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Article

Effect of N/O Elements on Microstructure and Mechanical Properties of Ti-N-O Alloy

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Abstract: A novel Ti-N-O composite was prepared by powder nitriding/oxy-nitriding combined with Spark-plasma Sintering (SPS) method. The effects of N/O on the microstructure and mechanical properties of Ti-N-O alloy were systematically studied. The results showed that the addition of N/O elements significantly improved the yield strength and the hardness of commercially pure titanium (cp-Ti). And the O element played a leading role in regulating the microstructure and morphology of Ti-N-O alloy. With the addition of O element, the microstructure showed equiaxed structure, and the characterization showed that this region is O-enriched region, and a small amount of nano-TiO₂ particles appeared in the alloy, which together led to the change of the microstructure. At the same time, more large-angle grain boundaries were generated in the Ti-N-O alloy.

Keywords: powder nitriding/oxy-nitriding; Spark-plasma Sintering; commercially pure titanium; microstructure; mechanical properties

1. Introduction

Titanium and its alloys have low density, high strength, excellent biocompatibility along with high corrosion resistance, which are considered as a kind of light materials. Therefore, they have been widely used in aerospace, automobile, marine and biomedical industries [1–4]. Especially for commercial pure titanium (cp-Ti), it is often used as an implant material to replace damaged bone or tissue [5–8]. However, a critical demerit of cp-Ti is its intrinsically low strength caused by its hexagonal-close-packed (HCP) single-phase nature [9–11], which limits its applications. The ASTM standard classifies cp-Ti into four grades (1–4) based on its interstitial contents (especially oxygen). The mechanical properties of the different grades vary considerably. The yield strength (YS) of grade 4 is ~2.8 times that of grade 1, but the YS is still low (~480 MPa) [12].

In recent years, research efforts have been focused on enhancing cp-Ti surface in order to improve strength. Many organic and inorganic related solutions have been used for cp-Ti coating applications [13]. Mohammadi et al. performed thermochemical gas nitriding of cp-Ti in a pure nitrogen atmosphere under the pressure of 2.5×10^5 Pa at temperatures of 1123 K, 1223 K, and 1323 K for 8 hours. The δ -TiN_x, ϵ -Ti₂N, TiN_{0.3}, and α -Ti (N) phases were formed in the nitrided samples from the surface to depth sequentially, and the surface microhardnesses were 983 ± 87 HV, 1141 ± 106 HV, and 1278 ± 131 HV, respectively [14]. Korkel et al. controlled the formation of white rutile surface layers on cp-Ti by gaseous thermochemical oxidation and focused on a two-step oxidation process. The two-step oxidation process was found to result in the controlled growth of robust, dense, adherent white titanium oxide layers, and the hardness distribution in the oxide layer exhibited a plateau at 800–1000 HV_{0.01} [15]. Ye et al. fabricated nanoporous TiO₂-TiN composite films with enhanced tribological properties on cp-Ti by combining electropulsing-assisted ultrasonic surface rolling process (EP-USRP) and an electrochemical process. The surface hardness was increased by

~295 HV (~41.1% over the untreated sample) and the hardening depth reached ~ 600 μm [16]. Yaskiv et al. carried out oxynitriding process on cp-Ti by introducing the controlled oxygen-containing medium into the system at finish stage of nitriding (during cooling). The mechanical properties such as hardness were improved[17]. Although the majority of the experimental processing methods used to create these coatings have been well consolidated, some of them, such as plasma spray or sputtering, which are commonly used to deposit thick coatings and submicrometric thin coatings, may necessitate a significant investment in equipment[18]. And the coatings cannot change the internal properties of the material.

Fang et al. added the multi-element Fe-Cr-Ni-Mo in the form of 316L steel into cp-Ti to prepare the bulk samples and realized the simultaneous enhancement of strength and uniform ductility[19]. In situ alloying of alloys with single elements like Cu[20] or Fe[21] has been employed to develop new alloys with promising mechanical properties. However, studies on the impact of N and O on microstructure and mechanical properties in Ti-N-O bulk materials are scarce. Powder nitriding/oxidation is an appropriate procedure because it allows nitrogen/oxygen to diffuse to the center of the powder at a sufficiently high rate in an interstitial diffusion manner[22]. Spark-plasma sintering (SPS) is a new technology for preparing functional materials. Fast and efficient sintering can be achieved under the combined action of spark discharge, Joule heating, electrical diffusion and plastic deformation effect in the SPS process[23,24]. SPS is characterized by uniform sintering, low grain growth, compaction-densification and better purification. It is considered a suitable process for consolidating a wide range of powder composites with high-density and homogeneous microstructures[25]. Energy consumption during the SPS consolidation process is less than a third of that of the conventional processes[26,27]. To ascertain the impact of N and O elements on the microstructure and mechanical properties of cp-Ti, a series of Ti-N-O alloys are prepared.

