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In situ statistical study of the nucleation, the variant selection and the orientation memory effect during the $\alpha \rightleftharpoons \beta$ titanium martensitic transformation

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The h c p → b c c and reverse phase transformation of titanium has been watched *in situ* and in real time by synchrotron X-ray topography from large α single crystals. Due to the large crystal volume investigated, the results can be considered as statistical. The heterogeneous nucleation character of this transformation has been shown and the orientation relationships between the two phases have been elucidated. This transformation is characterized by a severe selection of the variants. Very frequently, the transformation product, in the direct and reverse transformation, resolves into a texture composed of several little crystals with a same and sole orientation. An orientation memory effect of the titanium single crystals has been displayed. Also the sample geometric shape, the unit cell volumes, the shape deformation and the unusual temperature dependence of the vibrational entropy have been taken into account in discussing the results.

1. Introduction

The orientation relationships (OR) between two phases of different crystal structure play a crucial role in many metallurgical processes such as precipitation, epitaxial growth or martensitic transformations. In these examples, various attempts have been made to deduce, from the geometrical properties, the atomic displacements and the mechanisms by which they occur. Since the theoretical work of Mackenzie and Bowles [1–4], no general theory on the crystallography of the martensitic transformation has been proposed. Briefly they have resolved the atomic displacements in a homogeneous component defined by the shape change of the sample and in an inhomogeneous component where some additional displacements are required to generate the final lattice without visible shape change. From these considerations, they have deduced the OR. Numerous experiments on several systems have been realized to verify the validity of the mechanisms proposed. In this paper, we will restrict our discussion to the bcc $\rightleftharpoons$ hcp phase transformations for which titanium is the chosen example. The historical background of other transformations has been omitted.

The pure titanium undergoes a martensitic transformation around 870 °C. The high temperature phase has the bcc structure (β) while the low temperature phase is hcp (α). These hcp $\rightleftharpoons$ bcc transformations are less widely known than other phase transformations. Burgers [5], from simple geometric considerations, was the first to provide an OR. This approach was followed several years later by the Pitsch–Schrader [6] and Potter [7] proposals which were the most frequently reported in the literature. Another way to take up the bcc $\rightleftharpoons$ hcp (or other non-cubic structures) has been made by Zener [8] who was the first to suggest that the stability of the crystal lattice is closely related to its elastic anisotropy. The large softening of the shear elastic constants, at the transformation temperature, should induce the transformation. Recently [9, 10] it has been proposed that the strain field associated to crystalline defects should induce dynamical fluctuations of the lattice in the direction of the new phase, thus reducing the resistance of the crystalline net and favouring the transformation.

Some years ago, we successfully applied synchrotron X-ray topography to the *in situ* study of the titanium phase transformation and the first elements of OR during the $\alpha \rightarrow \beta$ transformation have been given [11]. In two recent papers [12, 13], we have shown that, during $\alpha \rightarrow \beta$ and reverse transformation, the nucleation was triggered by the residual stresses associated to complex crystalline defects. These results were in agreement both with the geometrical and the instability approach.

This paper relates the results obtained from the *in situ* study of the $\alpha \rightarrow \beta$ and $\beta \rightarrow \alpha$ reverse transformation of large α (or β) titanium single crystals. The large volume investigated by the X-ray beam allows elimination of the transformation peculiarities or artifacts. Complete OR have been determined by means of Laue diagrams. The variant selection during an $\alpha \rightleftharpoons \beta$ cycle and the orientation memory effect

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recorded have been connected with the experimental parameters and with the lattice softening at the transformation temperature.

