Precipitation Behavior of O Phase during Continuous Cooling of Ti-22Al-25Nb Alloy

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Abstract: The microstructure evolution and formation mechanism of the O phase in a Ti-22Al-25Nb (at.%) orthorhombic alloy resulting from different cooling rates were investigated. The results show that the morphology of the precipitated O phase is significantly affected by the cooling rate. As the cooling rate decreases, the floccular O, composed of many fine acicular O phases, gradually grows into the lamellar O phase. When the alloy is cooled from the B2 phase region, the grain boundary O (OGB) preferentially nucleates at the triple junctions and grain boundaries and forms the flat and the zig-zag OGB according to different cooling rates. The OGB consists of separated, flat OGB parts and unconnected, zig-zag OGB composed of multiple short, separated, flat OGB at a higher cooling rate. The zig-zag OGB presents a connected state due to the sufficient diffusion time at a lower cooling rate. When the alloy is cooled from the (B2 + α2) phase region, the increase of the phase boundary provides favorable conditions for the nucleation of the O phase due to the presence of α2 particles. The precipitated rim O phase appears on the periphery of the α2 particles at lower cooling rates. The analysis indicates that the Widmanstätten intragranular O (OIG) precipitated directly from the B2 phase maintains the plane relationship with the parent B2 phase, and the Widmanstätten grain boundary O (OGB) holds the specific orientation relationship with one of the two adjacent B2 grains. The OGB keeps the specific orientation relationship with one of the B2 grains as much as possible. When it cannot maintain the specific orientation relationship with one of the B2 grains, the OGB maintains a near-orientation relationship with B2 grains on both sides to reduce the nucleation activation energy. Moreover, there can be more than one nucleation site for the O phase on a single B2 grain boundary to form the OGB. The rim O phase formed through a decomposition reaction of α2 → α2 (Nb-lean) + O (Nb-rich) is controlled by a diffusional mechanism and maintains a specific orientation relationship, i.e., <001>O//<0001>α2 and <110>α2//<1120>α2, with the parent α2 particles.

Keywords: Ti-22Al-25Nb alloy; cooling rate; microstructure evolution; O phase formation; orientation relationship

1. Introduction

With the development of aerospace technology, more stringent requirements are being imposed on the high-temperature service performance of aeroengine materials. The orthorhombic Ti2AlNb-based alloys (titanium aluminides containing the O phase), discovered in the late 1980s by Banerjee [1], have received considerable attention and interest as potential advanced aerospace and elevated-temperature structural materials due to their low density, high specific strength, good creep resistance and elevated temperature strength [2–4]. Ti-22Al-25Nb (at.%) alloy, as one of the typical second-generation...
orthorhombic Ti$_2$AlNb-based alloys, has a superior balance combination of strength, room temperature ductility and fracture toughness [5,6]. It can be used for long periods of service at 650 °C to 750 °C or for short periods of service at higher temperatures. Therefore, many studies related to the Ti-22Al-25Nb alloy, such as studies of its phase transformation, microstructure evolution and the relationship between microstructure and mechanical properties, have been conducted by various researchers [7–9].

