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Solidification structure and high temperature oxidation resistance of nano titanium dioxide TiO$_2$ added Inconel 718 deposits by arc melt

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Abstract

In order to refine the microstructure of Inconel 718 and achieve high performance, nanometer TiO$_2$ particles (nano-TiO$_2$) were adopted to modify the solidification structure. After pretreating nano-TiO$_2$, oxide added 718 nickel alloy were prepared by using arc melting technology, and the microstructure and oxidation behavior were investigated in detail. The results show that the microstructures of Inconel 718 alloys with different content of nano-TiO$_2$ are all dendritic-like, and the microstructure of Inconel 718 and achieve high performance, nanometer TiO$_2$ particles (nano-TiO$_2$) were adopted to modify the solidification structure. After pretreating nano-TiO$_2$, oxide added 718 nickel alloy were prepared by using arc melting technology, and the microstructure and oxidation behavior were investigated in detail. The results show that the microstructures of Inconel 718 alloys with different content of nano-TiO$_2$ are all dendritic-like, and the size of dendrite gradually decreases and the shape tends to become equiaxed grain with the increase of TiO$_2$ content. The grain refinement effect is best for 0.6%TiO$_2$ added alloy. The precipitated phases become finer and more uniform due to grain refinement. The high temperature oxidation experiments of Inconel 718 alloy with different volume fractions of TiO$_2$ show that the main oxides are Cr$_2$O$_3$, accompanying with some Nb–Fe oxides. With the decrease of grain size, the size of oxides gradually decreases, and the oxidation layers are more and more compact, which effectively improves the oxidation resistance.

1. Introduction

Nickel-based superalloy has been widely used to manufacture gas turbines and aircraft engines in the fields of aerospace, energy and chemical engineering because of its good mechanical properties at 650 °C [1, 2]. As one kind of precipitation strengthening alloy, Inconel 718 has high content of Nb and a small amount of Ti and Al. The two principal strengthening phases are gamma double-prime ($\gamma''$-Ni$_3$Nb) and gamma prime ($\gamma'$-Ni$_3$(Ti, Al)). Due to the sluggish aging response of $\gamma''$, Inconel 718 has good resistance to strain-aged cracking during post-weld-heating and exhibits good weldability [3–5]. However, due to its poor thermal conductivity and low fluidity, the microstructure of welding deposits is always coarse, which easily leads to the formation of microcracks and affects the mechanical properties and high temperature oxidation resistance [6, 7]. So how to refine the microstructure is very crucial for the performance improvement of nickel alloy.

One point should be taken seriously is that the grain size influences the distribution of alloy elements [8]. Many researchers have studied the effect of alloy elements and grain size on high-temperature oxidation resistance. It is found that Cr plays a decisive role in the high-temperature oxidation resistance [9–11]. Because the diffusion speed of Cr along the grain boundaries is fast, microstructure refinement will accelerate the diffusion of Cr for the increase of total grain boundaries area and promote the formation of protective Cr$_2$O$_3$ layer. In addition, the protective layer is more compact for small-grain alloy.

By investigating the relationship between grain size and diffusion of Cr element [10, 12–14], it is found that the lateral diffusion of Cr proposed by Baer and Kim [8, 14] was coarse-grained and fine-grained, but the oxidation property of low Cr alloy decreases with the increase of grain size. However, the oxidation property of...
austenitic alloy with high Cr content increases with the decrease of grain size due to the higher diffusion of Cr along the grain boundary. Valerie Parry et al [15] indicated that grain refinement of Fe17.5Cr8.1Ni austenitic alloy by pre-plastic deformation leads to forming a fast diffusion network of Cr, thus forming a dense (Cr, Fe)\textsubscript{2}O\textsubscript{3} oxide film, which inhibits the diffusion of easily oxidized elements. In addition, Al element uniformly dispersed in the refined grain can form a protective layer to prevent further oxidation. This is because the increase of grain boundary area provides a large number of priority diffusion channels for easily oxidized elements, which increases their outward transmission speed and promotes the formation of protective continuous oxide film. The smaller the grain size is, the higher the nucleation density and the more uniform distribution of easily oxidized elements are, which is conducive to the formation of continuous and dense oxide film. Moreover, the increase of nucleation density of oxidation products is beneficial to reduce the grain size of oxide layer, that is, the oxide layer contains more grain boundaries as the material matrix. The diffusion of easily oxidized elements through grain boundaries or other short-circuit pathways is much faster than that in the lattice, accelerating the mass transfer of reactants in the oxide film, thus affecting the growth rate of the oxide film. Zheng et al [16] found that the fine NbCr\textsubscript{2} alloy with small grain size and high grain boundary concentration forms a fast diffusion network of Cr and Nb, which promotes the formation of oxides of Cr and Nb and prevents the inward diffusion of oxygen ions.

