JOURNAL OF SOLID STATE CHEMISTRY 111, 247–252 (1994)

Microstructural Study of Vanadium–Titanium Oxide Powders Obtained by Laser-Induced Synthesis

Laura E. Depero and Paolo Bonzi

Department of Materials Chemistry and Physics, University of Brescia, Italy

and

Mirella Musci and Cristina Casale

CISE Tecnologie Innovative POB 12081 Milano, Italy

Received February 26, 1993; in revised form August 30, 1993; accepted September 21, 1993

Using laser-induced pyrolysis, powder samples of pure TiO_2 and mixed oxides with different vanadium content were prepared and analyzed by XRD. The diffraction patterns were interpreted in microstructural terms by Fourier analysis of their peak profiles. The influence of vanadium on the phase transition was studied and the changes in the particle and microstrain distributions obtained at different temperatures were analyzed. There is an evident correlation between the initial microstrain distribution in the $Ti_{1-x}V_xO_2$ powder and the vanadium content. The segregation of the V_2O_5 phase causes a strain reduction into the anatase structure. We suggest that the previously observed lowering of the transition temperature for the anatase-to-rutile transformation in the presence of vanadium is due to distortions induced by this ion in the anatase structure. © 1994 Academic Press, Inc.

INTRODUCTION

Vanadium oxide supported by titanium dioxide (anatase) is one of the most efficient catalysts for the selective catalytic reduction (SCR) of nitrogen oxides with ammonia, and is extensively employed for the abatement of NOx emissions from combustion sources. A laser-induced process has been studied and developed for the synthesis either of pure TiO_2 powders, for use as a catalyst support (1), or of $Ti_{1-x}V_xO_2$ mixed oxides to be used directly as catalysts in the selective catalytic reduction of nitrogen oxides with ammonia (2). $Ti_{1-x}V_xO_2$ powders can be synthesized up to high vanadium content (x = 0.25) with specific surface areas even larger than $200 m^2/g$. It was shown that with a vanadium content lower than $x = 0.25$, $Ti_{1-x}V_xO_2$ can be obtained without segregation of V_2O_5 (2).

The aim of this work is to characterize and compare structure and microstructure of the anatase phase in catalysts obtained by vanadium oxides supported by pure TiO_2 and structure and microstructure of the $Ti_{1-x}V_xO_2$ mixed oxides. In a previous paper (3) we studied catalytic powder samples of pure TiO_2 obtained by laser-induced pyrolysis and then impregnated by conventional methods. The diffraction patterns were interpreted in microstructural terms by Fourier analysis of their peak profiles. In particular it has been observed that, on heating samples of the system V_2O_5–TiO_2, the anatase-to-rutile phase transformation takes place at temperatures well below that at which it occurs in the case of pure TiO_2–(anatase).

In this work we consider the mixed oxides obtained by a laser-induced process and we study the effects of thermal treatments on these powders. In particular we follow the phase transformations and determine the microstructure and the dimensions of the crystallites of vanadium–titanium-mixed oxides by using X-ray diffraction methods. Our goal is to understand the possible relationship between the V content in the oxide and the microstrain values in the lattice, in order to explain the already-reported (3) anatase-to-rutile transformation in the presence of V. It was shown (4, 5) that a possible substitution of V in the Ti sites could change the coordination geometry and, for this reason, may possibly induce a microstrain in the lattice. The thermal treatment should cause a relaxation of the lattice and a transformation to the thermodynamically more stable structure of rutile. It is also important to note that V and Ti could form mixed oxides (Magneli phases), with defective rutile structures, that cannot be distinguished experimentally with our experimental data.

II. EXPERIMENTS AND CALCULATIONS

Powder samples of pure titanium and vanadium–titanium-mixed oxides were obtained at CISE by laser-induced pyrolysis of titanium alkoxides. All the diffraction experiments were performed on a Philips MPD 1880 automated

0022-4596/94 $6.00

powder diffractometer with graphite-monochromated Cu$K\alpha$ radiation and with flat samples in the Bragg–Brentano parafocusing geometry. A silicon single-crystal holder was used in all the measurements with the exception of those performed at 400°C and 420°C for which a glass holder was utilized.