2. Experimental procedure

The ultra high vacuum heating camera and the white beam synchrotron topographic technique have been previously described [14]. At 1000 °C, in the β phase, the pressure is nearly 10^{-7}–10^{-8} Pa. The transformation temperature $T_{\alpha \rightleftharpoons \beta}$ is around 870 °C and the temperature gradient ΔT is of the order of 100 °C m^{-1}. When the DCI ring power is 2.9×10^{-10} J and the intensity 3×10^{-1} A the wavelength λ is comprised between 0.040 and 0.400 nm with a λ maxima equal to 0.160 nm. The cross-section of the beam is rectangular $(1.5 \times 0.8) \times 10^{-4}$ m^2. Diffracted spot evolutions are recorded either onto video tapes or photographic films or nuclear plates. In the last case, the time exposure can vary from 1 to 10 s. High purity (700, 40 and 13 atomic p.p.m.) α single crystals have been prepared by the cycling method [15].

Nucleation and OR linking of the low and high temperature phases during the $\alpha \rightarrow \beta$ and $\beta \rightarrow \alpha$ reverse transformation have been systematically studied so as to give results which have a statistical value. The experimental technique is such that the burst transformation has been avoided. When the first β nuclei are detected ($\alpha \rightarrow \beta$ transformation), the temperature is slowly increased in steps of 1 K until the transformation is achieved. To follow the crystal structure evolution during the transformation, topograms are realized at each step. When the transformation is achieved and the β structure stabilized, at 1000 °C, the temperature is slowly decreased and the $\beta \rightarrow \alpha$ transformation is studied in a same manner than the $\alpha \rightarrow \beta$ previous one.

3. Results

We have realized numerous *in situ* experiments. Figs 1 and 2 summarize the typical steps of the structure evolution occurring usually when a large α titanium single crystal is subjected to an $\alpha \rightleftharpoons \beta$ cycle.

3.1. 1/$\alpha \rightarrow \beta$ transformation

At the beginning of the transformation, owing to the low furnace gradient the β phase nucleation starts, in the α phase, simultaneously in various places. This fact is illustrated in Fig. 1a which is an enlargement of a diffraction spot given by the titanium α single crystal at the transformation temperature. β nuclei are detected by white contrasts due to the β phase out of reflection. The polychromatism of the synchrotron radiation also allows us to record, simultaneously, on the same diffraction diagram, the β diffraction spots. So Fig. 1b and c are photographic enlargements of the β diffraction spots during the transformation and when the transformation is nearly achieved. From Fig. 1a, b and c, we can ascertain that the new β phase nucleates by a classical heterogeneous nucleation process and not by a homogeneous or an autocatalytic burst one. Then the variants observed are "native" variants, directly bound to the initial crystalline state, and not variants triggered by the high stresses preceding the front of the burst transformation. Fig. 1b is the photographic enlargement of a reflection. It can be seen that all the diffraction spots, given by the little β crystals are grouped. This is due to the fact that all the diffracting β crystals have the same orientation. This crystalline state is comparable to a well defined texture or to a "pseudo-single crystal". This is more striking when the whole diffraction diagram of the stabilized β structure is considered, see Fig. 2c. A perfect α single crystal transforms in a "pseudo-β single crystal".

During the transformation, the well known parent shape deformation [16] is revealed in a reflection, Fig. 1a, by black contrasts due to the matrix deformation, surrounding the white "hole" due to the β crystal out of reflection. The diffraction spots of the β crystals are elsewhere in the diagram. Their careful examination has allowed us to display, during the $\alpha \rightarrow \beta$ transformation, a shape deformation of these crystals. At our knowledge, this result has never been quoted. At the outset of the transformation β crystals are isolated in the parent matrix, Fig. 1a; they have a good crystalline state, Fig. 1b. Their diffraction spots have a simple geometrical shape and a uniform intensity. When the transformation progresses, new β crystals appear between the original ones. This nucleation induces the deformation of the previous β crystals either by a mutual shape deformation or from the fact that adjacent little crystals have nearly the same orientation. Their common grain boundaries are low angle grain boundaries which are known to possess a long range stress field. The appearance of orientation spreading when the transformation is achieved is due to this effect.

