Experimental observations elucidating the mechanisms of structural bcc-hcp transformations in β -Ti alloys

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The formation mechanisms of two hcp α phase morphologies in Ti-4.5Fe-6.8Mo-1.5Al have been investigated by optical microscopy (OM), atomic force microscopy (AFM), electron probe microanalysis (EPMA) and dilatometry. At relatively high temperatures primary α forms predominantly on prior bcc β grain boundaries, whereas at lower temperatures so-called bainitic α plates nucleate both at grain boundaries and intragranularly. This morphological transition with decreasing temperature is associated with a change in transformation mechanism. The combined results of EPMA, OM and dilatometry show that the growth of these bainitic α plates is partitionless, and not accompanied by a volume change. Subsequently, a posttransformation redistribution of Fe takes place, which causes a dilatation that can be modelled based on the diffusion of Fe and the interface-area density. This mechanism as well as the formed microstructure are similar to bainite in steel, and therefore we chose to denote this transformation product as bainitic α . In addition, the AFM observations on bainitic α plates show an invariant plane strain surface relief with tilt angles that are consistent with the Burgers' transformation model based on shear. In contrast, the AFM results show that the formation of primary α is accompanied by an irregular dip on a free surface, which is in agreement with the volume decrease measured using dilatometry. Furthermore, the EPMA results show that primary α is formed by a partitioning transformation. The change in transformation mechanism with decreasing temperature is supported by the observed trend in both the dilatation and the volume fraction α as a function of temperature.

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I. INTRODUCTION

The nature of structural transformations in solids is of primary importance for controlling the multiphase microstructures of metals and alloys. Over the past decades, titanium alloys have become popular because of their high strength when compared to competitive materials such as aluminium-based alloys or stainless steel.¹ The need to improve its properties is stimulated by the highly specific demands for applications in, for instance, aerospace engineering and medical engineering.^{2,3} Therefore, it is very important to enhance our understanding of phase transformations in titanium.

Titanium alloys display different types of decomposition reactions when the high-temperature β -phase (bcc) is cooled down. The kind of transformations that will occur in a Ti alloy and the temperatures at which they take place depend on the alloying elements, and Ti alloys are classified accordingly.¹ The Ti-4.5Fe-6.8Mo-1.5Al alloy studied here is a so-called metastable β Ti alloy. During cooling in air, a small fraction of the β phase decomposes to athermal ω phase by a displacive mechanism;⁴⁻⁶ for Ti-4.5Fe-6.8Mo-1.5Al this transition occurs at approximately 400 °C. Upon further annealing the athermal ω phase particles transform to isothermal ω phase according to a diffusional reaction. A decomposition of the β phase to martensite, α' , has not been reported to occur in this class of Ti alloys. In addition, the minor O and C impurities commonly found Ti alloys can result in the formation of TiC and Ti₂O. Recently, highenergy x-ray diffraction was employed to study these precipitation processes.⁷

At relatively high annealing temperatures two α phase morphologies can be formed in metastable β Ti alloys.^{11,12}

When the undercooling below the transus temperature T_{β} is small, primary α plates are formed, which are sometimes called type 2 α (Refs. 13 and 14) or normal α plates.^{15,16} These α plates are generally irregularly shaped plates, which nucleate predominantly at the prior β grain boundaries. At somewhat lower temperatures a microstructure with a different α morphology is formed, which is very similar to bainite in steels as indicated previously by other investigators.^{17,18} In line with this morphological similarity we chose to denote this α morphology in Ti alloys as bainitic α plates. The bainitic α plates are relatively perfect thin plates, which nucleate both at grain boundaries and intragranularly. Bainitic α plates are observed in many metastable β Ti alloys such as Ti-(Cr, V, Mo, Mn),^{15,16} Ti-Mo-Al, Ti-Cu-Al,¹⁷ and Ti-Mo.¹⁹ In some papers this α morphology is denoted as type 1 α (Refs. 13 and 14) or black plates.^{15,16,19} Apart from the difference in morphology and nucleation behavior of the two types of α plates, a difference in etching characteristics is observed. Bainitic α plates appear dark after etching and etched primary α plates have a white appearance when examined with optical microscopy. One of the first explanations of the origin of bainitic α plates was given by Bunshah in 1958,¹⁷ who observed that with prolonged transformation time bainitic α plates thicken and lose their blackness. Therefore, he proposed that bainitic α plates are, in fact, supersaturated α plates and consequently have a different etching characteristic from primary α plates. Then, on holding for longer time, the solute is able to diffuse from the α plates into the matrix. As a result the bainitic α plates lose their blackness as they thicken. Bunshah's explanation has not been adopted ever since. In the present paper experimental evidence is provided, which shows that the formation of bainitic α plates evolves without partitioning of alloying elements.