2. Experimental Materials and Methods

2.1. Materials

The TA1 cp-Ti powder used in this study (prepared by PREP, showing good roundness, about 15-212 μm) had a composition (in mass %) of 0.150 O, 0.200 Fe, 0.030 N, 0.080 C, 0.013 H, and balance Ti. The powder nitriding and oxynitriding were used for the treatment of TA1 cp-Ti powder. The treated powder was prepared by SPS to obtain the bulk Ti-N-O alloys. The sample nomenclature and the corresponding specific process parameters are shown in Table 1. The nitriding temperature is generally chosen to be low, as very high temperature and long duration may cause detrimental microstructural changes[28]. Liu et al. used a cathodic cage in combination with the pulsed-biased system to realize nitriding of TA1 titanium at the cathodic potential below 660 $^{\circ}\text{C}$ [29]. Kikuchi et al. fabricated cp-Ti with a bimodal microstructure consisting of a substrate surrounded by a network structure of nitrogen diffusion phase by sintering nitrided powders, and demonstrated that the cp-Ti fabricated from powder nitrided at 600 $^{\circ}\text{C}$ has higher tensile strength as well as lower friction coefficient than compacts fabricated from as-received cp-Ti powder[30]. Based on the above, different heat treatments at 600 $^{\circ}\text{C}$ and 650 $^{\circ}\text{C}$ were selected for this study. The whole process of powder nitriding/oxynitriding was carried out in a well-type furnace under a gas atmosphere. The ammonia flow rate was maintained at 2 L/h throughout the powder nitriding process, while the air was added in the powder oxynitriding process, and the flow rate is 0.2 L/h. Ti-N-O alloys were prepared by SPS method. The sintering process involved heating to 1050 $^{\circ}\text{C}$ at a rate of 100 $^{\circ}\text{C}/\text{min}$ under 30 MPa pressure, with a 10-minute hold time. The final cylindrical sintered samples, each with a diameter of 20 mm.

Table 1. Processing parameters of Ti-N-O alloys.

Process of Powder Nitriding/Oxynitriding	Sample
	Raw
oxynitriding at 600℃ for 2h	600-2hNO
oxynitriding at 600℃ for 3h	600-3hNO
Cyclic nitriding at 650℃ for 3 h, keeping the first pure nitriding unchanged, and introducing air at the last 20 min of the second nitriding, that is, oxynitriding	650-3hN-2+O

2.2. Methods

The phase composition of the specimen was identified by X-ray diffraction (XRD) utilizing a PANalytical Empyrean X-ray which has a 20–80° range and a 0.02 step. The samples were applied standard processes for sand papering and polishing and then etched in the solution of HF, HNO3 and H2O with the ratio of 2:1:17, and the corrosion time is 5 to 10 seconds. The surface morphology of the sample was inspected by means of an optical microscope (OM) OLYMPUS GX51. A JSM 7800F Prime scanning electron microscopy (SEM) combined energy dispersive spectroscopy (EDS) and Oxford Symmetry S2 Electron Back-Scattered Diffraction (EBSD) , as well as a Thermo Scientific FEI Talos F200X transmission electron microscope (TEM) were adopted for assessing elemental distribution, chemical homogeneity, and microstructural characterization. Vickers hardness tests were performed using an HVS-1000 Vickers microhardness tester at a load of 100 gf and a dwell time of 15 s. Compressive tests were performed using a WDW-200 universal testing machine with a sample size with a diameter of 7.5 mm and a height of 11.25 mm at a cross-head speed of 1 mm/min.

