EXTENDED DEFECTS IN SLIGHTLY REDUCED RUTILE TiO₂

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Résumé :

L’objet de ce travail est l’étude de l’influence du réseau de dislocations, introduites par la déformation plastique, sur l’apparition de défauts étendus (plans de cisaillement cristallographique) dans le rutile sous-stœchiométrique TiO₂ₓ (x ∈ [0; 34.10⁻⁴] et à une température de 1050°C). À cette fin nous avons utilisé une installation permettant la déformation en compression à haute température et sous atmosphère réductrice contrôlée. Afin de conserver jusqu’à la température ambiante, la microstructure des échantillons obtenue à haute température, nous avons du mettre en place un système de trempe sous vide secondaire. L’observation au microscope électronique à transmission (M.E.T.) d’échantillons TiO₂ₓ trempés a permis, d’une part de vérifier l’efficacité de notre système de trempe et d’autre part de confirmer que ces structures peuvent être analysées en terme de solution solide de défauts ponctuels intrinsèques. En outre, nous avons pu observer des précipités du type Fe₅Tiₙ₋₂O₂n₋₂, en forme de plaquettes perpendiculaire à la direction [100]. Ces précipités apparaissent probablement à basse température.

L’observation au M.E.T. des échantillons réduits et déformés a montré la présence de défauts plans du type {132}. Ces défauts apparaissent lors du refroidissement de l’échantillon et sont favorisés par la présence du réseau de dislocations introduites par la déformation plastique.

Abstract :

The aim of this work is to study the influence of the dislocations network, introduced by plastic deformation on the formation of extended defects called crystallographic shear plans (c.s.p.). For this purpose, a rig allowing deformation under compression at high temperature and controlled reducing atmosphere, has been used. In order to preserve to ambient temperature, the obtained samples microstructures at high temperature, a quenching system under secondary vacuum, was set up. Observation under transmission electronic microscope of TiO₂₋ₓ quenched samples, has confirmed the efficiency of our quenching system and that these structures can be analysed as solid solution of intrinsic punctual defects. Precipitates of Fe₅Tiₙ₋₂O₂n₋₂ type in the shape of plates
perpendicular to [1 0 0] directions and appearing at low temperature could be observed in these compounds.
Observation under transmission electronic microscope of reduced then deformed samples has shown
plans defects presence of {132} type. These defects appears during the cooling of the sample and are
supported by the presence of network dislocations introduced by plastic deformation.

Mots clefs : rutile, deformation, stoechiometrie, défauts, compression

1 Introduction

The titanium oxide TiO$_2$ is considered at the present time as one of the most important element of
ceramics range. The study of rutile physical properties was largely oriented because of its aptitude to
lose its stoichiometry under oxygen partial pressure. This reduced rutile is noted TiO$_{2-x}$, x being the
gap to the stoichiometry.
The stoichiometry strong gaps (x >> 0.001) are interpreted in terms of two dimensions rearrangement
of rutile structure in extended defects called crystallographic shear plans (c.s.p.) . For stoichiometry
low gaps (x << 0.001), the rutile presents at high temperature a sub-stoichiometric field interpreted as
solid solution of intrinsic point defects, that means as oxygen vacancies or as titanium interstitials [1].
The purpose of this work is to study the influence of the dislocations network, introduced by plastic
deformation on the formation of the extended defects (c.s.p.).

2 Experimental technique

A compression system is provided to work at high temperature and under air. This system is designed
and set to allow the compression at high temperatures and under controlled reducing atmosphere(Figure 1).
The sub-stoichiometry is controlled by the application of oxygen partial pressures obtained by a
gaseous mixture of CO, CO$_2$ and N$_2$. The CO and CO$_2$ gases are mixed in the desired proportions by a
first measuring pump. This mixture is then dissolved in 90% of nitrogen by a second pump. For
stoichiometry low gaps, an isotherm at 1050° C giving a ratio O/ Ti according to oxygen partial
pressure is established from the measures carried out by thermo-gravimetric conduction by many
authors [3, 4, 5 and 6].
For the low partial pressures of oxygen (the studied case) and for temperatures ranging between 987°
C and 1480°C, Baumard [7] showed clearly on the isotherms of electric conductivity that the majority
intrinsic defect is interstitial titanium.
In order to preserve to room temperature the existing microstructures at high temperature, a quenching
system under secondary vacuum is designed(Figure 2). This system permits to eject the sample from
a zone where the temperature is 1050° C to the lower part of the compression system at a temperature
of about 100° C, during a very small time (about two seconds).
3 Results and discussions