II. TRANSFORMATION MECHANISMS

Regarding the formation of primary α plates, it is generally accepted that the growth is controlled by volume diffusion of alloving elements ahead of the interface. Although it is well known that the growth characteristics of bainitic α plates are significantly different from primary α plates, there seems to be consensus among researchers that also bainitic α plate formation is diffusion controlled.^{15,16,18} The diffusioncontrolled model for the formation of bainitic α plates was formulated by Menon and Aaronson¹⁵ based on thermodynamical data published by Murray.²⁰ They studied the Ti-6.6Cr system and observed a discontinuity in the lengthening kinetics associated with the transition from primary α to bainitic α plates, which was explained by the existence of a miscibility gap in the phase diagram. Under this assumption, the double-inflected free energy-composition curve for the β phase results in primary α at high temperature when the α phase equilibrates with a Ti-rich β phase, while at lower temperature bainitic α plates form when the α phase equilibrates with a Cr-rich β' phase. However, Aaronson and coworkers could not find experimental evidence for the existence of a Cr-rich β' phase.

The existence of a miscibility gap in the phase diagram of some Ti based alloys has become a matter of controversy recently. For the Ti-Mo system, which is important for the present study, it has been shown by transmission electron microscopy²¹ that the miscibility gap only exists at considerably lower temperatures than proposed by Murray.²⁰ Also the miscibility gap in the Ti-Cr and the Ti-V system, which was introduced by Murray and primarily based on the work of Nakano,⁹ could not be confirmed in later investigations. Prasad and Greer¹⁰ calculated, based on the Miedema model, that the miscibility gap in Ti-Cr alloys lies at temperatures and Cr concentrations that are much lower than assumed by Menon and Aaronson.¹⁵ A systematic investigation by Fuming and Flower on both high purity and diluted Ti-V alloys showed that the miscibility gap proposed earlier was caused by oxygen impurity.⁸ A high O content lowers the free energy of the α phase and this probably caused the artifact in the earlier experiments.⁷

In the present paper we present a comprehensive study of the $\beta \rightarrow \alpha + \beta$ transformation in Ti-4.5Fe-6.8Mo-1.5Al. In order to elucidate the nature of the formation mechanism of both the primary phase (α_p) and the bainitic phase (α_b) we combine various complementary experimental techniques. The growth rate of α phase has been determined from (*ex situ*) optical microscopy (OM) experiments, in which a series of samples is isothermally annealed for increasing times. The samples are heat treated in a dilatometer in order to measure the volume changes occurring during the transformation. By quenching the samples to room temperature, the hightemperature microstructure is frozen at several stages of the transformation. The optically determined volume fraction of bainitic α as a function of time is compared with the dilatometry results, and the observations are supported by a micro-

TABLE I. Composition of Ti-4.5Fe-6.8Mo-1.5Al.

	Мо	Fe	Al	Ti
wt. %	6.7	4.3	1.5	balance
at. %	3.4	3.8	2.7	balance

structural model. In addition, atomic force microscopy (AFM) and electron probe microanalysis (EPMA) have been employed to investigate the transformation mechanisms of the two α phase morphologies in Ti-4.5Fe-6.8Mo-1.5Al.

III. EXPERIMENTAL

The commercial Ti-4.5Fe-6.8Mo-1.5Al alloy used in this study was received in the form of a rod with a diameter of 15 mm. The chemical composition of this alloy is given in Table I. The concentrations of Fe, Mo, and Al were measured with XRF. Calculations with the thermodynamical programme Thermo-calc were performed using the Ti database to determine the β transus temperature T_{β} and the T_0 temperature, the temperature at which the free energies of β Ti and α Ti, both of the nominal composition, are equal. For the alloy composition, assuming typical concentrations of the interstitial alloying elements²² 0.12 wt. % O, 0.002 wt. % N, and 0.004 wt. % C, it is calculated that T_{β} =785 °C and T_0 =635 °C.

It is important to mention that if the concentration of impurities is higher than assumed above, then the T_{β} and the T_0 temperature can be significantly higher. For example, with 0.2 wt. % O both T_{β} and T_0 are 20 °C higher than calculated above. This also implies that when the impurities are distributed inhomogeneously, the transformation characteristics can differ locally in a sample.

The dilatation of the samples as a function of temperature and time was measured using a Bähr 805A/D dilatometer. A schematic drawing of the experimental setup and a detailed description of the instrument is given by Kop et al.²³ The cylindrical samples used in the dilatometer were 10 mm long with a diameter of 5 mm. Each sample was loosely held between quartz rods, and a thermocouple was spot welded onto the middle of the sample for measuring and controlling the temperature. The typical thermal gradient in the axial direction has been determined using a second thermocouple and is less than 3 °C. In the experiments, each sample is heated to a temperature of 900 °C, solution treated for 10 min, and subsequently cooled to the holding temperature at a pressure of less than 4×10^{-5} mbar. The cooling rate between 900 °C and the holding temperature was approximately 20 °C/s, which is fast enough to prevent transformation during cooling. After the thermal heat treatment in the dilatometer, each sample was cut in halves prior to the metallographic examination.