As a Ti-Al-Nb ternary alloy, the Ti-22Al-25Nb alloy mainly contains three different phases: the B2 phase as an ordered, body-centered cubic phase; the α$_2$ phase as a hexagonal, close-packed (base on Ti$_3$Al) phase; and the O phase as an orthorhombic (based on Ti$_2$AlNb) phase [10]. Due to the diversity of microstructures and the complexity of phase transformation, the microstructure and mechanical properties of the orthorhombic alloys are very sensitive to heat treatment. Boehlert [11] proposed that the ordered fully B2 microstructure exhibited room temperature strength up to 672 MPa and low elongations (<0.6 pct), and the ordered fully O (orthorhombic phase) microstructure exhibited intermediate strength (<704 MPa) and ε$_f$ (<1 pct). It was also found that fine O lamellae precipitated during aging provided significant strengthening for Ti-12Al-38Nb, and the (O + B2) microstructure exhibited better tensile property with strength up to 1125 MPa and large elongations (>12 pct). Zheng et al. [12] investigated the effect of three lamellar O of different sizes on tensile properties and found that fine acicular O precipitated during aging treatment improves the tensile strength (1057 MPa) in Ti-22Al-25Nb alloy. Wang et al. [13,14] investigated the mechanical properties of designed bimodal lamellar O + B2 microstructure, equiaxed O/α$_2$ + B2 microstructure and duplex microstructure. They reported tensile strengths of 1066 MPa–1172 MPa, 1050 MPa and 1111 MPa for lamellar microstructure, equiaxed microstructure and duplex microstructure, respectively. The morphology and formation mechanism of the O phase has always been an issue of concern to the scientific community. Previous investigations revealed that there are three possible transformation paths to form the O phase: (I) α$_2$→O, (II) B2→O and (III) α$_2$ + B2→O. For the first path, Muraleedharan et al. [15] investigated the α$_2$-to-O transformation in Ti-28.5Al-13Nb (at.%) and found the transformation of α$_2$→O is accomplished by a lattice distortion and a small composition change. Wu et al. [16] found the formation of the O phase is due to the niobium diffusion of the α$_2$ phase, which separates into niobium-lean and niobium-rich regions in Ti-24Al-14Nb-3V-0.5Mo (at.%). Wang et al. [17] investigated the formation mechanism of the fine, plate-like O phases within α$_2$-phases and the tensile behavior of an isothermally forged Ti-22Al-25Nb (at.%) orthorhombic alloy at 1040 °C during heat treatment, and they found the equiaxed α$_2$-phase was not stable and decomposed into O + α$_2$ phases. For the second path, Sadi et al. [18] found that the unit cell of the O phase can be directly derived from that of the B2 phase by a systematic TEM investigation in Ti-25Al-25Nb, Ti-22Al-28Nb and Ti-22Al-22Nb. Bendersky et al. [19,20] predicted there should be several possible decomposition paths of the β phase with the A2 (b.c.c.) symmetry. They lead to the same O phase but with different types and hierarchy of domain interfaces at room temperature. Muraleedharan et al. [21] found that the transformation of B2→O takes place in the temperature range at which the orthorhombic phase is stable and does not give rise to a change in composition; for this reason, the author concluded a massive transformation. Wei et al. [22] found that under the condition of B2 slow-cooling aging, there are two kinds of nucleation mechanisms of the O phase from the B2 grain boundary, i.e., sympathetic nucleation and interface instability nucleation. For the third path, according to research by Muraleedharan and coworkers [23], the O phase can be formed at the B2/α$_2$ interface by the eutectoid reaction in a Ti-24Al-15Nb alloy. As mentioned above, the properties of the Ti$_2$AlNb-based alloy are extremely sensitive to changes in the microstructure, which mainly depend on the thermomechanical treatment process parameters, especially the cooling rate during heat treatment. Therefore, it is essential to investigate the microstructure evolution of Ti-22Al-25Nb under different cooling rates during heat treatment. However, for a Ti-22Al-25Nb alloy, there is seldom systemic investigation that focuses on microstructure evolution and phase transformation during a continuous cooling process [24].
This paper reports research on microstructure evolution and the formation of the O phase of a Ti-22Al-25Nb (at.%) alloy cooled from different phase regions through accurate controlling of the cooling rate. The primary objective of this work is to investigate the formation mechanism of the precipitated O from the analysis of the morphological characteristics and orientation relationship with the parent phase. This information will be beneficial to obtain a better microstructure in practical production.