The profiles of the diffraction peaks were Fourier analyzed by means of a program developed by Lutterotti and Scardi (6) and based on a single-peak method derived by Nandi *et al.* (7). The single-peak Fourier profile analysis uses the intensity distribution of a single Bragg reflection, suitably corrected for the instrumental aberrations, for the determination, by Fourier transformation, of microstructural parameters, like crystallite sizes, M, and mean square microstrains, $\langle\varepsilon^2\rangle$. The equations

$$A_n = A_n^{\mathrm{S}} A_n^{\mathrm{D}},$$
$$A_n^{\mathrm{S}} = \exp(-d/M\,n), \quad A_n^{\mathrm{D}} = 1 - 2\pi^2 m^2 \langle\varepsilon^2\rangle n^2,$$

were used, where A_n is the Fourier cosine coefficient (for the harmonic number n), A_n^{S} and A_n^{D} are the corresponding size and microstrain coefficients, d is the interplanar spacing, and m is the order of the Bragg reflection. In order to reduce the errors of profile truncation and wrong evaluation of the background line (hook effect), straight line of maximum slope in the A_n vs n curve was chosen in all cases for obtaining A_0 by extrapolation to $n = 0$.

On this basis, and assuming small truncation and background errors (8) (the peaks are well separated), the microstrain values and crystallite sizes were calculated. The instrumental function, to be deconvoluted from the observed profile, was determined by measuring the diffraction pattern of a standard powder KCl (9). The half width at the half maximum (HWHM) for the standard reflection at $2\theta = 27°$ (reflection 200) is 0.05 (2θ) and the Gaussian content in the pseudo-Voigt function is 0.8. According to the hypothesis that the standard powder had no lattice distortions and that its crystallite sizes were large enough not to cause any broadening of its profile, it is possible to determine, by deconvolution, the broadening of the sample considered, thus allowing the derivation of the microstructural parameters $\langle M\rangle$ (average crystallite size) and $\langle e^2\rangle^{1/2}$ (mean-square root microstrain), and of the distribution function of the crystallite sizes.

TABLE 1

Sample	V content[a]
I	0.00
II	0.18
III	0.23
IV	0.30

[a] The vanadium content was determined by XPS measurements.

III. RESULTS AND DISCUSSION

In Table 1 a list of the analyzed samples (with values of V content) is reported. All samples were treated for 4