Sample preparation of titanium can be complicated. Due to its high ductility titanium deforms and scratches easily. Hydrogen absorption during electrolytic polishing can result in preparation artifacts^{7,13} and electrolytic polishing is therefore not used. Instead samples were polished according to

the metallographic preparation procedure recommended by Struers.²⁴ The first step is plane grinding with SiC paper up to a 2400 grid finish. The plane grinding is followed by chemical-mechanical polishing with a mixture of colloidal silica (OP-S) and hydrogen peroxide. In order to reveal the microstructure after polishing the Kroll etching solution was used.

The volume fraction of bainitic α plates as a function of time has been determined by means of optical microscopy (OM) for a large number of samples interrupted at different times during the transformation. The commercial software package ANALYSIS was used to quantify the volume fraction of α and β phase. In the present paper the volume fraction of bainitic α plates as a function of time is compared to the dilatation as a function of time at 615 and 540 °C. In addition, samples have been investigated at other temperatures in the range 540 to 760 °C in order to show the distinct differences in morphology, growth characteristics, transformed fraction, and dilatation between primary α and bainitic α plates in the temperature range 700 to 760 °C is discussed in more detail in another paper.²⁵

The local chemical composition of two samples, one partially transformed to bainitic α plates at T=615 °C and the other transformed to the equilibrium volume fraction of primary α plates at T=735 °C, were investigated by means of electron probe x-ray microanalysis (EPMA). The measurements were performed with a JEOL JXA 8900R microprobe using an electron beam with an energy of 15 keV and a current of 200 nA. The composition at each analysis location of the sample was determined using the x-ray intensities of the constituent elements Ti, Mo, Fe, Al after background correction relative to the corresponding intensities of pure metal reference materials. The intensity ratios thus obtained were processed with the matrix correction program CITZAF.²⁶ The spatial resolution of EPMA is dependent on the sharpness of the x-ray intensity peak. With the settings described above the spatial distribution of the x-ray intensity has a bell shape, which can be approximated with a Lorentzian with a width at half maximum of approximately 0.5 μ m. This width can be regarded as the effective spot diameter, and the spatial resolution is assumed to have the same value. In order to obtain an accurate concentration profile line scans were performed with points taken 0.25 μ m apart.

The surface relief observations of five samples, four partially transformed to bainitic α plates at T=630, 660, 680, and 690 °C, respectively, and the other transformed to primary α plates at T=750 °C, were made by atomic force microscopy (AFM). The experiments were performed using a Veeco MultiMode scanning probe microscope (SPM) in tapping mode AFM. The AFM measurements were performed in air with a scanning speed of about 20 μ m/s. Surface scans were made with a step size of 0.02 μ m for an accurate determination of the surface relief angles.

An overview of the various experiments at different temperatures is given in Fig. 1, which shows a schematic drawing of the phase diagram. The closed squares and the closed circles indicate the temperatures for respectively EPMA and AFM measurements. Dilatometry and OM measurements have been performed at various annealing temperatures in



FIG. 1. A schematic drawing of the quasibinary Ti-Fe phase diagram showing the regions where OM and dilatometry measurements were performed. The closed squares and the closed circles indicate the temperatures for, respectively, EPMA and AFM measurements.

the range of 540–760 $^{\circ}\mathrm{C}$ with steps of approximately 10 $^{\circ}\mathrm{C}.$

IV. RESULTS AND DISCUSSION

A. Growth kinetics

Figure 2 shows the microstructure at four stages of the transformation at 615 °C. It is seen that the bainitic α plates have nucleated both at former β grain boundaries and intragranularly. Comparison with the primary α plates formed at 735 °C (Fig. 3) shows significant differences in both the morphology and the growth characteristics. Primary α plates are predominantly formed at grain boundaries, have an irregular shape and their transformation kinetics are much slower. In addition, primary α plates have a white appearance, whereas bainitic α plates appear dark after etching. The possible origin of the difference in etching characteristics will be discussed later.

Based on a number of optical micrographs it is found that the thickness of bainitic α plates is in the range of 0.1–0.6 μ m. In comparison, a primary α plate has a thickness of approximately 0.3 μ m in the initial stage of transformation [Fig. 3(a)] and approximately 4 μ m when it has grown to its final size [Fig. 3(b)]. It is noteworthy to mention that the thickness values determined in the present study are in good agreement with the thickness of the two α morphologies extracted from the microstructures observed in Ti-Cr alloys.¹⁶

The fraction curve of bainitic α plates has been determined based on the microstructure of 12 samples transformed at T=615 °C for different holding times. The volume fraction as a function of time is plotted in Fig. 4 (open squares). Analysis of the optical micrographs shows that the incubation time τ for the formation of bainitic α plates is approximately 340 s.