2. Materials and Experimental Procedure

The alloy with a nominal composition of Ti-22Al-25Nb (at.%) was provided by Central Iron and Steel Research Institute (CISRI, Beijing, China) as a bar, and its chemical composition was determined by inductively coupled plasma atomic emission spectrometry (ICP-AES) as shown in Table 1. The bar was isothermally forged to a pancake with a diameter of 350 mm and a height of 40 mm at 960 °C (O + B2 phase regions). The microstructure of the alloy after isothermal forging is shown in Figure 1. The B2 transus temperature of the Ti-22Al-25Nb alloy was 1060 °C as determined by metallographic observations. It can be seen from the light microscopy (LM) image (Figure 1a) that the microstructure of the alloy after isothermal forging consists of the equiaxed $\alpha_2$/O particles, lamellar O and B2 matrix. The distribution of the equiaxed $\alpha_2$/O particles is random and homogeneous. Figure 1b presents the scanning electron microscope image of the as-received material. The dark regions represent $\alpha_2$ phases, the gray regions represent O phases and the light regions represent B2 phases in backscattered electron (BSE) mode. Continuous cooling specimens were cut from the pancake using a low-speed wire electrical discharge machine (DK7732HB, Posittec Equipment, Suzhou, China). The surface of each specimen was cut by lathe with a final dimension of Φ4 mm × 10 mm. A series of heat treatments were conducted in Bähr DIL805 A/D equipment (TA Instruments, New Castle, DE, USA), which is a high-precision differential dilatometer. In the following experiments, the specimens were heated to 1100 °C and 1020 °C at a rate of 50 °C/s for 20 min and then cooled to room temperature at different rates (0.1 °C/s, 0.4 °C/s, 1 °C/s, 4 °C/s and 10 °C/s). In order to better observe the changes in microstructure evolution and phase transformation, the specimens were sectioned in half at the location of the middle length, prepared through conventional metallographic techniques, i.e., the specimens were first coarsely ground on a metallographic pre-grinder with 80# metallographic sandpaper, then finely ground with 1000# metallographic sandpaper and finally polished with silica polishing agent (the dimension of the silica polishing agent is 0.05 microns) to reach the mirror surface. They were then etched with a corrosive of 11% HF, 33% HNO$_3$ and 56% H$_2$O in volume fraction. The microstructural evolution and phase morphologies of the alloy were examined using light microscopy (LM, OLYMPUS/PMG3, Olympus Corporation, Tokyo, Japan) and scanning electron microscope (SEM, ZEISS SUPRA55, Carl Zeiss AG, Jena, Germany) with backscattered electron (BSE) mode. The phase identification of the Ti-22Al-25Nb alloy under different cooling rates was made by X-ray diffraction (XRD, PANalytical X’Pert PRO, PANalytical B. V, Almelo, Netherlands) analysis through filtered Cu-Kα radiation. The diffraction angle (2θ) ranges from 30° to 80°. The XRD data were analyzed using Jade 6.0 software (Materials Data, Newtown Square, PA, USA). The orientation analysis was carried out by electron backscattered diffraction (EBSD) equipment installed on the Helios NanoLab G3 dual-beam electron microscope (FEI Company, Hillsboro, OR, USA). The specimens for EBSD testing were prepared via electrolytic polishing without etching. The components of the electrolyte were 10% perchloric acid, 35% n-butyl alcohol and 55% methanol in volume fraction. The electrolytic polishing process lasted for 40 sec at a voltage of 40 V and a current of under 1 A at 15 °C. During the EBSD testing, the samples were placed on a 70° sample stage. The step size, testing voltage and current of the EBSD analysis were 0.1 μm, 20kV and 6.4 nA, respectively. The micrographs were analyzed using a quantitative metallographic image analysis system (Image-Pro Plus 6 software, Media Cybernetics, Rockville, MD, USA) to measure the size of the precipitates.
The microhardness testing was performed at 5 different locations on each specimen with an HY-1000A microhardness tester. The loading weight and holding time for each testing location was 200 g and 15 s.

Table 1. Chemical composition of Ti-22Al-25Nb alloy.

|       | Al (at.% (wt. %)) | Nb (at.% (wt. %)) | O (ppm) | N (ppm) | H (ppm) | Ti       |
|-------|-------------------|-------------------|----------|----------|----------|----------|
|       | 22.3 (10.9)       | 25.7 (43.6)       | 430      | 52       | 9        | Bal.     |

Figure 1. Microstructure of the as-received Ti-22Al-25Nb alloy: (a) LM, (b) SEM.

3. Results and Discussion
3.1. The Effect of Cooling Rate on the Microstructure of Precipitated O Phase
3.1.1. The Effect of Cooling Rate on Microstructure following Heating at B2 Region

The light microscopic observations of the Ti-22Al-25Nb alloy cooled at different rates after solution treatment at 1100 °C are shown in Figure 2. As seen from Figure 2, the microstructure morphology has gone through a series of significant changes, which revealed that microstructural evolution is greatly affected by the cooling rates. The specimens cooled at 10 °C/s and 4 °C/s (Figure 2a,b) show the retention of the high-temperature β/B2 phase, in which the β phase is a disordered bcc phase and the B2 phase is an ordered cubic phase. Hagiwara et al. [25] found that the high-temperature single phase of a Ti-22Al-27Nb alloy at homogenization temperature (1200 °C) already turned to an ordered state, and this state can be maintained by quench. Thus, we considered the high-temperature phase retained by rapid cooling in our work as an ordered B2 phase. Based on Ref. [8], the types of phases were determined as shown in Figure 2f. The XRD pattern and metallographic images show that no second phase precipitated at the grain boundary or interior of the B2 phase. Huang et al. [24] discovered a similar phenomenon in a Ti-22Al-25Nb alloy subjected to solution treated at 1100 °C followed by water quenching. They proposed that rapid cooling suppresses the transformation related to long-range diffusion. According to the Ti-22Al-xNb alloy diagram depicted by Raghavan [26], the window for phase transformation to form a new α2 phase was narrow, and higher cooling rates resulted in a short time for element diffusion. When the cooling rate decreases to 1 °C/s and 0.4 °C/s (Figure 2c,d), it can be seen from the XRD pattern that the precipitates are O phase. There are two main characteristics of O phase precipitation: (1) fine acicular O phase non-uniformly precipitated directly from the B2 matrix and (2) the B2 grain boundary was decorated with the grain boundary O (O_{GB}) and the Widmanstätten grain boundary O (O_{WGB}) precipitated along the grain boundary. The fine acicular O phase gathered into
many clusters, which is called the floccular O in the present work. The microstructure is different from that of the Ti-24Al-15Nb alloy with a similar cooling rate (0.7 °C/s), which exhibits a fully lath microstructure [27]. This is mainly due to the difference in niobium content. The high niobium content decelerated diffusion processes in the Ti-22Al-25Nb alloy and led to sluggish phase transformations [28]. The dispersed floccular structure of the O phase is related to the diffusion processes of the B2→O transformation in a wide temperature range during the cooling process [29]. At a cooling rate of 0.1 °C/s (Figure 2e), the size of the acicular O phase changed greatly; both the thickness and the length increased to lamellar O and, a typical Widmanstätten structure appeared in the B2 grain. Kazantseva et al. [30] determined the temperature boundaries of phase transformations in Ti-22Al-26.6Nb, Ti-23.5Al-21Nb and Ti-24.6Al-22Nb, respectively. They found that as the aluminum content increases, the temperature range of existence of the orthorhombic O phase extends. Therefore, the formation of these microstructure was due to the fact that the O phase has a large temperature range of formation and sufficient time for nucleation and growth at a lower cooling rate for the Ti-22Al-25Nb alloy. In addition, the decrease in the cooling rate can improve the diffusion process of alloying elements, especially the diffusion of Nb.