In martensitic transformations, the habit plane (HP) and the shear direction are common both to the high and low temperature phases. Then, from simple geometrical considerations and symmetry relations in the Burger's OR, a titanium crystal can transform in 6 variants in the $\alpha \rightarrow \beta$ transformation and in 12 variants in the reverse $\beta \rightarrow \alpha$ transformation [5]. Comparing Fig. 2a and c, it can easily be checked that the previous remark concerning the numerous orientation variants is not satisfied. Fig. 2c is typically a diffraction diagram for a "single crystal". If other variants are present, their diffraction spots are not detected so they are either scarce or little developed and they must be considered as an exception to the general behaviour. Fig. 2b is the diffraction diagram at the transformation temperature. The two phases coexist. 1,...5 are the diffraction spots given by the α phase and 6...8 those given by the β phase.

Fig. 3a and b are, respectively, the stereographic projections of the titanium crystal in the α and β phases. It can be easily checked that the $(0\,0\,0\,1)_\alpha$ and $(1\,\bar{1}\,0)_\beta$ planes (CP) are in coincidence as well as the $[\bar{1}\,2\,\bar{1}\,0]_\alpha$ and $[1\,1\,1]_\beta$ directions (CD). These orientation relationships agree with the Burger's forecasts. The common shear plane being either the $(1\,0\,\bar{1}\,0)_\alpha$ plane in α phase or the $(\bar{1}\,\bar{1}\,2)_\beta$ plane in the β phase.

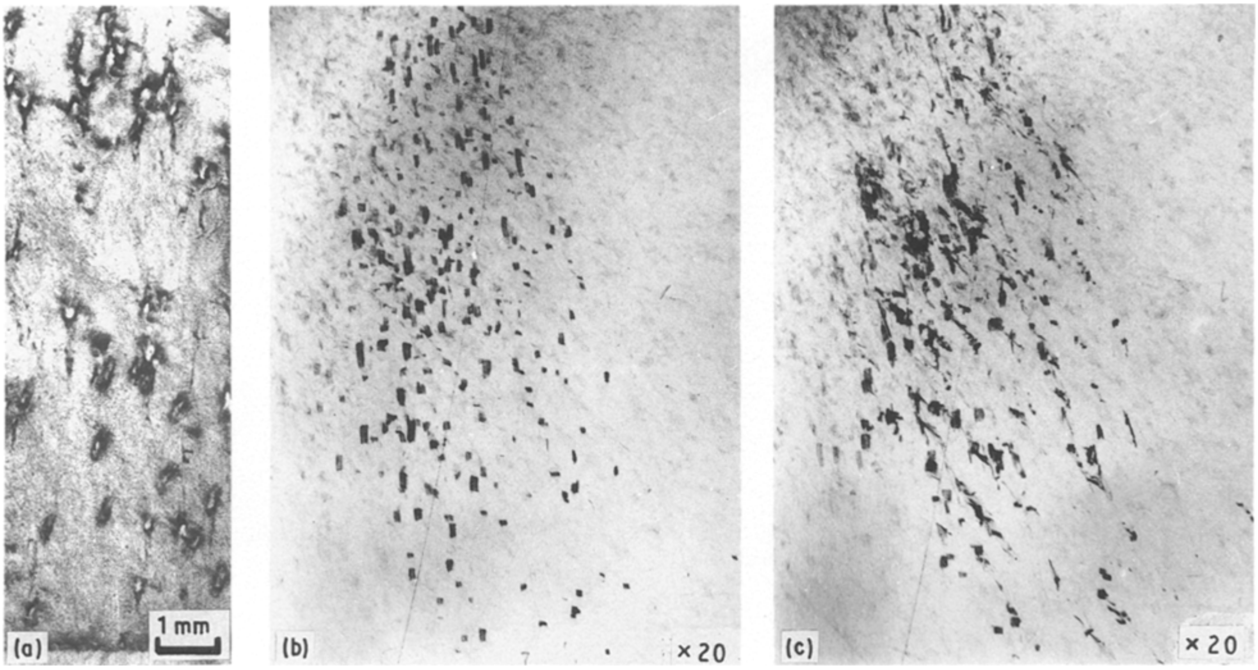

Figure 1 (a) X-ray topogram given by the single crystal in α phase from the outset of the $\alpha \rightarrow \beta$ transformation; (b) X-ray topogram given by the little β crystals from the outset of the $\alpha \rightarrow \beta$ transformation; (c) X-ray topogram given by the little β crystals when the $\alpha \rightarrow \beta$ transformation is practically achieved.