In addition, Fig. 4 shows the dilatation ΔL measured for a sample that is held at 615 °C (closed circles). Repeated mea-



FIG. 2. Optical micrographs showing the fraction of bainitic α plates formed at 615 °C (a) after 750 s, (b) 1080 s, (c) 1550 s, and (d) 4000 s.

surements under the same conditions showed that the dilatation measurements were highly reproducible. It is seen in Fig. 4 that no significant change in length is measured for t< 600 s. In contrast, optical microscopy shows that approximately 10 Vol % of bainitic α plates has already formed in the time interval $\tau < t < 600$ s. Figure 4 also shows that ΔL continues to increase significantly for t > 2000 s, whereas f^{α} does not increase anymore in this range. This remarkable discrepancy is seen to persist over the entire range of the transformation in a plot of dilatation against volume fraction bainitic α plates, as shown in Fig. 5 (open squares). The systematic deviation from the proportional behavior is a clear indication that ΔL is not primarily determined by f^{α} . This is also readily seen in the result for the isothermal transformation at 540 °C (open triangles), which is also plotted in Fig. 5. At this temperature the volume change during the entire transformation is approximately zero, which indicates that the atomic volume of the bainitic α plates is practically equal to the atomic volume of the β phase in which it is formed. This in its turn means that a low misfit between the lattice structures exists. The results of all measurements in the temperature range of bainitic α plate formation show that for decreasing temperatures the total dilatation decreases gradually from 5 μ m at 615 °C to zero at 540 °C, while the final volume fraction α increases from 92 to 97 vol %.



FIG. 3. The primary α plates formed at 735 °C (a) after 2100 s and (b) 100 000 s.

B. Compositional analysis

To investigate the partitioning of alloying elements during the formation of both primary and bainitic α , two samples, one partially transformed to bainitic α plates at T=615 °C and the other sample transformed to an equilibrium volume fraction of primary α plates at T=735 °C, were analyzed for composition fluctuations by EPMA. Figure 6(a) shows the result for a scan along line 2 in Fig. 3(b) across a primary α plate formed at 735 °C. For different locations in the sample transformed at T=615 °C line scans were made crossing several bainitic α plates. A typical result is shown in Fig. 6(b) for a scan as indicated by line 1 in Fig. 2(b): the microstructure after 1080 s with a volume fraction α of 44%. Figure 6(b) shows only a small elemental redistribution of Fe. In



FIG. 4. The dilatation of the sample and the volume fraction of bainitic α plates plotted against time during the isothermal transformation in Ti-4.5Fe-6.8Mo-1.5Al at 615 °C. The dashed line represents the least-squares fit through the optically determined fraction data with the JMAK equation. The solid line represents the best fit through the dilatation data with Eq. (6).



FIG. 5. The dilatation plotted against the volume fraction of bainitic α plates at 615 and 550 °C. The solid line represents the proportional behavior.

contrast, in primary α , formed by a partitioning transformation, the Fe and Mo concentrations drop to approximately 0.2 at. % as is seen in Fig. 6(a) for a line scan across a primary α plate formed at 735 °C. Therefore, it is concluded that the bainitic α plate formation is certainly not related to equilibrium conditions, and is close to partitionless. In addition, the EPMA results indicate that after the partitionless formation of a bainitic α plate some diffusion of the elements occurs, in particular Fe. The diffusion of Fe from the bainitic α plates to the β matrix causes the dilatation, and stabilizes the remaining β phase. In comparison, the elements Mo and Al do not partition significantly as is seen in Fig. 6(a), which can be well understood since the diffusivities of both Mo and Al are significantly lower than that of Fe.²⁷ Based on the temperature dependence of Fe diffusion it can be understood that both the dilatation and the volume fraction retained β phase decrease with decreasing temperature as mentioned above. It should be noted that the low misfit between the lattice structures, as indicated by dilatometry in conjunction with optical microscopy, is favorable for the partitionless transformation, i.e., it can occur at a low undercooling below T_0 .

C. Surface reliefs

Having found that the $\beta \rightarrow \alpha_b$ transformation is partitionless, we now will discuss the surface reliefs caused by both bainitic α and primary α , which have been measured using AFM. The characteristics of surface reliefs can give additional information on the transformation mechanisms of the formed phases. After polishing according to the procedures described in the section Experimental, one sample was solution treated and annealed at 630 °C for 720 s, and another sample was annealed at 750 °C for 2 h.

In Fig. 7(a) the AFM image of primary α formed at a grain boundary is shown. The surface relief along the line 1 in Fig. 7(a) is given in Fig. 7(b). It is seen that the formation of primary α phase has caused an irregular dip at the surface. This observation is consistent with the diffusional character of the transformation. Furthermore, the AFM image shows a net local volume decrease, which is in good agreement with the decrease of the sample length measured using dilatometry during the $\beta \rightarrow \alpha_p$ transformation.