3. Results and Discussion

3.1. Mechanical Properties

Figure 1 shows the hardness curve of Ti-N-O samples. Compared with the raw sample, the hardness of the samples has been greatly improved by adding N and O elements, and the 600-3hNO sample has the largest increase (304.3 HV0.1) , which is about 125% higher than that of the raw sample. At the same time, the effect of oxynitriding for 2 h or 3 h is not much different. Figure 2 shows the compression stress–strain curve of Ti-N-O samples. The raw sample is a very typical plastic material, and there is no failure phenomenon in the compression test. The fracture phenomenon of other three Ti-N-O samples is obvious. Among them, the plasticity of 600-3hNO and 650-3hN-2+O samples are similar, and the compressive strain is close to 0.4, but the hardness of 650-3hN-2+O sample is the lowest. The compressive strain of 600-2hNO samples is about 0.49, and the compressive yield strength of 600-2hNO and 600-3hNO samples is almost the same (666 MPa and 684 MPa respectively) , while the compressive strength of 600-2hNO sample is 282 MPa higher than that of 600-3hNO sample (2154 MPa and 1872 MPa respectively) . Moreover, compared with the Ti-N samples prepared by pure nitriding process, the yield strength of the 600-2hNO sample is 52 MPa higher than that of the Ti-N sample under the optimum process (650-3hN-2 sample) , which also shows that the addition of oxygen is more obvious and efficient than nitrogen in improving the strength of the sample under this experimental system. Combining hardness, compressibility and energy saving, it is obvious that the 600-2hNO process can obtain great performance in a short time, which is the best process for preparing Ti-N-O.

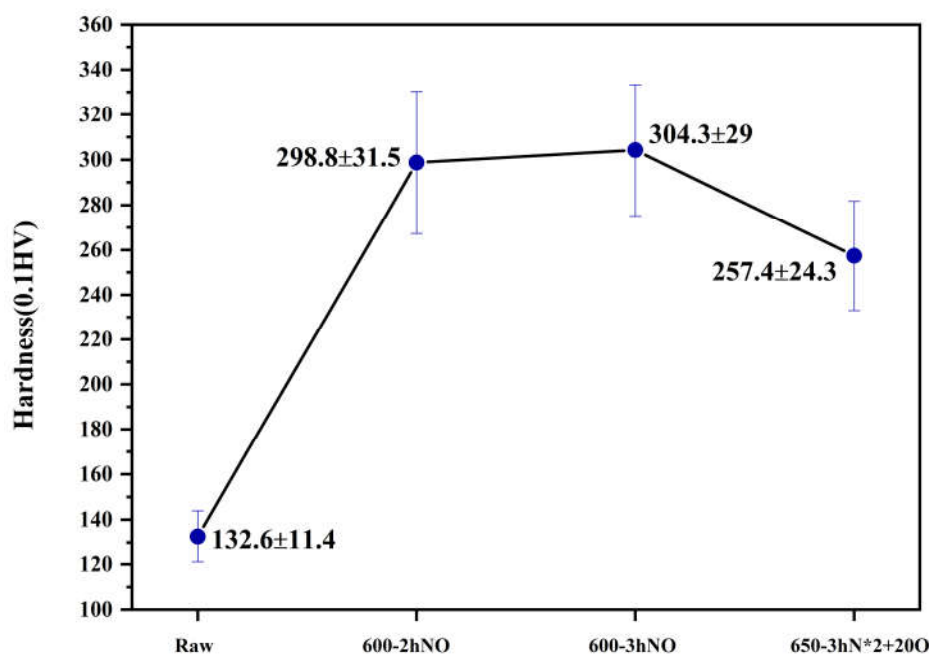


Figure 1. The hardness curve of Ti-N-O samples.

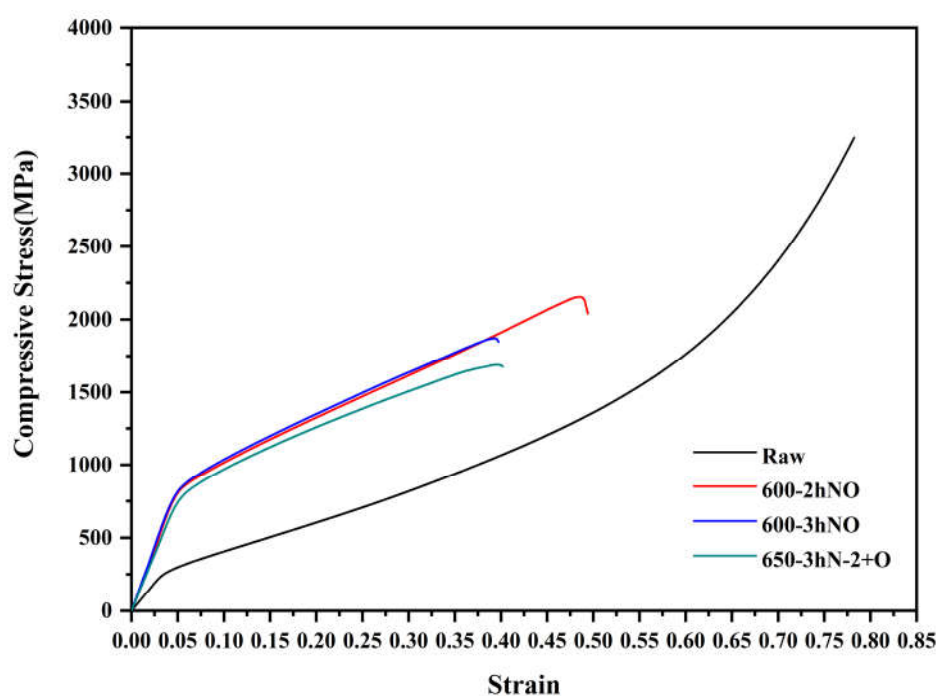


Figure 2. The compression stress-strain curve of Ti-N-O samples.