3.1 Characterization of non-deformed TiO$_2$$_x$ samples

The purpose of this operation is to have a reference state of the samples and to verify the efficiency of the quenching system. The samples are reduced then quenched (for different compositions). The observation of these samples by Transmission Electronic Microscope (T.E.M) of 100 kV did not
show any signs of extended defects. The cooling speed was quick enough to preserve the existing microstructure at high temperature.

As example, the Figure 3 presents a TiO$_{1.9985}$ sample microstructure. The thin blade is parallel to (0 1 0) plan, observed perpendicularly to the electronic rays. However, the presence of many irregular contrasts is observed. Supplementary stains of periodicity $1/3 \text{g} = [\bar{1} 0 1]$ in diffraction diagrams indicates that these are precipitates having the shape of small plates perpendicular to the [100] direction. Their sizes vary from 600 Å to 3000 Å. The analysis by Scanning Transmission Electronic Microscope (STEM) permitted to identify these precipitates as compounds of FeTi$_{n-2}$O$_{2n-2}$ types.

An annealing, in the air at 200°C during two hours was carried out on TiO$_{1.9985}$ sample. Figure 4 shows the microstructure of this sample observed by electronic microscopy. An increase of precipitates (sizes vary from 2300 Å to 5600 Å) and numerous precipitates deviations from <100> direction to another of the same type, was observed. This annealing has showed that the precipitates take place at low temperature during cooling of the sample after quenching.

![Figure 3. TiO$_{1.9985}$ quenched - cut (0 1 0)](image1)

![Figure 4. TiO$_{1.9985}$ annealed - cut (0 1 0)](image2)

This kind of precipitates have already been noticed by Bursill [8].

### 3.2 Compression in [111] orientation

The samples have been oriented by X ray by Laüe method.

The choice of these orientation has been motivated by the fact that the [111] direction is parallel to crystallographic shear plans of rutile $((132), (121), \ldots)$.

The samples present in this direction an important ductility. Figures 5 and 6 illustrate the evolution of flow stress $\sigma_e$ and activation volume $V_a$ depending on the composition.

The definition of the flow stress is the one that determines the stress for which the activation volume reaches a constant value [9]. The flow stress $\sigma_e$ is defined as stress of plastic flow at the beginning of plastic domain of linear hardening. This method doesn’t define the absolute flow stress, nevertheless it permits to follow the evolution of this parameter. To determine the activation volume experimentally, the method of relaxation was used [10]. The values are expressed in $b^3$ unit; $b$ is the Burgers vector of slipping dislocations.
It clearly appears a substoichiometric rutile softening compared to stoichiometric rutile. For rising gaps to stoichiometry, the flow stress and the activation volume of TiO$_2$ vary very slightly. In this case the deformation is controlled by dislocations climb and goes from a mechanism controlled by dislocations slip for TiO$_2$ to a process of dislocations climb for TiO$_{2-x}$.

This hypothesis has already been suggested by Duclos [11] and Castaing [12] to explain the softening observed in MgAl$_2$O$_4$ spinels and the NiO nickel oxide substoichiometric.

Observation by optic microscope of marks left by the emergence of dislocations on lateral sides of deformed samples allowed to determine the (110) <001> slip system activation.

3.3 Observation by T.E.M. of TiO$_{2-x}$ deformed samples

The observation by transmission electronic microscope TEM (100kv) of thin blades extracted from the two types of deformed samples revealed the presence of extended defects of (132) type, (figure 7).

This microstructure appears in contradiction with the observed microstructure in non deformed reduced samples (i.e. solid solution of point defects). The gap to stoichiometry was then verified by thermogravimetric measures which confirmed the expected values. These extended defects appear during the sample cooling and are assisted by the presence of the dislocations network introduced by the plastic deformation.
4 Conclusion

The observation by transmission electronic microscope of slightly reduced and deformed samples showed the presence of extended defects. These defects appear during the cooling of the sample and are assisted by the presence of dislocations network introduced by the plastic deformation.

Références