The AFM image showing the reliefs due to the formation of bainitic α plates is shown in Fig. 7(c). The image shows several bainitic α plates formed near a grain boundary. It is noted that the topography measured by AFM shows a microstructure that is very similar to microstructure seen in the optical micrographs of Fig. 2. Comparison shows that in the AFM image the plates are somewhat more isolated and surrounded by β phase. An image of such a region in which bainitic α plates are isolated was chosen deliberately in order to obtain a reference surface for the relief measurements. Figure 7(d) shows a line scan across five bainitic α plates as indicated by line 2 in Fig. 7(c). For each plate the relief angle is measured and the values are given in the figure. It is seen



FIG. 6. The Mo, Fe, and Al concentration profile (a) along path (2) in Fig. 3(b) across one primary α plate formed at 735 °C, (b) along path (1) in Fig. 2(b) across several bainitic α plates formed at 615 °C. The inaccuracy in the measured concentration of each element is ±0.1 at. %, which is very small in comparison to the absolute measured values. In order not to obstruct the clarity of the plots, error bars are only shown for one data point in the concentration profile of each element.



FIG. 7. (a) AFM image showing the surface relief due to primary α phase formed at 750 °C, (b) AFM scan along path (1) in (a), (c) AFM image showing the surface reliefs due to the formation of bainitic α plates at 630 °C, and (d) surface profile along path (2) in (c) of the IPS surface reliefs.

that for each plate in this group of parallel plates formed in the same β grain, the relief angle is approximately the same. This indicates that the plates have the same crystallographic orientation.

In 1934 Burgers²⁹ reported the orientation relationship (OR) between bcc Zr and hcp Zr, and proposed that the bcc-hcp transformation can be described by a shear mechanism. Some years later, this so-called Burgers OR was confirmed to hold also for the bcc-hcp transformation in Ti.³⁰ From Burgers' work it can be deduced that the maximum relief angle that can be observed at a free surface using AFM is 10.5° .³¹ This angle can only be observed when the habit plane of a bainitic α plate is perpendicular to the free surface.

The linescan in Fig. 7(d) shows that the surface profile is nearly perfectly linear at the position where a bainitic α plate intersects with the free surface. From the linescan it can be determined that the relief angle is 9.6°, and that the thickness of a bainitic α plate is approximately 0.2 μ m, which is in good agreement with OM observations. In the β matrix surrounding the plates the surface profile is much more irregular. This indicates that some plastic deformation in the β phase occurred to accommodate the shape strain due to the transformation.

For many bainitic α plates on a number of samples the relief angle was measured. In Fig. 8 the surface profiles of samples transformed at 660, 680, and 690 °C are shown. The results are very similar to the IPS surface reliefs shown in

Fig. 7(d), and also in this figure it is seen that each plate in a group of neighboring plates formed in the same β grain has approximately the same relief angle. From the analysis of bainitic α plates in all samples the maximum relief angle was found to be 10.1°, which is in good agreement with the maximum angle predicted on the basis of the Burgers OR.

The surface reliefs due to the formation of bainitic α discussed above are similar to the reliefs due to the formation of martensite in Ti systems,³¹ Fe-based alloys,³² and other systems.³³ Based on this analogy it is concluded that the transformation from β phase to bainitic α involves an invariant plane strain with a shear and dilatational component, which indicates that the transformation is displacive. It is noted that the dilatational component of the IPS is not accounted for in the present analysis, which is justified because the results of dilatometry showed that the volume change accompanying the transformation is very small. It is also interesting to mention that the results are in good agreement with the displacements caused by the formation of bainite in steel.^{34,35}

In addition to the transformation mechanism and the corresponding surface reliefs, the AFM observations provide also information about the typical thickness of bainitic α plates. In comparison to optical microscopy, AFM does not require etching to make the microstructure visible for analysis. Consequently, the possible influence of etching on the appearance of bainitic α plates is circumvented by using



FIG. 8. AFM line scans showing IPS surface reliefs due to the formation of bainitic α plates formed at (a) 660 °C, (b) 680 °C, and (c) 690 °C.

AFM. On the other hand, by using AFM the kinetics of bainitic α plates near a free surface are probed, which can be different from the bulk. It has been reported that the degree of transformation near the surface is more advanced than in the interior of a titanium specimen.³⁶ Most probably this is related to oxygen contamination occurring during processing. Since oxygen has a stabilizing effect on the α phase, the transformation temperatures T_{β} and T_0 near a surface can be higher than for the interior. Measurements have shown that both T_{β} and T_{0} are approximately 50 °C higher near a free surface compared to the calculated values for the bulk. This means that observations of the transformation kinetics occurring near a surface can not readily be compared to observations of the transformation in the bulk. The AFM results in Fig. 8 show that bainitic α plates with a thickness of approximately 0.5 µm are formed at 690 °C. Apparently, the thickness of α_b plates increases with increasing annealing temperature. These results are in good agreement with the results obtained by optical microscopy.