Grain refinement can be achieved by severe plastic deformation (SPD) and physical and chemical methods. Zhou et al [17] prepared AA1050 aluminum alloy bar by differential velocity sideways extrusion (DVSE) method. Compared with the billet, the grain refinement degree was larger and the mechanical properties of the material were improved. Zhou et al [18] found that under the same conditions, the effective strain of lateral extrusion was larger, the grain refinement was higher, and the comprehensive properties of materials were greatly improved. In addition, grain refinement can also be achieved by adding nanoparticles to promote nucleation. Based on the nucleation theory, John and Lu et al [19, 20] used the nano-functionalization technology to control the solidification structure of aluminum alloy and nitinol alloy additive manufacturing by adding zirconium-based nanoparticles and La\textsubscript{2}O\textsubscript{3}, and obtained fine equiaxial crystal structure. Nano Al\textsubscript{2}O\textsubscript{3} and TiO\textsubscript{2} added in nickel alloy can also effectively refine microstructure and reduce segregation, resulting in the increase of impact toughness and decrease of crack tendency [21, 22]. Y\textsubscript{2}O\textsubscript{3} added in Ni/Ni\textsubscript{3}Al has the same effect as Al\textsubscript{2}O\textsubscript{3} and TiO\textsubscript{2}, and the high temperature oxidation resistance at 1000 °C increases evidently [23]. However, the effect of grain size on oxidation resistance of Inconel 718 alloy is rarely studied. In this work, nano-TiO\textsubscript{2} particles were used to refine microstructure of Inconel 718 alloy. This work aims to study the effect of different content of nano-TiO\textsubscript{2} inoculant on solidification microstructure and precipitation, establish the relationship between high-temperature oxidation and grain size and further understand the high temperature oxidation mechanism of Inconel 718.
2. Experiment

In order to avoid aggregation, nanometer TiO$_2$ (nano-TiO$_2$) powders were coated on the surface of pure nickel particles by LPG High Speed Centrifugal Spray Dryer, as shown in Figure 1. The coating process is as follows. Firstly, the adhesives composed of carboxymethylcellulose sodium and deionized water in the ratio of 1:100 were heated at 90°C for 1.5–2 h. Secondly, nano-TiO$_2$ with particle size of 100 nm was added in carboxymethylcellulose sodium and sodium polyphosphate (worked as dispersant) and stirred for 10–20 min at 90°C. Then, ultrasonic vibrator was adopted to make nano-TiO$_2$ uniformly distribute in the adhesives. Thirdly,

|   | C   | Mn | Fe | P   | S   | Si  | Al  | Ti  | Cr  | Nb | Mo | Ni   | TiO$_2$ |
|---|-----|----|----|-----|-----|-----|-----|-----|-----|----|----|------|--------|
|   | 0.05| 0.1| 20  | 0.01 | 0.001 | 0.06 | 0.45 | 17.4 | 5   | 3  | 3    | Bal    | 0–1.0  |

Figure 2. Microstructures of the fusion zone with different nano-TiO$_2$: (a) 0 wt%, (b) 0.2 wt%, (c) 0.4 wt%, (d) 0.6 wt%, (e) 0.8 wt%, (f) 1.0 wt%.
pure (99.9% minimum) nickel powders (100 um) were added into the solution and stirred for 1.5–2 h. Lastly, the Ni/TiO₂ particles were prepared by LPG High Speed Centrifugal Spray Dryer.