3.2. Microstructure

Figure 3 shows the XRD patterns obtained from 600-2hNO powder, 600-2hNO sample, and raw powder. The raw powder is mainly made up of α -Ti phase. The diffraction peaks of TiO_2 appeared in the 600-2hNO powder, which was attributed to the formation of TiO_2 after the oxygen content of the surface layer exceeded the solid solution limit of titanium during nitrocarburizing. The diffraction peaks of 600-2hNO sample are basically the same as that of raw powder, which is thought to be the result of TiO_2 decomposed under Joule heat, and oxygen atoms diffused to low concentration region, finally forming α -Ti solid solution containing N/O after SPS. In fact, during the whole sintering

process, the sample undergoes $\alpha \rightarrow \beta \rightarrow \alpha$ transformation (α phase to β phase and then α phase), which will be discussed in detail later. Figure 4 shows the SEM images of the surface of 600-2hNO powder. 600-2hNO powder represents a rougher surface than the raw powder, and some scattered bright white particles less than 1 μm in diameter can be found. Combined with XRD patterns, it is inferred that these are generated TiO_2 particles.

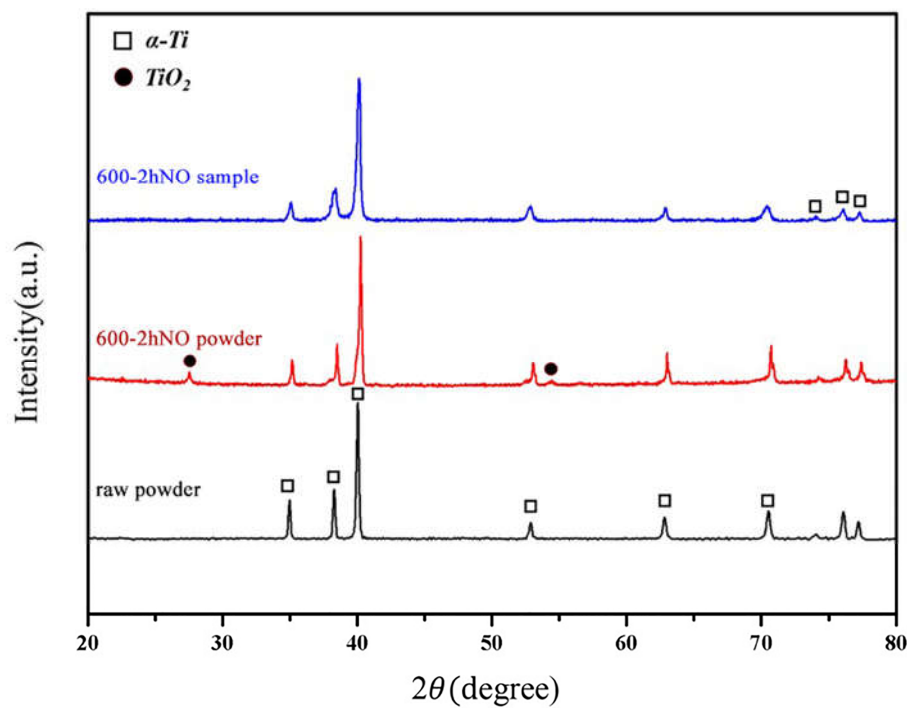


Figure 3. The XRD patterns obtained from 600-2hNO powder, 600-2hNO sample and raw powder.