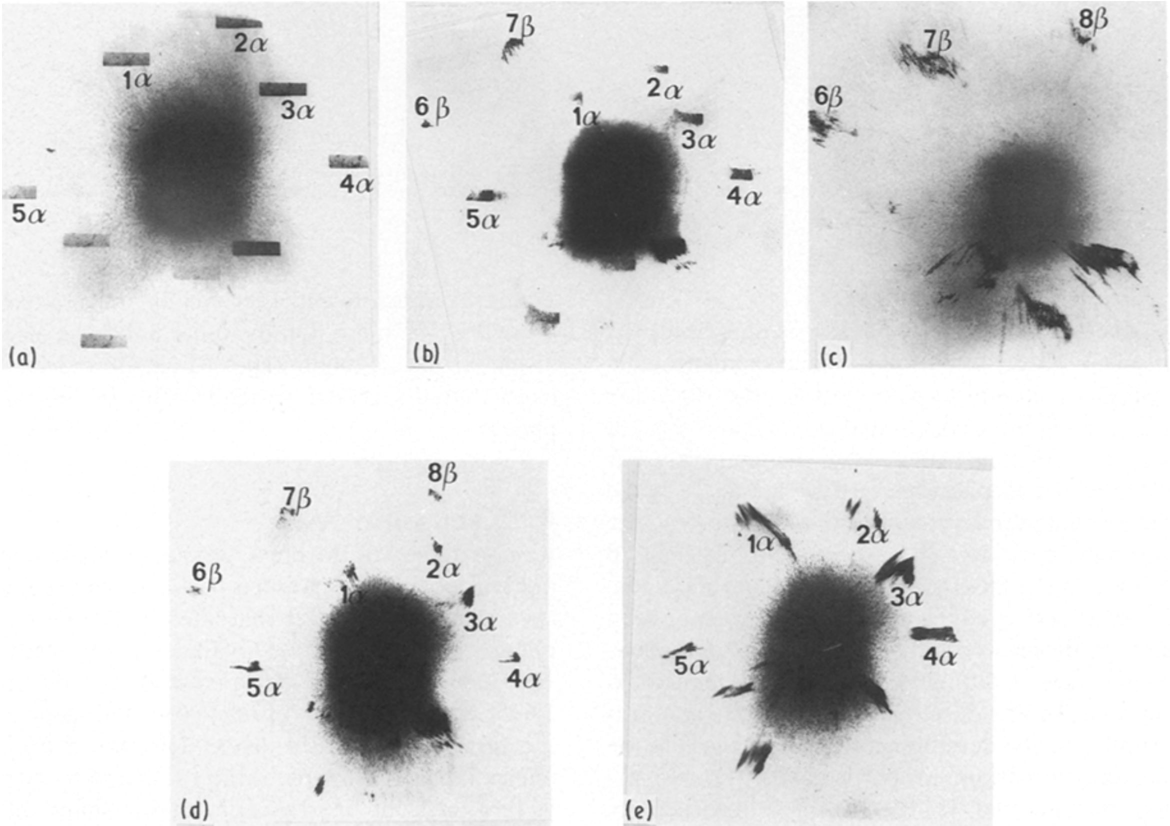

Figure 2 X-ray diffraction diagrams showing the structure evolution of an α titanium single crystal submitted to an $\alpha \rightleftharpoons \beta$ transformation. The X-ray reflections have been marked 1, . . . 8. (a) Initial state at room temperature. α spots 1, . . . 5; (b) During the $\alpha \rightarrow \beta$ transformation temperature. α spots 1, . . . 5 and β spots 6, . . . 8 are simultaneously visible; (c) At $\sim 1000\,^{\circ}\mathrm{C}$. The $\alpha \rightarrow \beta$ transformation is achieved. α diffraction spots marked 1, . . . 5 have disappeared. Only β diffraction spots marked 6, . . . 