![Figure 2.](image_url) Light microscope images and phase identification of Ti-22Al-25Nb alloy cooled at different rates from 1100 °C: (a) 10 °C/s, (b) 4 °C/s, (c) 1 °C/s, (d) 0.4 °C/s, (e) 0.1 °C/s, (f) XRD pattern.
To further confirm the characteristics of the precipitates on the B2 grain boundary at lower cooling rates following heat treatment at 1100 °C, SEM with BSE mode observations are shown in Figure 3. At a cooling rate of 1 °C/s (Figure 3a), part of the B2 grain boundary was decorated with flat O\(_{\text{GB}}\) and zig-zag O\(_{\text{GB}}\), which appeared around the triple junctions (TJs) preferentially. The grain boundary, especially the TJs, as a typical crystal defect, was conductive to nucleation and the growth of O\(_{\text{GB}}\) due to the high defect energy. The flat O\(_{\text{GB}}\) precipitated partially along the B2 grain boundary and formed two separated, flat O\(_{\text{GB}}\) parts as shown in Figure 3a. Figure 3b is a partial, enlarged view of Figure 3a. As seen from Figure 3b, the zig-zag O\(_{\text{GB}}\) was composed of multiple short, separated, flat O\(_{\text{GB}}\) in an unconnected state. It is noteworthy that the growth direction of these short, separated, flat O\(_{\text{GB}}\) is not consistent with the direction of the B2 grain boundary extension line (white dotted line). Sun et al. [31] observed the flat and zig-zag morphology of α\(_{\text{GB}}\) in a TA 15 alloy, and proposed that the flat and zig-zag α\(_{\text{GB}}\) had a competitive growth relationship. As the cooling rate decreased to 0.4 °C/s (Figure 3c), the flat and zig-zag O\(_{\text{GB}}\) decorated one B2 grain boundary simultaneously, forming a mixed O\(_{\text{GB}}\). This indicated that the O\(_{\text{GB}}\) could nucleate separately and simultaneously on one B2 grain boundary. Moreover, there is a competitive relationship between the growth of flat and zig-zag O\(_{\text{GB}}\). The O\(_{\text{WGB}}\) were found near the zig-zag O\(_{\text{GB}}\). As the cooling rate decreased further (Figure 3d), the B2 grain boundary was decorated with a different morphology of O\(_{\text{GB}}\), and the zig-zag O\(_{\text{GB}}\) presented a connected state. This was mainly due to the lower cooling rate, which allowed the O\(_{\text{GB}}\) to have sufficient time to nucleate, grow and form the flat or connected zig-zag O\(_{\text{GB}}\) to decorate the entire B2 grain boundary [32]. Compared with the microstructure at higher cooling rates, more Widmanstätten grain boundary O (O\(_{\text{WGB}}\)) and Widmanstätten intragranular O (O\(_{\text{WI}}\)) appeared at a cooling rate of 0.1 °C/s. The similar characteristic, which was the growth direction of the zig-zag O\(_{\text{GB}}\) deflected from the extension line of the B2 grain boundary, existed in unconnected, zig-zag O\(_{\text{GB}}\) and connected zig-zag O\(_{\text{GB}}\). As seen in Figure 3c,d, the O\(_{\text{WGB}}\), which precipitated from the O\(_{\text{GB}}\), grew to one of the two adjacent B2 grains. It was known that the O phase followed a certain variant selection (VS) in relation to the parent B2 phase as [001]O//[110]B2 and <110>O//<111>B2 [33]. The orientation relationship between the precipitated O and B2 matrix will be discussed in detail later.