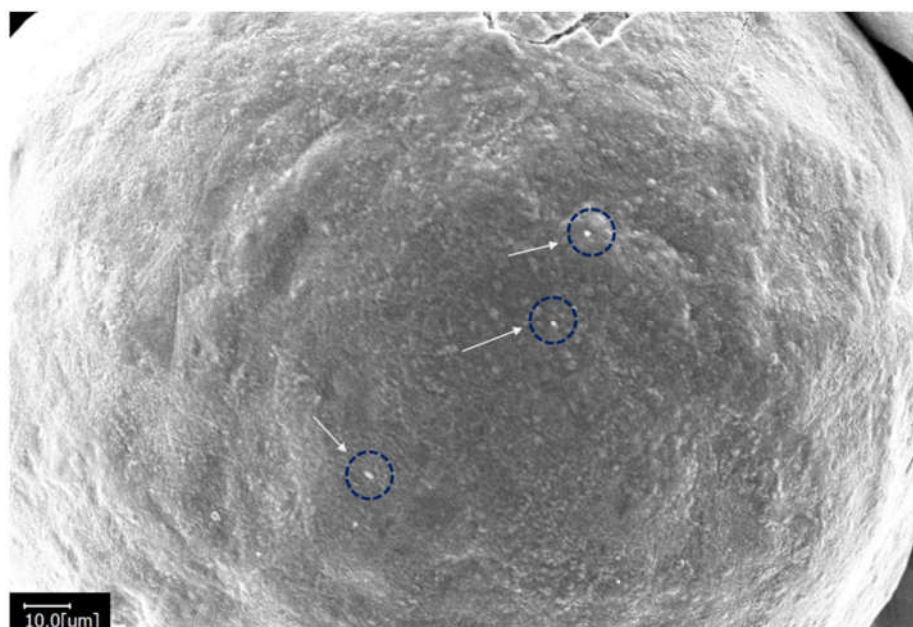


Figure 4. The SEM images of the surface of 600-2hNO powder.

Figure 5 shows the OM images of 600-2hNO sample and the raw sample. All the samples showed lath structures with different thicknesses, while equiaxed structures were found in the 600-2hNO sample. Figure 6 shows the SEM image and EDS analysis of 600-2hNO sample. A thin strip “bump” which is different from the morphology on both sides is shown. Energy dispersive spectroscopy

(EDS) was used to determine the composition of different morphologies. It can be seen that the oxygen content of points A and B, which represent the bump area, is several times higher than that of point C, referring to similar work done by predecessors[31]. The “bump” is the so-called α -phase reserved area, which is also the oxygen-enriched area, while the two sides represented by point C experienced the transformation from α to β and then to α -phase during sintering. Combined with metallography, we infer that most areas experienced the transformation from α to β to α during sintering, and these boundaries different from lath structure should be solid solution element-enriched areas. Oxygen, as a stable element of α -phase, was enriched in the local grain boundary region during sintering, which keeps α phase from $\alpha \rightarrow \beta \rightarrow \alpha$ transformation, hinders the formation of lath morphology and presents an equiaxed morphology, which together with the lath α phase constitutes the microstructure. In addition, the N element was not detected by the EDS, and it may be that oxygen atoms occupy most gaps so that the existence space of nitrogen atoms is small, so the O element plays a leading role in regulating the microstructure and morphology of Ti-N-O alloy.

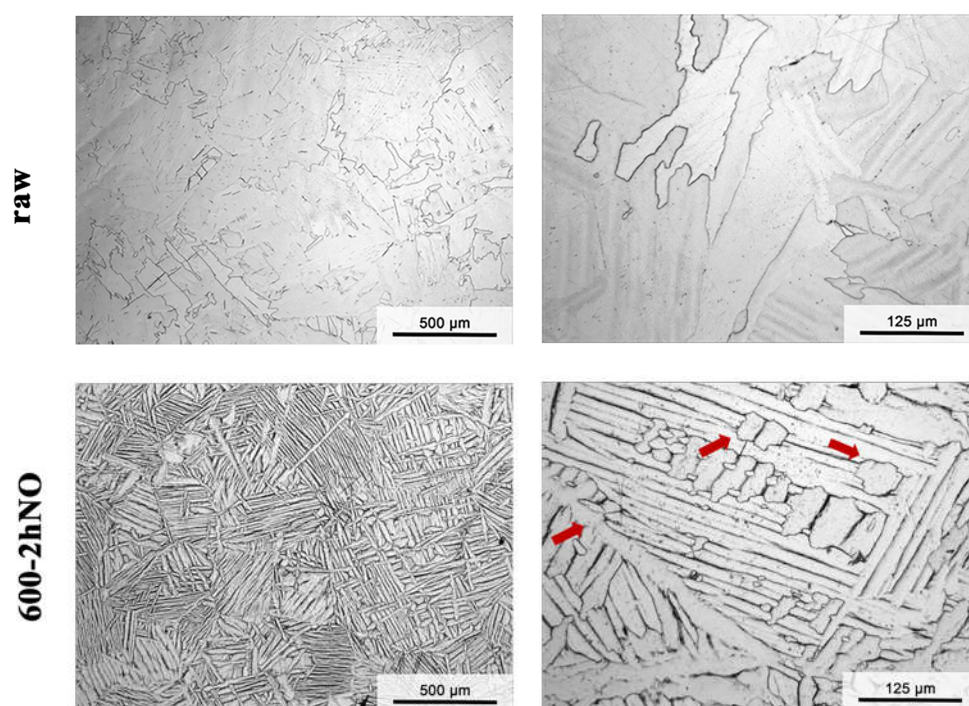


Figure 5. The OM images of 600-2hNO sample and the raw sample.