8 are visible; (d) During the $\beta \rightarrow \alpha$ reverse transformation. β (6, . . . 8) diffraction spots are visible while α ones (1. . . 5) reappeared; (e) At room temperature in α phase. Compare Fig. 1a and e.

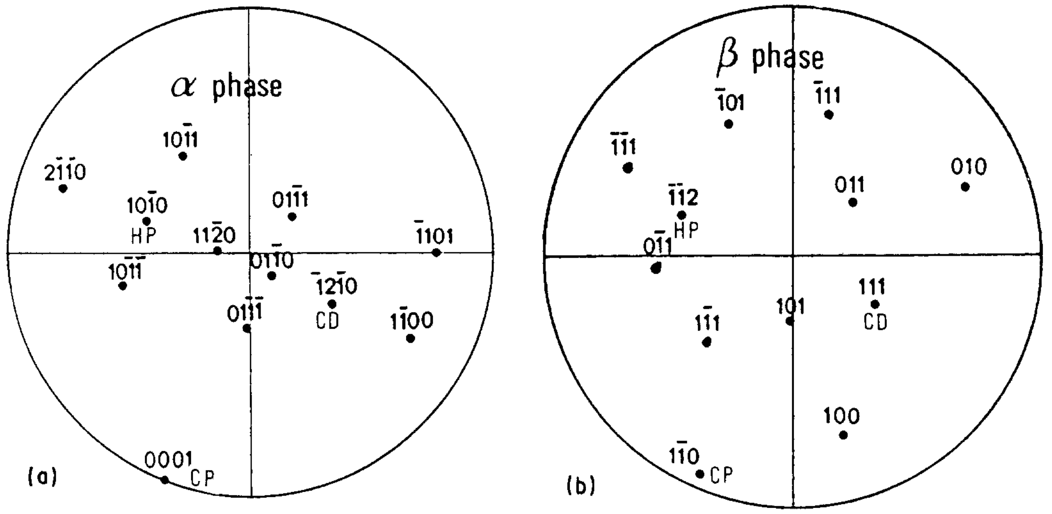

Figure 3 Stereographic projections. HP = Habit plane; CP = common plane; CD = common direction. (a) Initial state. α single crystals; (b) β "single pseudo-monocrystal". After α → β transformation.

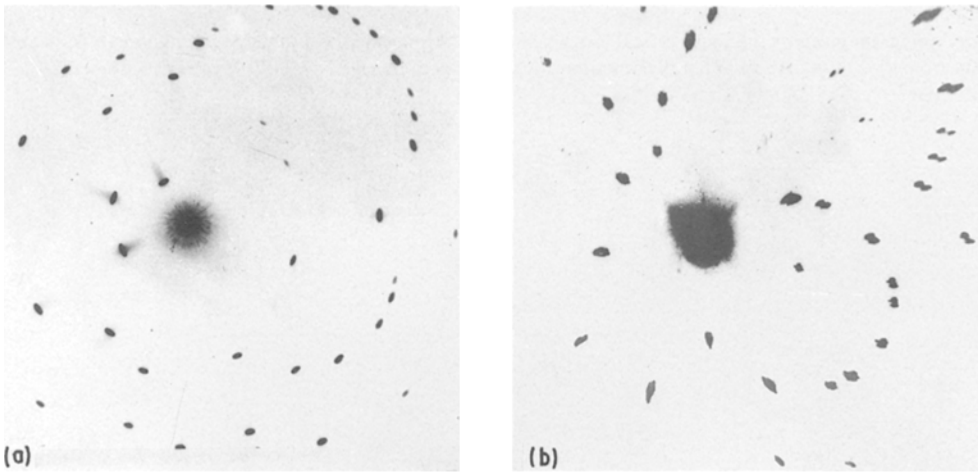

Figure 4 Orientation memory effect. (a) Laue diagram. Initial state; (b) Laue diagram. After a complete α ⇄ β transformation cycle.