3.1.2. The Effect of Cooling Rate on Microstructure following Heating at (B2 + α\(_2\)) Region

Light microscope images of the Ti-22Al-25Nb alloy solution treated at 1020 °C for 20 min and cooled at different rates are shown in Figure 4. When the specimen was cooled at a high rate (10 °C/s or 4 °C/s) as shown in Figure 4a,b, the high-temperature B2 phase and α\(_2\) particles were retained in the alloy. According to Ref. [7], we determined the types of phases shown in Figure 4f. It can also be seen from the XRD pattern that the O phase does not exist at this time. The size of the particles is slightly smaller than the particles in the as-received Ti-22Al-25Nb alloy due to rim O dissolution of the initial α\(_2\)/O particles after heating at the (B2 + α\(_2\)) region. Compared with a high cooling rate following heat treatment at the B2 region, the B2 grain size was smaller when heated at the (B2 + α\(_2\)) region. This was mainly caused by the combination of a low heating temperature and the pinning effect of the α\(_2\) particle [34]. When the cooling rate was 1 °C/s (Figure 4c), acicular O were precipitated from the B2 matrix, B2 grain boundaries and around α\(_2\) particles. Similar to cooling from 1100 °C, these fine, needle-like O lamellae cluster together, forming a floccular microstructure. When cooled from the two-phase region, the increase of the phase boundary provides favorable conditions for the nucleation of the O phase due to the presence of α\(_2\) particles in the grains. As the cooling rate decreases to 0.4 °C/s (Figure 4d), the volume fraction of the floccular O phase precipitated in the B2 grains and around the α\(_2\) particles increased, and it was observed that the diameter of the α\(_2\) particles decreased, as shown by the white arrows. As the cooling rate was deceased further (Figure 4e), the O\(_{\text{W}}\) and the O phase precipitated around the α\(_2\) particles were significantly coarsened, and the volume fraction of the α\(_2\) particles decreased.
With further decreases in the cooling rate (Figure 5d), rim O phase appeared around almost was discovered by Wang et al. [17], who found that α phase + (Figure 5b), a small amount of floccular O phase appeared in the B2 matrix and around the α plate-like O phase + α. α is the orientation characteristics of the precipitated O phase in different B2 grains has significant effect. The morphology and area. As seen from the inverse pole figure (IPF) of B2 phases in Figure 6b, there are three different crystallographic orientation B2 grains at the triple junctions. The morphology and orientation characteristics of the precipitated O phase in different B2 grains has significant

Figure 3. The morphology of Ti-22Al-25Nb alloy cooled at different rates from 1100 °C: (a,b) 1 °C/s, (c) 0.4 °C/s, (d) 0.1 °C/s.

Typical scanning electron microscopy micrographs on microstructure changes after cooling from 1020 °C at different rates are shown in Figure 5. It can be observed that at a relatively high cooling rate (Figure 5a), there was no rim O phase around the α particles, and the surface of the equiaxed particles was relatively smooth. When cooled at 1 °C/s (Figure 5b), a small amount of floccular O phase appeared in the B2 matrix and around the α particles. As the cooling rate decreased (Figure 5c), a large number of floccular O phases appeared around the α particles, and rim O phase appeared around a few α particles. With further decreases in the cooling rate (Figure 5d), rim O phase appeared around almost all α particles, and the α particles were no longer smooth. Meanwhile, it is observed that some α particles were being dissolved. A similar α decomposition phenomenon was discovered by Wang et al. [17], who found that α particles decomposed into the fine, plate-like O phase + α phase during aging treatment.

3.2. O Phase Precipitation Mechanism
3.2.1. O Phase Precipitation Mechanism from B2 Matrix

To investigate the relationship between the precipitated O phase and the parent B2 matrix, EBSD analysis of Ti-22Al-25Nb alloy cooled at 0.1 °C/s from 1100 °C is shown in Figure 6. Figure 6a is the scanning electron microscope image of the EBSD analysis area. As seen from the inverse pole figure (IPF) of B2 phases in Figure 6b, there are three different crystallographic orientation B2 grains at the triple junctions. The morphology and orientation characteristics of the precipitated O phase in different B2 grains has significant
changes, as shown in Figure 6c. On the #1 B2 grain boundary, lamellar O\textsubscript{WGB} phase precipitated along grain boundaries and grew into #1 B2 grain, (mark by the red rectangle). In the #2 B2 grain, the clustered lamellar O\textsubscript{WGB} phase with different crystallographic orientations formed visual parallel colony structures, as marked by the black arrows. It is worth noting that on the grain boundary between the #1 B2 grain and #2 B2 grain (marked by the black rectangle), the precipitated O\textsubscript{WGB} grew into different B2 grains, #1 B2 grain and #2 B2 grain, respectively. No colony structure observed on the #3 B2 grain boundary and fine acicular O phase in the B2 grain precipitated directly from the parent B2 matrix, and there was no obvious visual orientation.