D. Etching characteristics

In order to show that bainitic and primary α plates appear different after etching even when they have approximately the same thickness, a two-step annealing treatment was applied to a single sample in order to obtain a microstructure with both primary and bainitic α plates. The main advantage of such an investigation of both α morphologies in a single sample is that the possible influence of sample preparation or etching time on the etching characteristics can be minimized. In this two-step treatment using the dilatometer the sample was first annealed at 730 °C for 2400 s during which primary α phase is formed predominantly at grain boundaries (see Fig. 9). Subsequently, the transformation to primary α plates was interrupted by quenching to 620 °C. During the second annealing at 620 °C for 900 s bainitic α plates are formed, mainly intragranularly. In Fig. 9 it is seen that at some locations the primary α phase (white) has a thickness of less than 1 μ m, which comparable to the size of a typical bainitic α plate (dark). This illustrates that a distinct difference in etching characteristics exists between primary and bainitic α plates, independent of the thickness of the two α morphologies.

Based on the experimental results discussed above, it is argued that the dark etching of bainitic α plates can not be

explained by the fact that they are unresolvably thin as proposed elsewhere.³⁷ Instead, the differences in etching are probably a consequence of differences in chemical composition between bainitic α plates and primary α plates as discussed below and already suggested by Bunshah many years ago.¹⁷

E. Similarities with bainite in steel

Not only do similarities exist between the microstructure of bainitic α plates in Ti and bainitic ferrite in steel as mentioned earlier, also a similar controversy exists in the steel community regarding the formation mechanism of bainitic ferrite. The debate between the two schools of thought, the displacive school and the diffusional school, is ongoing since the discovery of bainite by Bain in the 1930s. Titanium alloys have been studied much less extensively than steel and the most recent literature on titanium seems to suggest that



FIG. 9. Microstructure with both primary and bainitic α plates, which is obtained after a two-step annealing treatment. The primary α plates observed at the grain boundaries are formed at 730 °C in 2400 s. The transformation to primary α phase is interrupted by quenching to 620 °C. Subsequently, the bainitic α plates are formed during the second annealing at 620 °C in 900 s.

the diffusional interpretation is widely accepted although it can not explain all experimental observations as discussed earlier. In the present paper the diffusional interpretation is counteracted and the experimental evidence shown above indicates that the formation of bainite in titanium is displacive. This transformation behaviour of the supersaturated bainitic α plates is very similar to the displacive transformation mechanism of bainitic ferrite in carbon steel.²⁸ In the displacive school of thought it is assumed that bainitic ferrite is formed diffusionless and that subsequently carbon escapes from the supersaturated ferrite. Thus this transformation model concerns two processes: a lattice transformation and partitioning of carbon. In contrast, in the diffusion-controlled transformation model the diffusion of carbon ahead of the interface controls the lattice transformation. The fast diffusion of carbon makes the displacive transformation model difficult to prove. In the metastable β Ti alloy studied in the present paper, however, the diffusion of Fe is much slower and therefore the supersaturated bainitic α plates can be retained at room temperature when the transformation is interrupted. It has been shown that the Fe content in bainitic α plates is somewhat lower than the overall Fe concentration, which indicates that a phase transformation can, in principle, evolve via a lattice change without diffusion and subsequently a post-transformation diffusion of an alloving element. We believe that the observations of bainite in titanium can help to enhance our understanding of bainite in steel.

F. Modeling of the dilatation signal

Having argued that the dilatation observed is not due to the transformation itself but is related to the Fe partitioning, we will now try and build a quantitative model to describe the observed kinetics. The rate of partitioning of Fe after the partitionless formation of bainitic α plates is controlled by the diffusion of Fe in the β phase.²⁷ The redistribution of Fe changes the atomic volume of both the α and the β phase. It is known that the escape of Fe from the supersaturated bainitic α plates results in an increase of the atomic volume of the α phase. The simultaneous enrichment of Fe in the β phase decreases the atomic volume of the β phase. Unfortunately, there are no quantitative literature data for the Ti-Fe system about the dependence of the β and α atomic volume on the concentration Fe. Presumably, as in Ti-Mo (Refs. 20 and 38) and Ti-V (Ref. 38) systems, and as indicated by the expansion of the sample, the dependence of the atomic volume on the Fe concentration is stronger for the α phase than for the β phase.

Now a model is developed that can describe the measured dilatation signal quantitatively. First, the simple case of Fe diffusion from one bainitic α plate in a semi-infinite medium will be described. Subsequently, the Fe partitioning process will be linked to the measured dilatation, and an expression will be derived describing the time dependence of the partitioning process for a system in which a large number of bainitic α plates have been formed at the same time. Finally, the model will be related to the actual time dependence of bainitic α plate formation.