3.2. 2/β → α transformation

When the high temperature phase is stabilized, the reverse β → α transformation is undertaken and, as in the previous α → β transformation, the structure evolution is followed *in situ* and in real time. Fig. 2d shows an intermediate stage when the temperature is such that the two phases are present. Fig. 2e is the diffraction diagram of the crystal when its structure wholly came back in α phase after a complete α ⇄ β cycle. Due to the fact that the β crystalline state, Fig. 2c, is not as perfect as the initial state, it has not been possible to detect where the β nucleation took place. From the new α diffraction spots, it is possible to deduce that the new development phase follows a process similar to the development of the β phase in the direct transformation. In particular, if 12 variants should be expected in the β → α transformation, Fig. 2e shows that experimentally this rule is not satisfied. As in the previous and direct transformation, we obtain a single crystal after an α ⇄ β cycle. Fig. 2e shows that after such a cycle, the crystal orientation is comparable to the single crystal orientation before cycling. This observation is confirmed with Laue diagrams taken before and after cycling at room temperature: Fig. 4a and b. On the other hand, the asterism visible in the diffraction spots, Figs 4b and 2e, indicates that the crystal structure after cycling is less perfect.

4. Discussion

Results quoted in the previous chapter show that the martensitic transformation is particular in titanium. It is surprising to discover that after an α → β or β → α phase transformation we obtain, generally, only one variant and moreover after an α ⇄ β cycle the crystal comes back to its initial orientation. This property is the result either of the nuclei selection during the nucleation process or the variant selection by extrinsic factors such as crystal orientation, shape of the sample. . . .

In previous papers, we have shown that the nucleation was triggered by the stress field associated to crystalline defects and not by their core structure [12, 13]. The heterogeneous character of the nucleation is visible in Fig. 1a although the regular distribution of nuclei in the whole crystal could be attributed to an homogeneous nucleation process. In fact, we can ascertain that the nucleation process has an heterogeneous character. Nuclei are distributed over the whole crystal and for a given temperature, owing to the low furnace gradient, some of them spread out. Martensitic transformation being a diffusionless transformation, the growth of nuclei is instantaneous and the size of the crystals of the new phase is rapidly limited by the crystal surface. In the example of Fig. 1a, if the shear plane orientation and the sample thickness are taken into account, it is easy to demonstrate that this size is limited to 200 μm. This size is well in accordance with the experimental result. At this stage the transformation is stopped. To carry on the crystal transformation, it is necessary to raise the temperature. A temperature interval of 15 °C separates the transformation start from the transformation end. The question asked is 'whether the selection of one variant results from the presence of only one nucleus type in the crystal or from the existence of extrinsic limiting factors which authorize the growth of one nucleus type only?' The X-ray topography does not allow an answer to this question. The new phase is detected only when the size of the crystals is the order of a few micrometers. But, if it can be supposed that in $\alpha \rightarrow \beta$ transformation there exists in the highly perfect single crystal a predominant family of nuclei, owing to the absence of extrinsic crystalline defects such as grain boundaries, strained regions. . . , giving a same transformation variant (the nuclei being successively activated until the transformation is achieved), we think that in the reverse transformation this assumption is highly improbable. Indeed, contrary to the $\alpha \rightarrow \beta$ transformation, in the $\beta \rightarrow \alpha$ transformation the matrix consists of numerous little strained crystals separated by low angle grain boundaries. All these crystalline defects are known to be potential nuclei centres. An hypothesis of the presence in the crystal of only one nucleus type is not realistic, other factors as now described must be taken into account:

(i) The shape of the sample may play a role in the variant selection in favouring the better oriented shear system. Effectively, among the three potential shear planes, the $(1\bar{1}00)$ and the $10\bar{1}0)$ planes, making respectively 80° and 50° with the great external surfaces, are the more probable active prismatic shear planes. So, taking the shear direction also into account, from a simple geometrical approach it is easy to demonstrate that all the variants are not equivalent and that the sample geometry operates its own selection.