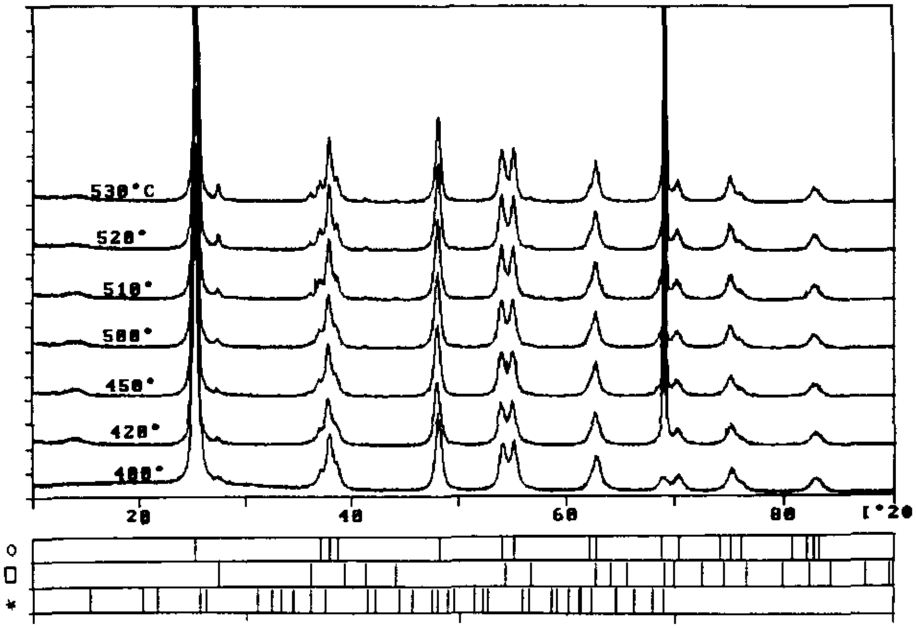

FIG. 1. XRD patterns of sample I for the indicated treatments (for 4 hr). These patterns and those of the other figures are presented with the following common features and conventions: (i) the intensities are given in arbitrary units; (ii) the vertical bars in the three strips reported below each pattern represent 2θ (Bragg) positions for anatase (O), rutile (□), and V_2O_5 (*), as given in JPDC cards 211272, 211276, and 90387, respectively; (iii) the very strong reflection at about 69° (2θ) is due to the Si sample holder.

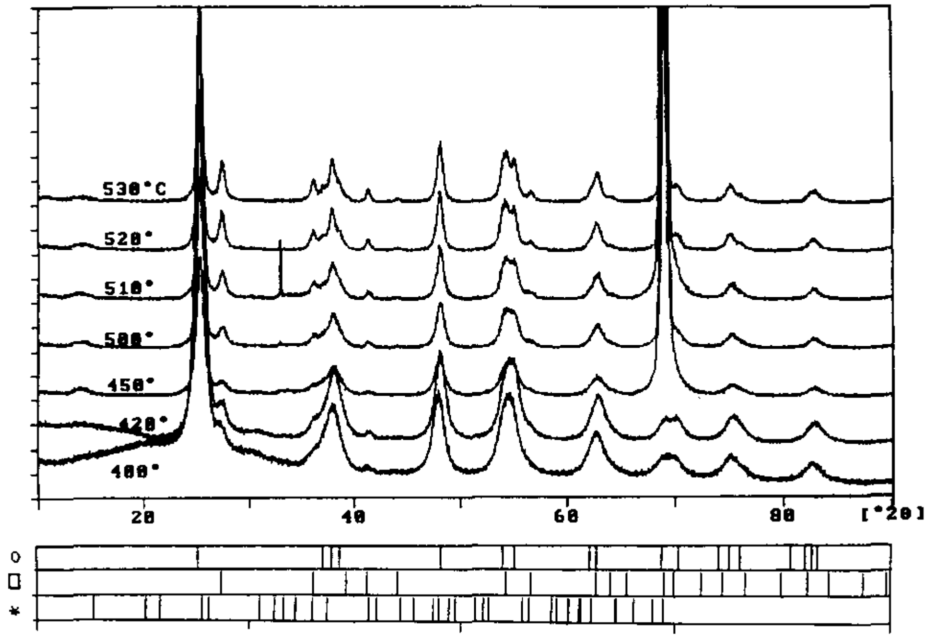

FIG. 2. XRD patterns of sample II for the indicated thermal treatments (for 4 hr).

hr at temperatures of 400, 420, 450, 500, 510, 520, and 530°C. The same sample was treated at different temperatures in sequence, as indicated. In Fig. 1 the XRD patterns of pure TiO_2 are reported. Here, and in all the following patterns, the reflection at about 69°(2θ) and the halo at 14°(2θ) are due to the sample holder made of a silicon single crystal. As the temperature rises, only a small narrowing of the peaks is observed, as can be seen by looking at the separation of the two peaks at about 55° (2θ). A small percentage of the rutile phase is present in all the patterns and does not change with the temperature. In Fig. 2 the patterns obtained for sample II after the thermal treatment are reported. Here the narrowing of all peaks is more evident than that observed in pure TiO_2, as is the increase of the rutile content in the samples (the reflection at 32° (2θ) in the pattern obtained after the treatment at 510°C is spurious). In Fig. 3 the patterns relative to sample III are shown. The first three patterns, obtained after the treatments at 400, 420, and 450°C, are very similar to those obtained for sample II treated in the same way. In