The chemical composition of Inconel 718 alloy used in experiment is listed in table 1.

The samples of nickel alloy with different nano-TiO₂ content were prepared by arc melting furnace. The shielded gas is argon and the gas flow was 15 l min⁻¹. The current is 150 A. The effect of TiO₂ on grain refinement and high-temperature oxidation was studied. The grain refinement effect was evaluated by secondary dendrite arm spacing (SDAS), which is the distance between two adjacent secondary dendrites. The relationship between the high-temperature oxidation resistance and grain refinement was also investigated in detail.

In order to investigate the oxidation resistance, the samples were oxidized at 650 °C for 3 h, 12 h, 36 h, 60 h, 84 h and 120 h, respectively in Muffle furnace. The weight gain was measured by electronic balance with a resolution of 10⁻⁶ mg. The microstructure morphology was examined by Olycia M3 optical microscopy (OM) and EVO MA15 scanning electron microscopy (SEM). The SDAS was measured by Image-Pro Plus. X-ray diffraction (XRD) was used to analyze the phases of coated powders, nickel alloy and oxidation layers. Energy dispersive spectrometer (EDS) was used to analyze the chemical composition of phases and oxides.

Figure 3. The SDAS of nickel alloy with different nano-TiO₂: (a) 0 wt%; (b) 0.2 wt%; (c) 0.4 wt%; (d) 0.6 wt%; (e) 0.8 wt%; (f) 1.0 wt%.

Figure 4. XRD patterns of the fusion zone with different nano-TiO₂.
3. Results

3.1. Microstructure

Figure 2 presents the optical microstructures of Inconel 718 with different TiO$_2$ content. It can be seen that the morphologies of the six samples are all dendritic. For the sample without TiO$_2$, coarse dendrites are observed in figure 2(a). With the increase of TiO$_2$ content, dendrite arms become shorter and the growing directivity of dendrites is not obvious (as shown in figures 2(b) and (c)). Figure 2(d) shows that when the content of the nano-TiO$_2$ is 0.6%, the directivity disappears. However, when the addition of nano-TiO$_2$ is more than 0.6%, the directivity becomes more obvious again, as shown in figures 2(e) and (f).
SDAS is used to evaluate grain refinement effect. From figure 3, it can be seen that SDAS becomes smaller for the TiO2 added alloy. The SDAS decreases firstly and then increases with the increase of weight percent of nano-TiO2. Compared to the alloy without TiO2, the SDAS for 0.6% added one is 5.69 μm, about half of the none TiO2 added one (10.24 μm). However, when the addition is more than 0.6%, the SDAS becomes larger and the SDAS is 8.53 μm for 1.0% added alloy.

It is worth noting that the uniformity of microstructure for the case of 0.8% and 1.0% is getting worse (as shown in figures 2(e) and (f)), which can be explained by nonuniform distribution of nano-TiO2 resulting in poor grain refinement.

The addition of nano-TiO2 can not only refine the grain size but also have significant influence on the composition, distribution and size of the precipitated phases. XRD results (as shown in figure 4) show that the γ, strengthening phase γ’ and γ'' are detected in all the samples. Besides, the NbC is found in the samples with the addition of nano-TiO2, and the strongest peak is got when the addition of TiO2 is 0.6%.

The precipitated phases of none TiO2 added alloy distribute along the grain boundary (interdendritic boundary) in the form of cluster particles (as shown in figure 5(a)). With the increase of TiO2, the precipitated phases distribute more homogeneously due to grain refinement and the shape of precipitated phases become short rods, irregular small bulks, and small spherical shape, as shown in figures 5(b)–(d). The small spherical shape particles are precipitated uniformly at the grain boundary (interdendritic boundary) and in the grains. However, with the further increase of TiO2, most of the precipitated phases are interconnected in the form of

![Figure 6. OXIDE weight gain curve after curve fitting of the samples with different nano-TiO2.](image-url)