(ii) After nucleation, the growth of the new phase involves the deformation of the surrounding matrix because the volume of the unit cells of the two phases are different. This effect is known as shape deformation. Generally, shape deformation is relaxed by the nucleation of new variants so that the mutual deformations are self-compensating. Then the growth of the "original" variant is frequently accompanied by the nucleation and growth of other variants. But in titanium, this effect is inoperative because the unit cell volumes are not very different and especially so because its entropy has an unusual temperature dependence [8]. Near the transformation temperature, it has been shown [17] that the C_{66} and C_{44} shear moduli, in the α phase, are the most temperature sensitive and when the decreasing of the C_{66} value is the order of 75% the C_{44} decreases by 42%. The C_{66} modulus is precisely the $\{10\bar{1}0\}\langle 11\bar{2}0\rangle$ shear system active in the $\alpha \rightarrow \beta$ transformation. Then the structural forces (shape deformation and interfacial surface energy) opposing to a phase transformation, directly related to the shear moduli, decrease rapidly at this temperature.* This effect, also observed in the $\beta \rightarrow \alpha$ transformation [19], can explain the non-multiplication of variants during the titanium transformation and the development of a sole variant in favouring the plastic accommodation of the shape strain. We think that this entropy dependence with the temperature is the preponderant factor in the variant selection.

The orientation memory effect quoted in [20, 21] is directly bound to the previous effect. It may be explained from the existence of crystalline defects common to the two structures. For example, when Burger's OR are satisfied the $\{0001\}_\alpha$ plane transforms in a $\{110\}_\beta$ plane and the $\langle 11\bar{2}0\rangle_\alpha$ direction transforms in a $\langle 111\rangle_\beta$ direction. These two directions are the Burger vector directions of perfect dislocations in α and β phase, respectively. Then, during the transformation, the Burger vector direction is not modified. We can imagine a perfect pinned dislocation common to both phases and remaining during the $\alpha \rightleftharpoons \beta$ phase transformation. If the stress field associated to this crystalline defect triggers the phase transformation, we can imagine that during the $\beta \rightarrow \alpha$ reverse transformation the initial orientation is found again.

5. Conclusion

Nucleation, orientation relationships and peculiarities of the structure evolution of large α titanium single crystals during the high temperature $\alpha \rightleftharpoons \beta$ martensitic transformation have been studied *in situ* by synchrotron X-ray topography.

Results given in this paper are representative of the structure evolutions of α titanium single crystals submitted to an $\alpha \rightleftharpoons \beta$ cycle. Due to the large crystal volume investigated, they can be considered as statistical results.

The β or α phase nucleation is heterogeneous. Even when several kinds of potential nuclei are present, as well as in the $\alpha \rightarrow \beta$ or $\beta \rightarrow \alpha$ transformation, frequently we obtain a single transformation variant. We have shown that several factors act in this direction: a small volume variation of the unit cells during the transformation, a variant selection by the geometric shape of the sample and particularly, in titanium, the relaxation of the shape deformation due to the dependence of the vibrational entropy with the temperature which induces a softening of the shear systems.

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* F. Willaime and C. Massobrio have recently studied the hcp–bcc transformation in Zr by lattice and molecular dynamics. Their results [18] confirm these results.

We think that the observed orientation memory effect is directly bound to these properties provided that some crystalline defects are common to both phases and remain during the transformation.

Finally, the most frequent orientation relationships found between the two phases are in accordance with those of Burger's.

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