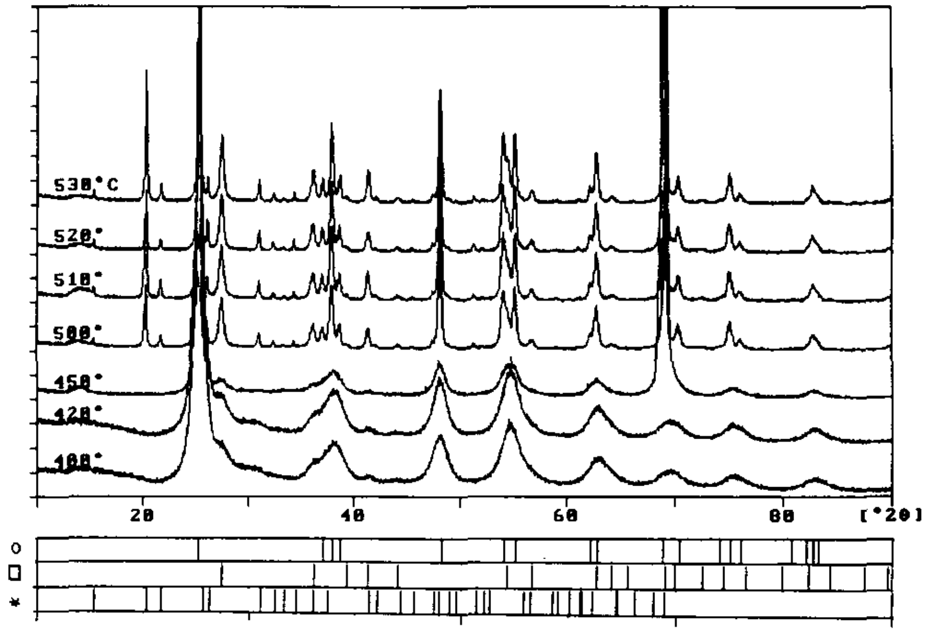

FIG. 3. XRD patterns of sample III for the indicated thermal treatments (for 4 hr).

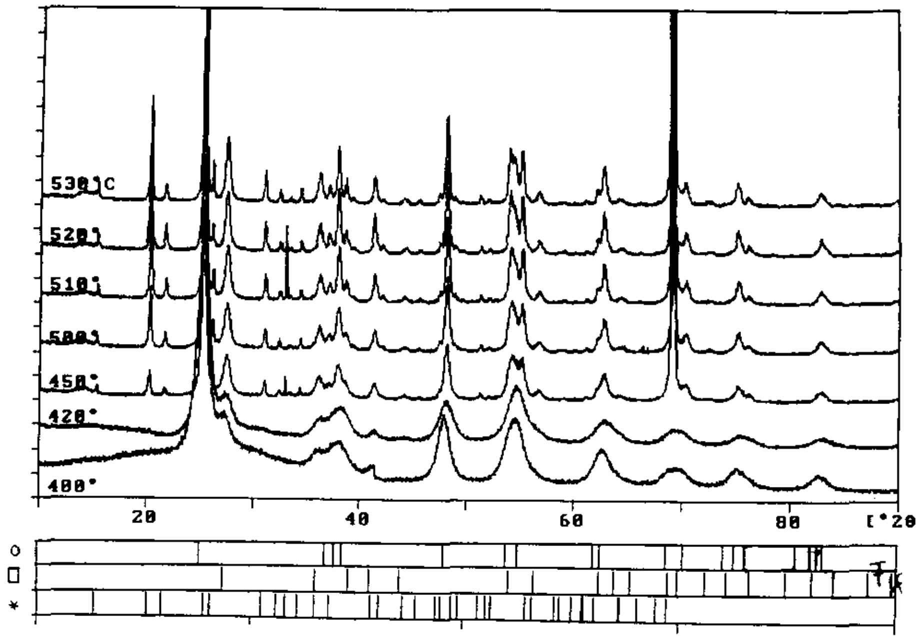

FIG. 4. XRD patterns of sample IV for the indicated thermal treatments (for 4 hr).