**Table 2. Chemical composition of the precipitated phases (wt.%).**

|   | C  | Cr | Fe | Ni | Nb | Si | Ti | Al | O  |
|---|----|----|----|----|----|----|----|----|----|
| a-1 | 16.9 | 14.4 | 17.9 | 40.0 | 10.8 |
| a-2 | 14.1 | 17.3 | 57.9 | 10.1 | 0.6 |
| a-3 | 1.4 | 0.8 | 13.4 | 22.6 | 61.8 |
| a-4 | 46.2 | 6.4 | 3.9 | 11.2 | 32.3 |
| b-1 | 36.7 | 12.6 | 13.7 | 20.9 | 16.1 |
| b-2 | 16.4 | 18.9 | 45.6 | 18.5 | 0.6 |
| b-3 | 9.1 | 1.7 | 19.3 | 5.6 | 64.3 |
| b-4 | 46.2 | 6.4 | 3.9 | 11.2 | 32.3 |
| c-1 | 19.7 | 14.1 | 15.4 | 36.5 | 14.3 |
| c-2 | 15.4 | 17.9 | 41.1 | 25.1 | 0.5 |
| c-3 | 11.7 | 2.00 | 15.9 | 5.2 | 63.9 |
| c-4 | 25.7 | 13.6 | 13.8 | 22.8 | 24.1 |
| d-1 | 23.6 | 10.2 | 12.4 | 33.3 | 20.4 |
| d-2 | 21.9 | 21.7 | 44.6 | 11.3 | 0.5 |
| d-3 | 7.4 | 3.7 | 18.9 | 8.7 | 61.3 |
| d-4 | 41.3 | 7.4 | 6.1 | 9.4 | 35.9 |
| e-1 | 25.1 | 13.1 | 18.5 | 34.6 | 8.7 |
| e-2 | 19.8 | 18.7 | 45.0 | 13.3 | 3.2 |
| e-3 | 6.3 | 1.1 | 17.4 | 6.4 | 67.9 |
| e-4 | 30.9 | 10.6 | 7.5 | 10.5 | 40.5 |
| f-1 | 10.6 | 15.9 | 26.4 | 37.9 | 9.2 |
| f-2 | 19.8 | 18.7 | 45.0 | 13.3 | 3.2 |
| f-3 | 7.6 | 1.0 | 18.2 | 9.8 | 63.4 |
| f-4 | 36.9 | 5.8 | 4.0 | 8.6 | 44.7 |
large bulk and the distribution uniformity of the precipitated phases is getting worse (as shown in figures 5(e) and (f)).

The small spherical particles mainly containing O, Ti, Al, Nb and Cr may be Ti-Al oxides. Al is the main element in Ti-Al oxides for the sample without TiO$_2$ (in figure 5 Point (a-3)). After adding nano-TiO$_2$, Ti is the principal element of the Ti-Al oxides, and Ti oxides may be Ti$_2$O$_3$ (in figure 5 point (b-3), (c-3), (d-3), (e-3) and (f-3)). Ti$_2$O$_3$ can be taken as the refiners to refine microstructure of invar alloy [24]. The quantity of small spherical-like particles is highest when the content of TiO$_2$ is 0.6% because of selection oxidation of alloying elements.

As shown in table 2, the alloying elements of cluster particles (point (a-2)) are Ni, Cr, Fe, Nb and Si, which can be easily formed in $\gamma +$ Laves eutectic [25]. Similar chemical composition of precipitated phases is found in the samples with the addition of nano-TiO$_2$. However, due to grain refinement, the morphology and distribution of precipitated phases change, and short rod and small bulk precipitated phase form, as shown in figures 5(b)–(f). Due to the EDS results, the short rod particles are $\gamma$ + Ni$_3$Nb (point (a-1), (b-1), (c-1), (e-1) and (f-1)). The bulk precipitated phases are mainly composed of Nb and C (point (a-4), (b-4), (c-4), (e-4) and (f-4)). Because the niobium is a kind of carbide-forming element, carbon element can easily react with niobium to form NbC, which leads to the formation of $\gamma +$ NbC eutectic [26].

For the alloy of adding nano-TiO$_2$, $\gamma +$ Laves eutectic and $\gamma +$ NbC eutectic can also be found in figures 5(b)–(f), but the morphology, distribution and amount have changed greatly. The amount of $\gamma +$ Laves eutectic and $\gamma +$ NbC eutectic decreases with the decrease of grain size. Moreover, the amount of irregular small bulks increases with the decrease of SDAS.