![Figure 4.](image)

**Figure 4.** Light microscope images and phase identification of Ti-22Al-25Nb alloy cooled at different rates from 1020 °C: (a) 10 °C/s, (b) 4 °C/s, (c) 1 °C/s, (d) 0.4 °C/s, (e) 0.1 °C/s, (f) XRD pattern.
Figure 5. Scanning electron micrographs of Ti-22Al-25Nb alloy cooled at different rates from 1020 °C: (a) 4 °C/s, (b) 1 °C/s, (c) 0.4 °C/s, (d) 0.1 °C/s.

Figure 6. EBSD observations of Ti-22Al-25Nb alloy cooled at 0.1 °C/s from 1100 °C (a) scanning area, (b) IPF of B2 phase, (c) IPF of O phase.

The EBSD analysis in the #3 B2 grain and the pole figure of the B2 phase and O phase are shown in Figure 7. As a body-centered cubic unit, a single B2 phase unit cell contained six equivalent [110] crystal planes. As an orthorhombic unit, an O phase unit cell contained only one equivalent (001) O plane and one equivalent [110] O direction due to the lattice parameters a = 0.6089 nm, b = 0.9569 nm and c = 0.4666 nm, respectively [35]. The positions of the six focusing points in the (001)O pole figure (Figure 7c) are the same as those in the [110]B2 pole figure (Figure 7b), indicating that the O_WI phase follows the plane relation (001)O//[110]B2 during a continuous cooling process. Zheng et al. [36] found that the lamellar O phase follows the plane relation [001]O//[110]B2, and all 12 variants of lamellar O phases appear during the second solution treatment. Even if there was no obvious visual orientation priority, the O_WI phase still maintained the plane relation with the parent B2 phase. Therefore, this indicated that the precipitation probability of each O phase variant is approximately equal, and there was no obvious O phase variant selection effect in the #3 B2 grain.
As shown in Figure 8a, the purple lamellar O phase formed a cluster structure and grew into the #1 B2 grain. The pole figures of the purple O_{WGB} with the #1 B2 pole figure are shown in Figure 8b. The [001] plane of the purple O_{WGB} is parallel to the [110] plane of the #1 B2 grain, and the <110> direction of the O_{WGB} is also parallel to the <111> direction of the #1 B2 grain. Thus, the O_{WGB} maintained the specific orientation relationship, i.e., (001)O//[110]B2 and <110>O//<111>B2, with one of the two adjacent B2 grains. The grain boundary was decorated by O phases with different colors as shown in Figure 8a by the black arrows. This indicated that different crystallographic variants of the O phase precipitated simultaneously at one B2 grain boundary and formed the O_{GB}. It is known that the positions where the grain boundary and crystal defects gather are possible nucleation sites. Therefore, it can be inferred that there can be more than one nucleation site for the O phase on a single B2 grain boundary during the cooling process. The pole figures of the orange O_{GB} and the cyan O_{GB} with the #1 B2 pole figure are shown in Figure 8c,d, respectively. Similar to the purple O_{WGB}, the orange O_{GB} kept a specific orientation relationship with the #1 B2 grain. As seen from Figure 8d, the cyan O_{GB} did not have a specific orientation relationship because the <110> direction of the cyan O_{GB} is not strictly parallel to the <111> direction of the #1 B2 grain. However, the [001] plane of the cyan O_{GB} is parallel to the [110] plane of the #1 B2 grain. This indicated that the cyan O_{GB} held a near-orientation relationship with the #1 B2 grain based on this plane relation. It was pointed out that the products held a specific orientation relationship with the parents during the precipitation process, minimizing the interfacial energy [32] and nucleation activation energy [37]. A previous investigation [36] suggested that precipitates tried to maintain the orientation relationship with the parent phase grain as much as possible to reduce the nucleation activation energy when the O_{GB} cannot maintain a specific orientation relationship with a certain B2 grain.