the pattern obtained at 500°C the V_2O_5 phase is present. It is interesting to note that a drastic narrowing of all the peaks occurs with this segregation. The percentage of the rutile phase is not substantially different from that obtained in the case of sample II. In Fig. 4 the same behavior is shown for sample IV, but at a lower temperature (450°C). Likewise in this case the rutile content is very similar to that shown in the previous figures. The total quantity of segregating V_2O_5 is different in samples III and IV depending on the different initial vanadium content in the two samples. In both samples the patterns obtained at 520 and 530°C are identical. This means that all V is segregated as V_2O_5 or that there is a maximum amount of vanadium that can be present in the rutile and anatase phases.

The microstructural parameters $\langle M \rangle$ (average crystallite size) and $\langle e^2 \rangle^{1/2}$ (mean-square root microstrain) for the anatase phase are calculated using the 110 reflections. In Figs. 5a and 5b the average dimensions of the crystallites and the microstrain values are reported as a function of temperature of treatment. In all the samples the dimensions at 400°C are very similar. The slope of the curve of the crystallite sizes vs the temperature is strongly dependent on the V content. In the pure TiO_2 sample the dimensions are almost constant, while the slope increases with the V content. At 400°C a direct correlation between the V content and the value of the microstrain is evident (Fig. 5b). This fact shows that in these oxides the V ions enter the structure of the anatase phase substituting the Ti ions. At the temperature of the V_2O_5 segregation, 500 and 450°C for III and IV, respectively, a drastic reduction of the HWHM of the reflections in the patterns corresponds

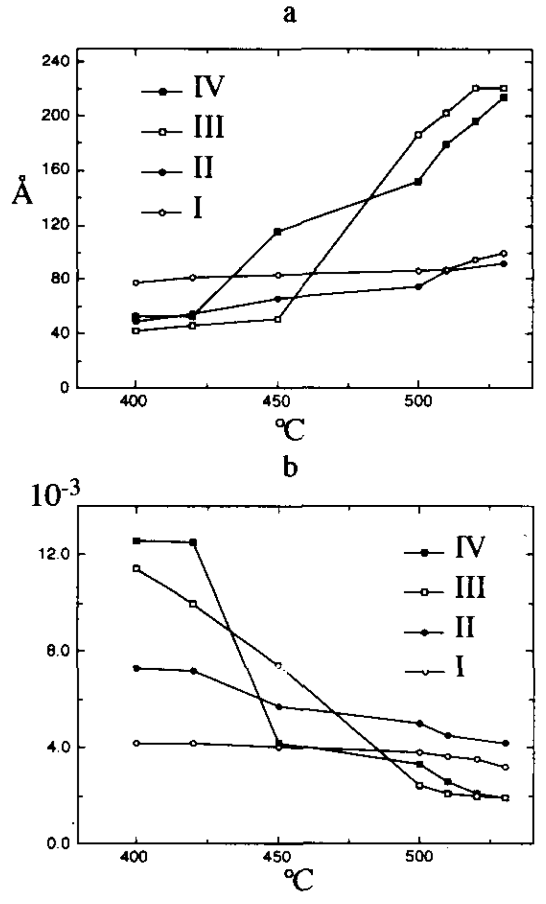

FIG. 5. (a) Average crystallite sizes as a function of the treatment temperature. (b) Average microstrain values as a function of the treatment temperature.