3.2. Oxidation kinetics

Figure 6(a) shows the oxide weight gain of the samples holding at 650 °C for 3 h, 12 h, 36 h, 60 h, 84 h and 120 h, respectively. It can be seen that the oxidation curve of the Inconel 718 followed a parabolic law at 650 °C. The samples have a high oxide rate during the initial period (before 12 h), after which follows a gentle growing process in the later stage of oxidation. The first 12 h are the initial nucleation stage of the oxide, also known as the incubation stage. The main influencing factor at this stage is the chemical reaction between metal and oxygen molecules. Grain refinement makes the easy oxidation element such as Cr, Nb distribute uniformly in nickel alloy and increases the total grain boundaries area, which will supply the rapid diffusion channels for metal elements and oxygen and promote the formation of oxides. Because the content of Nb element content is lower, the oxide film on the weld surface is Cr oxide at the initial stage of oxidation. However, the forming oxide film has low density resulting in poor oxidation resistance, so the oxidation weight gain rate is high in the early stage of oxidation. With the increase of oxidation time, the thickness of oxidation film increases gradually and the oxide layer becomes dense. Because the oxide film separates the oxygen from base metal, it can protect nickel alloy from further oxidation and enhance high temperature oxidation resistance, and the oxidation weight gain rate reduces. The weight gain decrease with the decrease of SDAS (as shown in figure 6(b)). However, the oxide
rate of the small SDAS sample is higher than the samples with large SDAS during the initial stage, which can be explained by the fast diffusion of Cr and O along the grain boundaries to form oxides.

The oxidation kinetic curve is also shown in figure 7. It can be seen that the relation between the square of the oxidation weight gain and oxidation time is basically linear. However, alloys with different TiO2 content have different weight gain coefficients of oxidation. According to the oxidation kinetics, the parabolic rate constant \( k_p \) is widely used to characterize the growth rate of mass weight gain and evaluate the oxidation resistance of materials and \( k_p \) is defined as:

\[
\left( \frac{\Delta m}{s} \right)^2 = k_p t \quad [27]
\]

The coefficient of the sample without nano-TiO2 is 0.0058 (figure 7(a)). As the content of nano-TiO2 increases, the oxidation weight gain coefficient gradually decreases (as shown in figures 7(b) and (c)). The coefficient reaches to a minimum 0.0047 when the content of the nano-TiO2 is 0.6%, which means that the oxidation resistance reaches to the best (figure 7(d)). However, when the addition amount is greater than 0.6%, the oxidation weight gain coefficient begins to rise again (as shown in figures 7(e) and (f)).

3.3. Oxidation layer

The surface morphologies of nickel alloy with different mass fractions of nano-TiO2 are shown in figure 8. Large granular particles form at the initial time (at 3 h). With the increase of holding time, cotton-shaped particles form and distribute homogeneously on the surface of nickel alloy (at 84 h and 120 h). It can also be seen that the content of the large granular particles decreases with the decrease of the SDAS (figures 8(b) and (c)). And the sizes of the granular particles become smaller. Moreover, the cotton-shaped particles become dense due to grain refinement (as shown in figures 8(e) and (f)). The fast diffusion of Cr along the grain boundary promotes the formation of \( \text{Cr}_2\text{O}_3 \), and the interface between oxides and matrix also promotes the formation of \( \text{Cr}_2\text{O}_3 \). Therefore, with the increase of holding time, the compact oxide layer form.

Based on the analyses of the EDS, it is shown that the main elements of the granular particles are Cr and O, which means that the granular particles are chromium oxides. The elements of the cotton-shaped particles are

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Figure 8. Surface morphologies and the oxides of the samples with different nano-TiO2 after oxide at 3 h, 84 h and 120 h: (a) 0 wt%; (b) 0.2 wt%; (c) 0.4 wt%; (d) 0.6 wt%; (e) 0.8 wt%; (f) 1.0 wt%. 
Figure 10. Energy-dispersive spectroscopy analysis result of the element distribution of the sample’s cross section line scan with 0.6% nano-TiO₂ after oxide 84 h.

