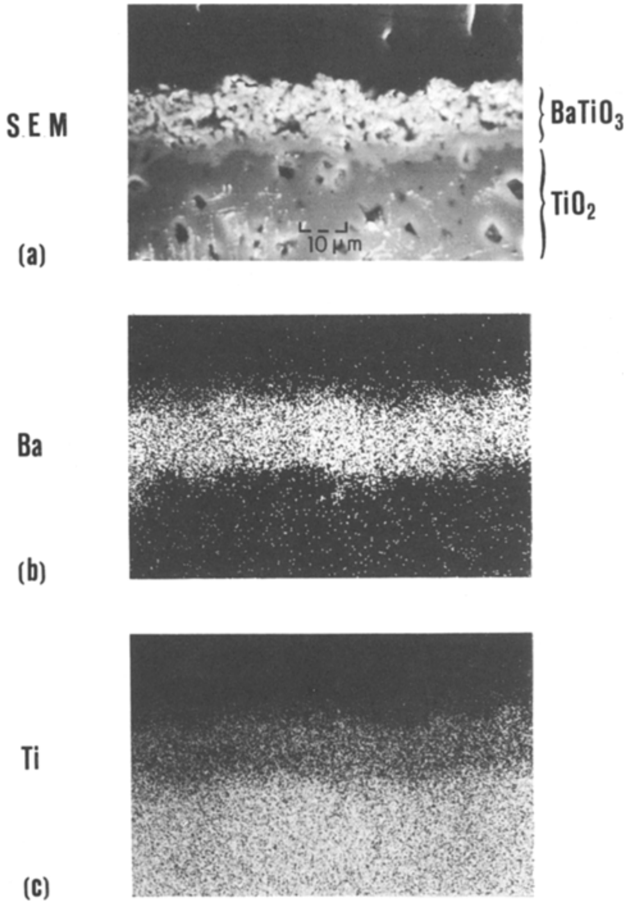

Figure 8 Ba_2TiO_4–TiO_2 interface after treatment ($T = 1100°$ C, $P = 1$ atm air, $t = 92$ h). Result: Formation of $BaTiO_3$ into the TiO_2 ceramic.

converted into $BaTiO_3$; simultaneously, a substance containing barium, no titanium, penetrates into the $BaTiO_3$ layer.

It is reasonable to interpret both observations as follows:

(a) there would be decomposition of orthotitanate at the Ba_2TiO_4–$BaTiO_3$ interface according to

$$Ba_2TiO_4 \rightarrow BaTiO_3 + \text{“BaO”}$$

In this reaction “BaO” designates a compound corresponding to the stoichiometric composition BaO which could only be characterized by electron microprobe analysis, i.e. a chemical species containing barium but no titanium;

(b) at the $BaTiO_3$–TiO_2 interface the following reaction would occur

$$\text{“BaO”} + TiO_2 \rightarrow BaTiO_3$$

This reaction could be detected only by studying the Ba_2TiO_4–TiO_2 interface; as already mentioned, studying the $BaTiO_3$–TiO_2 interface has not detected this reaction probably due to the excessive thickness of the $BaTiO_3$ layer.

Experimental result supports this interpretation. The conversion of Ba_2TiO_4 into $BaTiO_3$ and simultaneously the diffusion, through $BaTiO_3$, of a barium-rich species which contains no titanium occur only if titanium oxide (or any other oxide, e.g. ZrO_2) is present on the other face of the $BaTiO_3$ ceramic. Indeed, heat treatment (under the same conditions as a C sample) of a sample consisting only of a Ba_2TiO_4–$BaTiO_3$ reaction couple resulted in only minor interface changes.

5. Conclusion

The above study, although it was achieved under experimental conditions (temperature, nature and size of reaction interfaces, etc.) largely different from those characterizing industrial calcination and laboratory tests [1, 2] yielded results confirming and supporting the assumptions made to explain the formation of barium metatitanate from powder mixtures of barium carbonate and titanium oxide.

The observations related to the formation of $BaTiO_3$ by diffusion of barium through TiO_2 supplement those made on monocrystals [4]; the assumption of the formation of orthotitanate by a similar mechanism of barium diffusion through metatitanate is confirmed. Additionally, the transformation of Ba_2TiO_4 into $BaTiO_3$ with release of barium oxide, which could be deduced from the chemical balance of the reaction, is here clearly validated.

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