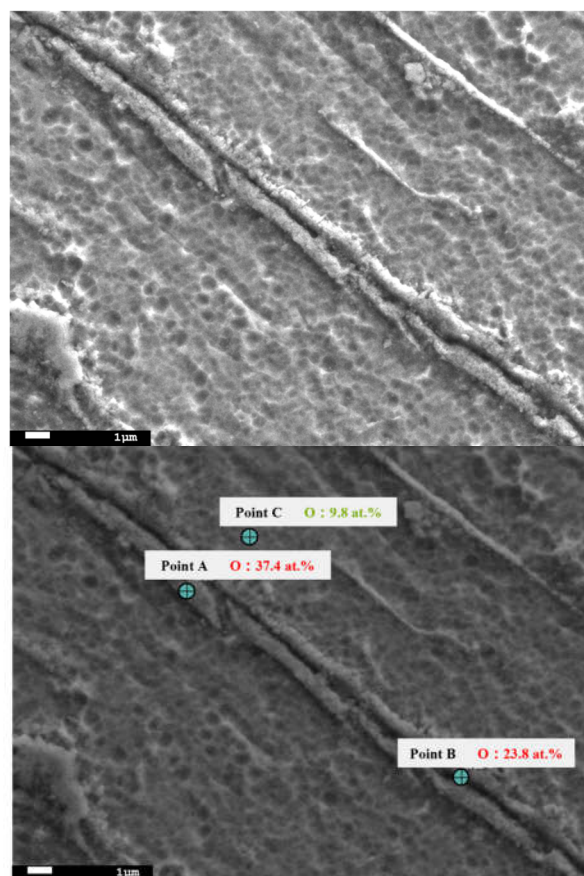


Figure 6. The SEM image and EDS analysis of 600-2hNO sample.

Figure 7a shows the TEM image of 600-2hNO sample. The shooting area is the intersection of the precipitated phase and the matrix. The two areas in the figure, b and c, are subjected to selective Fourier transform, and the precipitated phase is determined to be nano-TiO₂ particles after calibration, which corresponds to the previous discussion. The crystal plane direction and crystal plane spacing corresponding to α -Ti phase and selected TiO₂ precipitation phase are also marked in Figure 7b and c. The (2 0 -1 2) crystal plane of TiO₂ and the (1 0 -1 3) crystal plane of α -Ti are transformed by inverse Fourier transform, and the corresponding inverse Fourier images shown in Figure 7d and e are obtained. It can be clearly seen that there are basically no dislocations in the selected crystal plane direction in the TiO₂, and only a small lattice distortion exists, which is indicated by the red arrow. While more dislocations are displayed near the α -Ti end of the TiO₂ phase. Because dislocation movement is hindered by the hard phase, the atomic arrangement in α -Ti matrix region is disordered and the Fourier facula is blurred. Another possibility is that oxygen atoms diffuse to the matrix induced by partial decomposition of the secondary phase at high temperature, and the concentration of oxygen near the secondary phase is high (similar to alloy G-P region[32]), and the semi-coherent high solid solution region of its near-precipitation state intensifies atomic disorder due to lattice distortion.