Figure 9. XRD patterns of the samples with 0.6% nano-TiO₂ after oxide at 3 h, 84 h and 120 h.

Figure 11. Schematic diagram of oxidation behavior of samples containing 0.6% nano-TiO₂ at 650 °C.
4. Discussion

4.1. Grain refinement

The grain refinement effect depends on the lattice misfit between the refiner and the nucleated phase, the smaller the mismatch, the better the nucleation on the surface of the refiner surface. Therefore, the smaller the lattice mismatch between the refiner and the nucleated phase, the better the grain refinement [28]. When TiO\textsubscript{2} is added into nickel alloy, it will be decomposed into Ti and O first and then more stable oxide Ti\textsubscript{2}O\textsubscript{3} will form during arc melting and the following solidification.

The Ti\textsubscript{2}O\textsubscript{3} can serve as an effective refiner to refine microstructure [24]. The crystallographic data of Ti\textsubscript{2}O\textsubscript{3} and Inconel 718 are listed in table 3.

In order to study the lattice mismatch between Ti\textsubscript{2}O\textsubscript{3} and Inconel 718, the two-dimensional lattice mismatch proposed by Bramfitt was used [28], as expressed by equation (1):

\[
\delta(nhkl)_{(nhkl)_{n}} = \sum_{i=1}^{n} \left( \frac{d_{uvw} - d_{uvw_{n}}}{d_{uvw}} \right) \times 100
\]

where, \(\delta\) is the lattice mismatch between the refiner and the substrate, (nhkl)\textsubscript{n} and (nhkl)\textsubscript{h} are the low index of the substrate and the nucleated solid, [uvw]\textsubscript{n} and [uvw]\textsubscript{h} are the low index direction of them respectively. \(d_{uvw}\textsubscript{n}\) and \(d_{uvw}\textsubscript{h}\) are the interatomic spacing along [uvw]n and [uvw]h. \(\theta\) is the angle between the [uvw] and [uvw]n.

According to equation (1) and table 4, the lattice mismatch between the refiner and the substrate is shown in table 3. The lattice mismatch between (0001) of Ti\textsubscript{2}O\textsubscript{3} and (111) of Inconel 718 is 1.41%. Ti\textsubscript{2}O\textsubscript{3} has a low lattice mismatch with the matrix, which means that the Ti\textsubscript{2}O\textsubscript{3} can serve as the core of heterogeneous nucleation. Besides, the Ti\textsubscript{2}O\textsubscript{3} particles are located at the grain boundary, which can inhibit grain growth and refine the grain size.

Moreover, the precipitated phases at the grain boundary (interdendritic boundary) and in the grains become finer and uniformly disperse in the matrix. They can also act as the core of heterogeneous nucleation and inhibit grain growth, which contribute to grain refinement.

4.2. Effect of grain size on oxidation resistance

For samples with different SDAS in the present work, the oxides in oxidation layer are composed of Cr\textsubscript{2}O\textsubscript{3}, (Cr, Fe)\textsubscript{2}O\textsubscript{3} and FeNbO\textsubscript{4}. The oxides in outer layer are granular Cr\textsubscript{2}O\textsubscript{3}, and the particles size and content decrease with the decreasing SDAS after 120 h oxidation. That can be explained by the distribution of alloying elements. Grain refinement can eliminate the segregation of alloy elements and make the distribution of Cr uniform. The formation of Cr\textsubscript{2}O\textsubscript{3} is controlled by outward cation diffusion (Cr\textsuperscript{3+}) and inward anion diffusion (O\textsuperscript{2–}), so the uniform distribution of Cr can promote the formation of fine oxide particles, and oxide layer becomes homogeneous.