Consider that a supersaturated bainitic α plate has been formed partitionless, at $t=\tau$, in an infinite medium. The time required for the Fe concentration to reach the equilibrium concentration at each side of the interface is defined as the delay time t_d of the process. The concentration of Fe in the β phase at a distance x from the interface C_x at time t is given by

$$\frac{C_x - C_0}{C_i - C_0} = 1 - \operatorname{erf}\left(\frac{x}{2\sqrt{D(t - t_d - \tau)}}\right) \tag{1}$$

with *D* the diffusion coefficient of Fe in the β phase, C_i the concentration at the interface, which has a constant value, and C_0 the bulk concentration. Evidently, the concentration profile given by Eq. (1) scales with $\sqrt{D(t-t_d-\tau)}$, and the total amount of Fe partitioning from α to β is therefore proportional to $\sqrt{D(t-t_d-\tau)}$, which can be regarded as the average diffusion length \overline{x} .

The change of the average atomic volume of a bainitic α plate and of its surrounding β matrix is proportional to the partitioning of Fe, and thus proportional to \bar{x} . The measured dilatation ΔL of the sample is the macroscopic result of the partitioning of Fe from all bainitic α plates to the neighboring β matrix. In order to account for overlapping diffusion fields, a boundary condition is introduced that limits the change of \bar{x} with time; \bar{x} has a maximum value \bar{x}_{f} that is reflected in dilatometry by L_{f} , the final length of the sample. Generally, the fraction of the partitioning process f^{Fe} can be written as

$$f^{\rm Fe} = \frac{\overline{x}(t)}{\overline{x}_{\rm f}} = \frac{L(t) - L_0}{L_{\rm f} - L_0} = \frac{\Delta L}{\Delta L_{\rm max}}$$
(2)

with L_0 the initial length.

It is assumed that the change in depleted/enriched volume fraction with time is proportional to $(1-f^{\text{Fe}})$ (the remaining volume fraction available for depletion/enrichment of Fe), χ (the interface area per unit volume) and a characteristic velocity $\sqrt{D/(t-t_d-\tau)}$, leading to

$$\frac{df^{\rm Fe}}{dt} = (1 - f^{\rm Fe})\chi \sqrt{\frac{D}{(t - t_d - \tau)}}.$$
(3)

Integrating Eq. (3) from 0 to t gives

$$f^{\text{Fe}} = 1 - \exp[-2\chi\sqrt{D(t - t_d - \tau)}].$$
 (4)

One can readily see that this expression for the depleted/ enriched volume fraction obeys the boundary condition mentioned earlier: f^{Fe} approaches unity as $t \rightarrow \infty$, i.e., in the final stage of the partitioning process.

It should be remembered that equation Eq. (4) is only valid for the case that at $t=\tau$ all bainitic α plates are formed instantaneously. Therefore, Eq. (4) needs to be modified to account for the increasing number of bainitic α plates playing a role when the transformation progresses. The volume fraction of bainitic α plates as a function of time has been experimentally determined by optical microscopy, and can be mathematically described by

$$f^{\alpha}(t) = f^{\alpha}_{\text{final}} \{1 - \exp[-k^n(t-\tau)^n]\}$$
(5)

with *n* the rate coefficient, *k* the rate constant, τ the incubation time of the transformation, and $f_{\text{final}}^{\alpha}$ the final volume

fraction observed by optical microscopy. In Fig. 4, the dotted line through the optically determined fraction data represents the least-squares fit of Eq. (5).

By using Eq. (5) as a prefactor to Eq. (4), the dilatation of the sample due to the post-transformation Fe diffusion can be written as

$$f^{\text{Fe}} = \frac{\Delta L}{\Delta L_{\text{max}}} = \{1 - \exp[-k^n (t - \tau)^n]\}$$
$$\times \{1 - \exp[-2\chi \sqrt{D(t - \tau - t_d)}]\}. \tag{6}$$

The solid line in Fig. 4 shows that the dilatation data as a function of time *t* can be fitted to Eq. (6) with good accuracy. From the least-squares fit with $D=4.9 \times 10^{-16} \text{ m}^2/\text{s}$ for Fe in the β phase²⁷ it follows that $\chi=1.5 \times 10^6 \text{ m}^{-1}$, $t_d=460 \text{ s}$, $\tau=340 \text{ s}$, n=2.2, and $k=1.2 \times 10^{-3} \text{ s}^{-1}$.

The value found for the interface-area density $\chi = 1.5 \times 10^6 \text{ m}^{-1}$, means that on average 7.5 bainitic α plates form in a cube of $10 \times 10 \times 10 \ \mu\text{m}^3$. This is in good agreement with the actual number of bainitic α plates per 100 $\ \mu\text{m}^2$ as seen in the micrographs (see Fig. 2).

The measured relative dilatation of approximately 5×10^{-4} is the net result of an increase of the atomic volume of the α phase due to depletion of Fe, and a decrease of the atomic volume of the β phase due to enrichment of Fe. It is known that due to enrichment of Fe in the β phase the lattice parameter decreases approximately 0.3%/at. % Fe;²⁰ for the simultaneous increase of the lattice parameter of the α phase due to depletion of Fe the dependence is estimated somewhat stronger, 0.4%/at. % Fe. Due to partitioning, the Fe increase in the β phase is $f^{\alpha}/(1-f^{\alpha})$ times the Fe decrease in the α phase. Then it can be calculated that the Fe-decrease in the α phase is approximately 0.5at.%, which is a realistic value and in fair agreement with the concentration profile shown in Fig. 6(a).