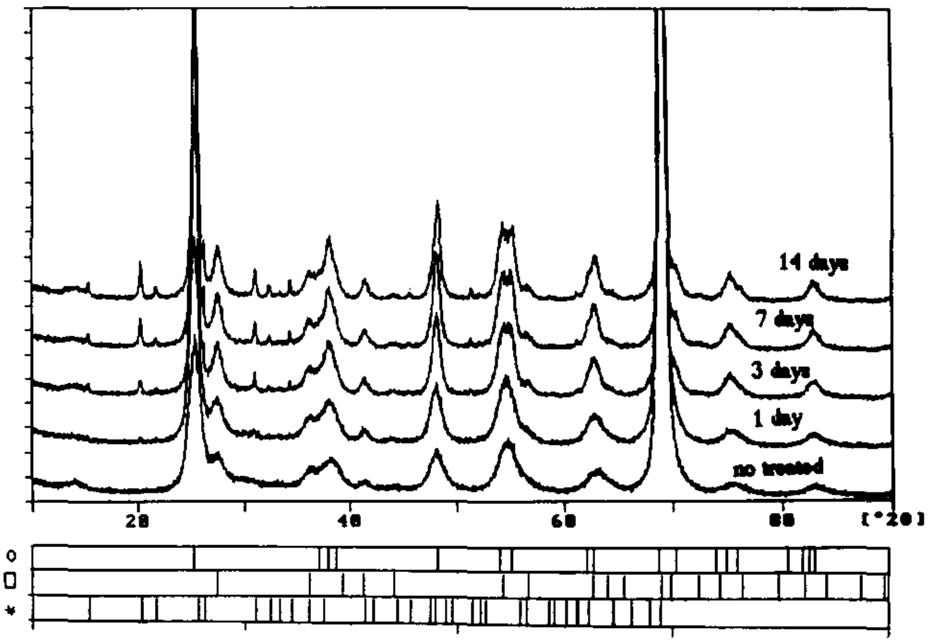

FIG. 6. XRD patterns of sample IV for the indicated periods of thermal treatment at 400°C.

to a collapse in the microstrain and an increase in the crystallite dimensions. All these experimental observations suggest that vanadium introduces distortions in the anatase structure. It was previously discussed (4) that vanadium may have a coordination geometry different from the octahedral geometry, shown by Ti in the anatase phase. This fact may be the cause of the distortions. In sample II there is no segregation and the behavior of both the crystallite dimensions and microstrain distribution is very similar to that obtained in pure TiO_2. This fact supports the idea that a minimum amount of V is necessary for segregation to occur, even if we cannot exclude that the amount of the segregated phase is not enough to be detected. Without doubt, in sample II we have no evidence of the drastic reduction of microstrains in the structure as we have in samples III and IV.

In order to understand if the segregation of the V_2O_5 phase is a thermodynamical or kinetic phenomenon, a thermal treatment at a fixed temperature of 400°C was performed for different periods on sample IV. In Fig. 6 the corresponding XRD patterns are shown. After 3 days the V_2O_5 phase appears and its content goes to a plateau asymptotically. The total amount of V_2O_5 is less than that obtained by the same sample in the previous treatments. This fact could indicate that the segregation is both a kinetic and a thermodynamic phenomenon. In these patterns the narrowing of the reflections is gradual. This behavior is different from that of the same sample treated at different temperatures (see Fig. 5). In Fig. 7 the calculation of the dimensions and the microstrain value of the anatase phase, calculated using the 110 reflection, are reported on the same scale of Fig. 5. For comparison the