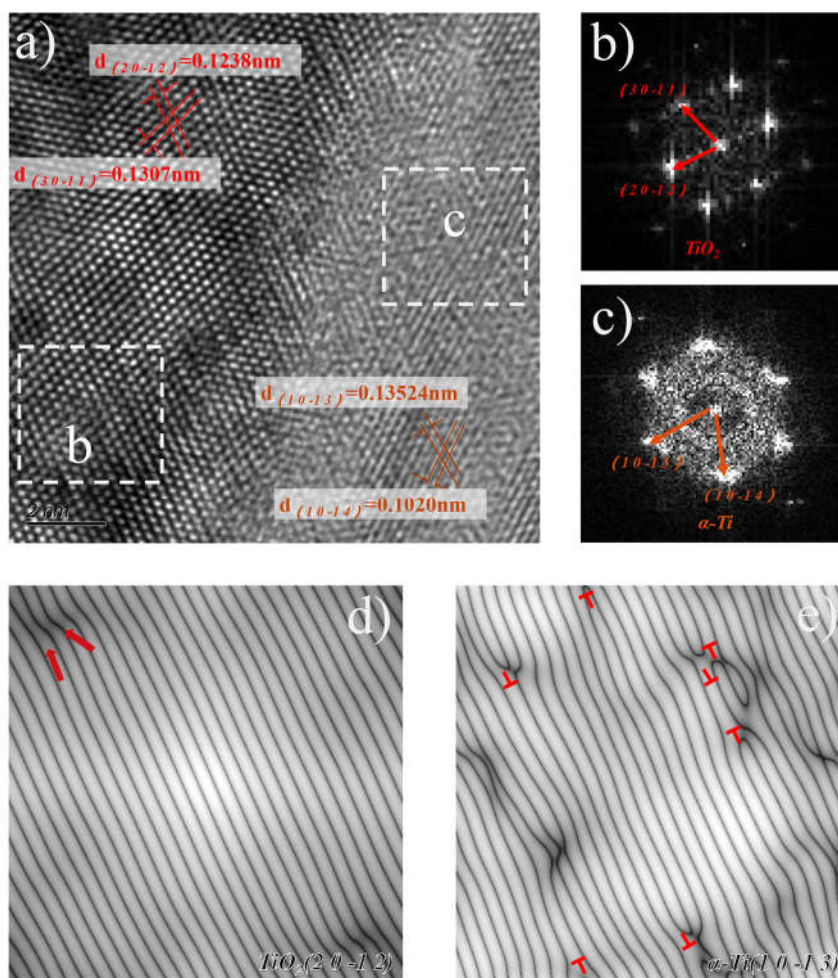


Figure 7. (a) The TEM image of 600-2hNO sample; (b) the Fourier images of b; (b) the Fourier images of c; (d) the inverse Fourier images of b; (e) the inverse Fourier images of c.

Figure 8 shows GB images of raw sample and 600-2hNO sample taken under EBSD. The red, green, and blue lines represent grain boundaries with angles of $2 \sim 5^\circ$, $5 \sim 15^\circ$ and above 15° respectively. The extrusion deformation between powders leads to the edge breaking, and the sintering temperature rise is equivalent to recrystallization, so many dense large-angle grain boundaries appear locally after sintering. It is calculated by software that the total length of grain boundaries in 600-2hNO sample is not much different from that of the raw sample, but the total length of large-angle grain boundaries is 1.14 cm more than that of the raw sample, which also proves that more large-angle grain boundaries are produced in 600-2hNO sample after sintering.

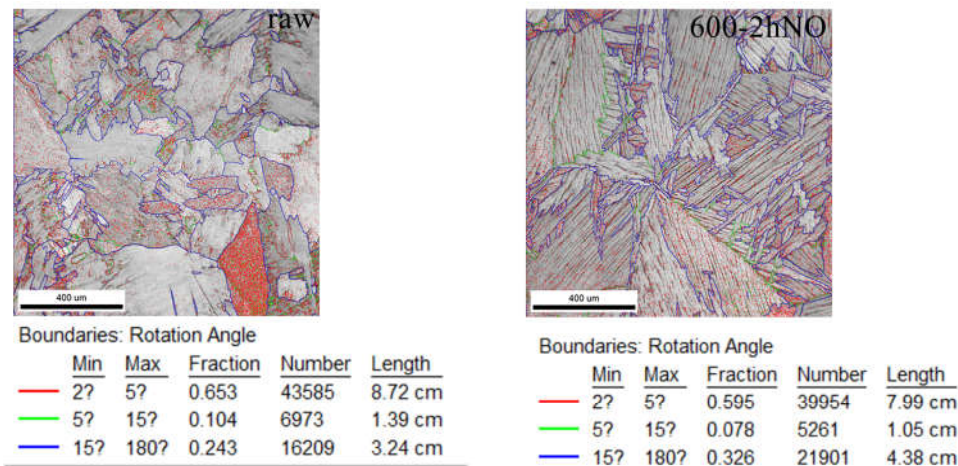


Figure 8. The GB images of raw sample and 600-2hNO sample taken under EBSD.