3.2.2. O Phase Precipitation Mechanism from α2 Particles

The EBSD analysis of the Ti-22Al-25Nb alloy cooled at 0.1 °C/s from 1020 °C is shown in Figure 9. The green and pink rim O phases appeared when the α2 particles when the cooling rate decreased to 0.1 °C/s as marked by black arrows in Figure 9a. The [110] and <111> pole figures of the B2 phase are shown in Figure 9b. There are six focusing points on the [110] B2 planes as shown in Figure 9b, indicated that all α2 particles and precipitated O phases are in one single B2 grain. Figures 10 and 11 show the crystallographic plane and crystallographic direction pole figures corresponding to the B2 phase and lamellar O phase and the α2 phase and precipitated rim O phase, respectively. As seen from Figure 10, the [001] and <110> pole figures of the red lamellar O phase coincide with the [110] and <111> pole figures of the B2 phase. Therefore, it can be concluded that in a single B2 grain, the lamellar O phase keeps the specific orientation relationship with the B2 phase. The [001] plane of the green rim O phase is parallel to the [0001] plane of the purple α2 particle, and one <110> direction of rim O is also parallel to one <1120> direction of the α2 particle, as shown in Figure 11. This suggests that the newly precipitated rim O phase holds the specific orientation relationship with the parent α2 particles during the cooling process.
The diameter of the $\alpha_2$ and ($O + \alpha_2$) particles and the thicknesses of the lamellar $O$ depicted in Figure 4 are all listed in Table 2. The diameter of the $\alpha_2$ particles without rim $O$ ($10 \, ^\circ\text{C/s}$ and $4 \, ^\circ\text{C/s}$) is almost equal to those of ($O + \alpha_2$) particles ($1 \, ^\circ\text{C/s}$, $0.4 \, ^\circ\text{C/s}$ and $0.1 \, ^\circ\text{C/s}$), indicating that the rim $O$ phase formed through a decomposition reaction: $\alpha_2 \rightarrow \alpha_2 + O$. Muraleedharan et al. [15,21] found that the formation of the $O$ phase precipitated on the periphery of the $\alpha_2$ particles is caused by the diffusional kinetics of the $\alpha_2$ phase. As a result of the Nb diffusion, the $\alpha_2$ phase contained supersaturation of niobium elements separated into two regions, one being the Nb-rich region and the other the Nb-lean region. Nb-rich regions with composition closer to Ti$_2$AlNb transformed to the $O$ phase [16,38], which maintains a specific orientation relationship with the parent $\alpha_2$ particles, and Nb-lean regions remained untransformed, that is, they retained the $\alpha_2$ phase. Wu et al. [39] considered that the $O$ phase is a pseudohexagonal phase with a lattice distortion caused by a supersaturation of the $\alpha_2$ phase. In order to accommodate the excess Nb, the crystalline cell of the hexagonal phase $\alpha_2$ had a slight distortion and transformed to
O lattice [40], which means the $\alpha_2$ transformed to $\alpha_2$ (Nb-lean) and O (Nb-rich). Therefore, the rim O phase formed on the periphery of the $\alpha_2$ particles is controlled by a diffusion mechanism. It is difficult to form rim O in a short time due to the need for a large amount of Nb diffusion. Thus, no rim O phase appeared on the periphery of the $\alpha_2$ particles at high cooling rates during cooling from the (B2 + $\alpha_2$) region. The newly precipitated rim O phase provides fresh nucleation sites for other O phases. Thus, the precipitated rim O is conducive to the nucleation, growth and coarsening of the O lamellae around rim O. According to the analysis above, the schematic of the formation process of the precipitated O phase with cooling from the B2 and (B2 + $\alpha_2$) region was shown in Figure 12. Figure 13 shows the comparison of microhardness versus cooling rate plots for the Ti-22Al-25Nb alloy. At cooling rates of 4 °C/s and 10 °C/s, the microhardness of the ($\alpha_2$ + B2) microstructure is larger than that of the B2 single phase. This is mainly because the fully B2 phase exhibits low strength, and equiaxed $\alpha_2$ particles have a strengthening effect. As the cooling rate decreases to 1 °C/s, either cooled from 1100 °C or 1020 °C, the microhardness of the alloy increases. From the previous analysis, a more needle-like O phase precipitates from the B2 matrix when the cooling rate is less than 4 °C/s. According to Ref. [11], the precipitated O phase is beneficial to the strength but detrimental to the plasticity of a Ti$_2$AlNb-based alloy. A similar phenomenon is also seen in Ref. [22]. Therefore, the increase in microhardness at lower cooling rates is due to the strengthening of the precipitated O phase. In addition, the microhardness of the (O + B2) microstructure is larger than that of the ($\alpha_2$ + B2 + O) at a lower cooling rate. This is mainly because the $\alpha_2$ particles located on the grain boundary are detrimental to the mechanical properties of a Ti$_2$AlNb-based alloy, according to Ref. [2]. At a cooling rate of 0.1 °C/s, there is a substantial decrease in microhardness either cooled from 1100 °C or 1020 °C. According to EBSD analysis, the volume fraction of the O phase is 72.9% (cooled from 1100 °C) and 61.8% (cooled from 1020 °C) when the cooling rate is decreased to 0.1 °C/s. According to references [11,12,22], it is harmful to the strength of the alloy when the volume fraction of the precipitated O phase reaches a relatively large degree. In summary, the microstructure of the lamellar O + B2 matrix has good microhardness and can be further examined as an ideal microstructure. The influence of the O phase lamellae size, the ratio of coarse lamellae to fine lamellae and the appropriate O phase volume fraction on the mechanical properties of a Ti-22Al-25Nb alloy will be further investigated in the future.