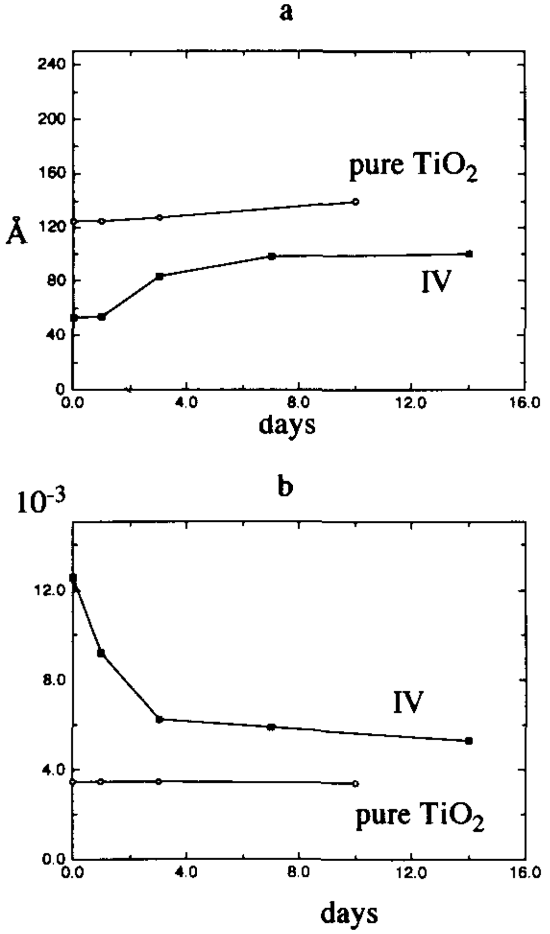

FIG. 7. (a) Average crystallite sizes of sample IV and of a pure anatase sample as a function of the period of the thermal treatment. (b) Average microstrain values for sample IV and for a pure anatase sample as a function of the period of the thermal treatment.

results for the pure TiO_2 anatase phase are shown in the same figure. The effect of segregation in this case is principally the reduction of the lattice strain. After segregation, strain values for sample IV are very similar to those found in the case of pure anatase (sample I). This fact suggests that the crystallite growth observed in Fig. 5 is principally due to a lattice reconstruction, probably facilitated by the thermal mobility in the structure.

IV. CONCLUSIONS

In this paper we confirmed the results already reported (3) about the influence of V in the structure and microstructure of the anatase phase in the catalysts based on TiO_2. In particular it was shown that there is a direct correlation between the vanadium content and the microstrain present at the initial states in the mixed oxide catalysts. This effect confirms that in these materials V substitutes Ti in the anatase structure, introducing distortions, which will finally cause the formation of the rutile phase or the segregation of V_2O_5. The appearance of the V_2O_5 phase in the treatment at constant temperature (400°C) after a few days indicates that the phenomenon has a kinetic nature. Nevertheless, the total amount of segregated phase is less than that obtained at higher temperatures, indicating also a thermodynamical effect. When segregation appears, there is always a drastic reduction of the strain in the anatase lattice. On the contrary, the increase of the crystallite sizes strongly depends on the temperature.

ACKNOWLEDGMENTS

We thank Prof. Marcello Zocchi for useful discussions and acknowledge financial support by the "Progetto Finalizzato Materiali Speciali per Tecnologie Avanzate" CNR, Rome, Italy.

REFERENCES

1. F. Curcio, M. Musci, N. Notaro, and G. De Michele, *Appl. Surf. Sci.* **46,** 225 (1990).
2. M. Musci, M. Notaro, F. Curcio, C. Casale, and G. De Michele, *J. Mater. Res.* **7,** 2846 (1992).
3. L. E. Depero, P. Bonzi, M. Zocchi, C. Casale, and G. De Michele, *J. Mater. Res.* **8,** 2713 (1993).
4. L. E. Depero, *J. Solid State Chem.* **103,** 528 (1993).
5. L. E. Depero, *J. Solid State Chem.* **104,** 470 (1993).
6. The calculations were performed using the two programs by L. Luterotti and P. Scardi, General Peak Separation Routine: MARQFIT (1990) and Line Broadening Analysis by W. A. X. S. (1992).
7. R. K. Nandi, H. K. Kuo, W. Shosberg, G. Wissler, J. B. Cohen, and B. Crist, Jr., *J. Appl. Crystallogr.* **17,** 22 (1984).
8. M. Zocchi, *Acta Crystallogr., Sect. A* **36,** 164 (1980).
9. The standard sample was kindly provided by P. Scardi.