3.3. Organization Formation of Ti-N-O Alloys During Sintering

Figure 9 shows the schematic diagram of the *Organization* growth of Ti-N-O alloys throughout the sintering process. Firstly, powders with solid solution elements distributed in a stepwise manner from outside to inside are prepared. Among them, the N and O contents of each powder varies due to the different infiltration conditions of different powders. Immediately thereafter, the prepared powders are sintered. At this point a sintered neck starts to form between the powders. Electric current and Joule heat are transferred between the powders, and energy converges throughout the interior of the embryo. Solid solution atoms begin to migrate at this time, diffusing in all directions toward the matrix while large angular grain boundaries and regions of high deformation become their preferred destinations. Although the temperatures in all regions of the embryo have not reached the β -phase transition point, the rapid temperature increase of 150 °C/min does not leave much time for the atoms to migrate. The oxygen-poor and oxygen-rich distribution has been identified. The oxygen-rich interface is marked with a thick red line in the figure. After reaching 1100 °C, the vast majority of the α -phase inside the embryo reaches the β -phase transition point. However, a small number of oxygen-rich interfaces retain the α -phase in this small region due to the stabilizing effect of O (marked by the thick orange line in the figure). During cooling to room temperature, the transient β -phase transforms back into the α -phase, which starts to form the typical α -Ti lath shape during this process. This is hindered by the α -phase, which has not been involved in the phase transition throughout the process (marked by the white dashed line in the figure). In some places, the growth of the lath-like morphology is limited, showing an equiaxed rather than an lath-like morphology. These equiaxed *Organization* intersect with the surrounding lath-like *Organization*, which ultimately make up the *Organization* morphology of the Ti-N-O alloys.

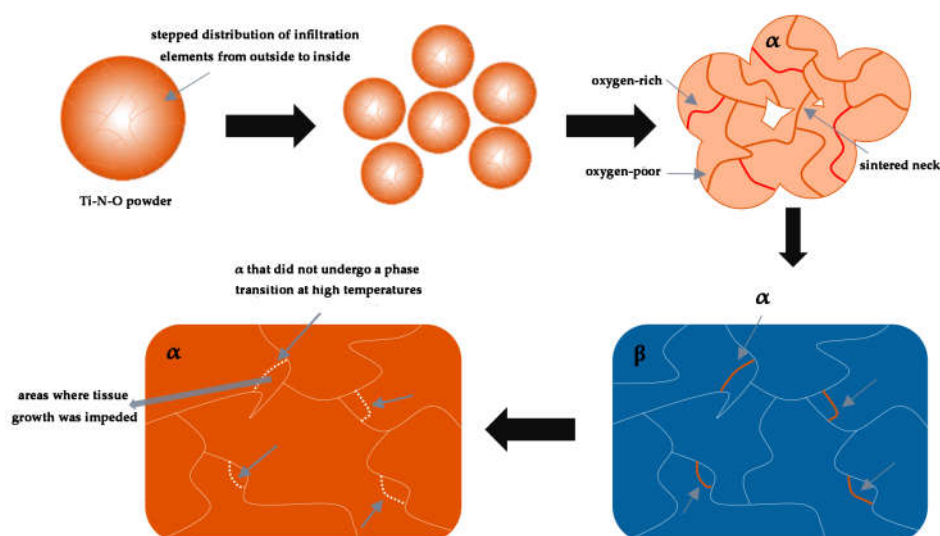


Figure 9. The schematic diagram of the *Organization* growth of Ti-N-O alloys throughout the sintering process.

4. Conclusions

In this work, the effects of N/O on the microstructure and mechanical properties of Ti-N-O alloy were reported. The main conclusions were as follows:

1. The yield strength of Ti-N-O alloy prepared by powder oxynitriding at 600°C for 2 hours was 666 MPa, which was 203% higher than that of cp-Ti, and the hardness was 298.8 HV0.1, which was 125% higher.
2. In the process of preparing Ti-N-O powder, TiO₂ was formed on the surface of powders. After the powder was sintered into a bulk, TiO₂ did not completely disappear, forming a second phase strengthening effect on the matrix, and a large number of dislocations could be observed nearby.
3. The local O element aggregation played a stabilizing role, and the original morphology of α phase was partially preserved, showing a lath + equiaxed α phase structure.
4. More large-angle grain boundaries were produced in the Ti-N-O alloy, which was due to the extrusion deformation between powders leading to the edge breaking, and the sintering temperature rise was equivalent to recrystallization.

Author Contributions: M.S. : Methodology, formal analysis, and writing—original draft. R.C. : Experiment development, data collation, and analysis. C.Z. and G.C. : Research ideas and methods, resources, supervision, project administration, and funding acquisition. Z.X. : Data curation. H.H. : Formal analysis. X.Z. : Formal analysis.

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Data Availability Statement: The raw/processed data required to reproduce these findings cannot be shared at this time as the data also forms part of an ongoing study.

Conflicts of Interest: The authors declare no conflict of interest.

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