**Figure 9.** EBSD observation of Ti-22Al-25Nb alloy cooled at 0.1 °C/s from 1020 °C (a) IPF map of O phase, (b) {110} and <111> pole figures of the B2 phase.

**Figure 10.** (a) {110} and <111> pole figures of the B2 phase, (b) {001} and <110> pole figures of the red lamellar O phase.
Figure 9. EBSD observation of Ti-22Al-25Nb alloy cooled at 0.1 °C/s from 1020 °C (a) IPF map of O phase, (b) {110} and <111> pole figures of the B2 phase.

Figure 10. (a) {110} and <111> pole figures of the B2 phase, (b) {001} and <110> pole figures of the red lamellar O phase.

Figure 11. (a) {0001} and <112̅0> pole figures of the purple α2 phase, (b) {001} and <110> pole figures of the green rim O phase.

Table 2. dα2 (μm) under different cooling rates. dα2 is the diameter of the α2 particles, rim O is the thickness of precipitated rim O and dm is the diameter of the (O + α2) particles.

| Cooling Rate (°C/s) | dα2  | rim O | dm   |
|---------------------|------|-------|------|
| 10                  | 5.81 | 0     | 5.81 |
| 4                   | 5.79 | 0     | 5.79 |
| 1                   | 4.98 | 0.4   | 5.78 |
| 0.4                 | 4.36 | 0.7   | 5.76 |
| 0.1                 | 4.15 | 0.8   | 5.75 |

Figure 12. The schematic of the formation process of precipitated O phase with cooling from (a) B2 region, (b) B2 + α2 region.
4. Conclusions

In summary, the present research investigated the microstructural evolution of the O phase in a Ti-22Al-25Nb (at.%) alloy during cooling at different cooling rates from different phase regions. It also summarized the precipitated formation mechanism of the O phase on B2 grain boundaries and within B2 grains and $\alpha_2$ grains. The main conclusions of this paper are as follows:

1) Microstructure observation indicated that the cooling rates have a significant influence on the morphology of the precipitated O phase. As the cooling rate decreased, more floccular O phases precipitated directly from the B2 matrix, and the Widmanstätten grain boundary O precipitated along the grain boundary.

2) When cooled from the (B2 + $\alpha_2$) region, the increase of the phase boundary provided favorable conditions for the nucleation of the O phase due to the presence of $\alpha_2$ particles. The precipitated rim O phase appeared on the periphery of the $\alpha_2$ particles at lower cooling rates.

3) The O$_{WI}$ phase maintained the plane relation with the parent B2 phase, and the O$_{WCB}$ maintained the specific orientation relationship, i.e., $\langle 001 \rangle_O//\langle 110 \rangle_B$ and $\langle 110 \rangle_O//\langle 111 \rangle_B$, with one of the two adjacent B2 grains. The O$_{GB}$ keeps the specific orientation relationship with one of the B2 grains as much as possible. When it cannot maintain the specific orientation relationship with one of the B2 grains, the O$_{GB}$ maintains a near-orientation relationship with B2 grains on both sides to reduce the nucleation activation energy. There can be more than one nucleation site for the O phase on a single B2 grain boundary to form the O$_{GB}$.

4) The rim O phase formed through a decomposition reaction of $\alpha_2 \rightarrow \alpha_2$ (Nb-lean) + O (Nb-rich) is controlled by a diffusion mechanism and maintains specific orientation relationship, i.e., $\langle 001 \rangle_O//\langle 0001 \rangle_\alpha$ and $\langle 110 \rangle_O//\langle 11-20 \rangle_\alpha$, with the parent $\alpha_2$ particles.

Author Contributions: Conceptualization, D.L.; formal analysis, F.Z.; methodology, J.X.; project administration, W.Z.; investigation, D.L.; writing—original draft preparation, D.L.; resources, X.M.; supervision, X.L. All authors have read and agreed to the published version of the manuscript.

Funding: This work is financially supported by the Program of National Key Research and Development Plan of China (2016YFB0301203), the Natural Science Foundation of Shaanxi province of China (2020JQ-156) and the Fundamental Research Funds for the Central Universities (3102019TS0404).

Data Availability Statement: The data are not publicly available due to the fact that these data are part of an ongoing study.

Acknowledgments: We would like to thank the Analytical & Testing Center of Northwestern Polytechnical University for the convenience of the experimental tests.
Conflicts of Interest: The authors declare no conflict of interest.

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