G. The transition from primary α plates to bainitic α plates

In the previous sections it has been shown that bainitic α plates form without partitioning, and that subsequently Fe diffuses from the supersaturated α plates, which causes the measured positive dilatation of the sample. In contrast, the formation of primary α plates is diffusion controlled and accompanied by a negative dilatation.²⁵ Apparently, when all alloying elements (Fe, Mo, and Al) partition during the reconstructive growth of primary α phase a net decrease in volume occurs. On the other hand, Fe partitioning causes a positive change in volume. This indicates that when primary α phase is formed the volume change due to partitioning of Mo and Al is dominating, which results in a net decrease in volume. In this section the transition from primary α plates to bainitic α plates will be studied in more detail. The results of both the dilatation and the volume fraction of α phase as a function of temperature are discussed.

For a large number of samples the dilatation has been measured during the isothermal $\beta \rightarrow \alpha + \beta$ transformation in the temperature range 540–760 °C. The total length change as a function of isothermal transformation temperature is plotted in Fig. 10(a). A gradual transition from negative to



FIG. 10. (a) The total dilatation measured during the β to α transformation and (b) the volume fraction of α as a function of temperature; the solid line represents the calculated fraction and the filled circles are the measured values.

positive dilatation is seen with decreasing temperature. This dependence on temperature is strange compared to results obtained for other metal alloys in which the high temperature phase decomposes in the two-phase region. Normally, the total dilatation increases or decreases monotonically with decreasing transformation temperature since the volume fraction of product phase increases. With decreasing temperatures below 700 down to 630 °C the dilatation changes from negative to positive because primary α phase is formed by a diffusional mechanism, in which alloying elements partition, whereas the bainitic α phase formed at lower temperatures grows according to a displacive mechanism without compositional changes. This is supported by metallographic analysis of samples transformed in this temperature range. It should be noted that the observed trend in the dilatation signal can only be understood on the basis of a change in the transformation mechanism of the α phase. If, on the other hand, it is assumed that bainitic α plates are formed by a diffusion-controlled mechanism, the chemical composition of the bainitic α plates would be approximately the same as that of the primary α plates, and the dilatation would be negative too. Below approximately 620 °C the dilatation again decreases because the diffusivity of Fe decreases. When the diffusion of Fe becomes much slower than the partitionless growth rate of bainitic α plates, stabilization of the remaining β phase cannot occur. Consequently, the volume fraction retained β phase and the dilatation decrease with decreasing temperature.

In addition to the dilatation, the volume fraction α was determined from the micrographs and is plotted in Fig. 10(b). The predicted volume fraction based on thermodynamical calculations using THERMO-CALC is also plotted in this figure. It is seen that the β transus temperature calculated using THERMO-CALC, yielding T_{β} =785 °C, is in good agreement with experimental results. This indicates that the Ti database gives reliable results for the studied alloy composition with estimated O, N, and C concentrations. For temperatures above 700 °C the measured fraction values agree well with calculated values. However, from 700 down to 630 °C the measured volume fraction increases strongly from 30 to 90 %, whereas the calculated fraction gradually increases to only 50%. This trend reflects the transition from diffusion-controlled to partitionless formation of the α phase.

V. CONCLUSIONS

The concentration profiles measured by EPMA show that the growth of bainitic α plates occurs without partitioning of alloying elements. In addition, the AFM measurements show that the formation of bainitic α plates involves a IPS shape change, which means that the lattice transformation is displacive. The results of dilatometry in conjunction with optical microscopy indicate that the atomic volumes of the decomposing β phase and the formed supersaturated bainitic α plates are approximately equal. This means that a low misfit between the lattice structures exists, which is favourable for a partitionless transformation. For relatively high transformation temperatures Fe diffuses from the bainitic α plates to the β matrix, which causes dilatation effects. Furthermore, the Fe redistribution stabilizes the remaining β phase. Due to the

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temperature dependence of Fe diffusion, the dilatation and the volume fraction β decrease for lower transformation temperatures. The measured dilatation signal can be modelled based on the diffusion of Fe and the interface-area density. In view of both the partitionless growth and post-transformation diffusion, bainitic α plates can be regarded as the titanium counterpart of bainite in steels.

In contrast to the bainitic α plates, the EPMA results show that the primary α plates formed above 700 °C grow by a diffusion-controlled mechanism. Metallographic analysis shows that with decreasing temperature the primary α plates are gradually replaced by bainitic α plates. The trend in both the dilatation and the volume fraction α as a function of temperature indicates that the morphological transition is associated with a change in transformation mechanism.

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