The diffusion of oxygen and chromium has two ways: lattice diffusivity (D\textsubscript{l}) and grain boundaries diffusion (D\textsubscript{gb}). Both for oxygen and chromium, diffusion speed of D\textsubscript{gb} is much faster than that of D\textsubscript{l}. [9, 10, 12, 14]
because the grain boundaries work as short-circuit diffusion path. Therefore, it is easier and faster for the Cr2O3 to form at grain boundaries. It can be used to explain why the oxide rate of the sample with small SDAS is higher than the samples with large SDAS at the initial stage. Besides, chromium can diffuse laterally from grain boundaries to the whole alloy [9, 14] which contributes to the formation of a densely protective Cr2O3 layer with refined grains. The boundaries between the oxides and matrix can be also acted as short-circuit for the formation of Cr2O3. Therefore, the samples with the smallest SDAS form a dense protective oxide layer. The schematic model is established to demonstrate the oxidation mechanism of Inconel 718 with different grain sizes, as shown in figures 12 (a) and (b).

The EDS and XRD analysis show the presence of Nb oxides, which is FeNbO4. The rank of alloying elements reacting with O at 650 °C is as follows: Al > Ti > Nb > Cr > Fe [29]. However, there are no Al and Ti oxidation products in the oxide layer. That is because of the presence of Ti-Al oxides in nickel alloy, which prevent further oxidation. Nb reacts more easily with O than Cr, so we can find the Niobium oxides in the inner oxide layer.

Cr2O3 is stable below 800 °C, so it can improve the oxidation resistance of material when a densely protective film forms [30]. In this study, the grain size is effectively refined by adding 0.6% nano-TiO2. The grain refinement can not only promote the uniform distribution of Cr but also accelerate the diffusion speed of Cr and O by the short-circuit diffusion path. As a result, the dense and protective oxide film was formed to improve the oxidation resistance.

### 5. Conclusion

Inconel 718 with the different content of TiO2 was prepared by arc melting furnace. The aim is to analyze the solidification microstructure and high temperature oxidation behavior of different prepared alloys and further understand the relationship between grain refinement and oxidation resistance. The obtained results are as follows:

| Table 4. Lattice misfit between refiner (Ti2O3) and the substrate (Inconel 718). |
|-------------------------------|------------------|------------------|------------------|------------------|------------------|
| Ti2O3//Inconel 718            | (hkl)Ti2O3       | (hkl)Inconel 718 | d_hardTi2O3       | d_hardInconel 718 | θ/°               | δ/%               |
| (0001)Ti2O3// (100) Inconel 718 | [120]Ti2O3       | [010]Inconel 718 | 5.125            | 3.601            | 0                 | 30.86             |
|                               | [2110]Ti2O3      | [110]Inconel 718 | 10.25            | 8.051            | 5.91              |                   |
|                               | [1010]Ti2O3      | [100]Inconel 718 | 8.876            | 7.18             | 0                 |                   |
| (0001)Ti2O3// (110) Inconel 718 | [2130]Ti2O3      | [001]Inconel 718 | 5.125            | 3.601            | 0                 | 26.44             |
|                               | [2110]Ti2O3      | [332]Inconel 718 | 10.25            | 8.446            | 4.76              |                   |
|                               | [1010]Ti2O3      | [110]Inconel 718 | 8.876            | 7.635            | 0                 |                   |
| (0001)Ti2O3// (111) Inconel 718 | [2130]Ti2O3      | [110]Inconel 718 | 5.125            | 5.023            | 0                 | 1.41              |
|                               | [1100]Ti2O3      | [211]Inconel 718 | 8.876            | 8.844            | 0                 |                   |
|                               | [2110]Ti2O3      | [101]Inconel 718 | 5.125            | 5.023            | 0                 |                   |

Figure 12. Schematic models representing the oxidation mechanisms of samples with coarse and fine grain size.
(1) Nano-TiO$_2$ effectively refines the solidification microstructure of Inconel alloy. The dendrites tend to become equiaxed grain and the SDAS become lower with the addition of nano-TiO$_2$. For 0.6% added alloy, the SDAS reduces to 5.69 $\mu$m, which is only about half of the SDAS of no oxide added alloy (10.24 $\mu$m). Moreover, the content of the precipitated phases increases, the precipitated phases are also getting finer and the distribution becomes homogeneously with the decrease of grain size.

(2) Oxidation of Inconel 718 followed a parabolic law at 650 °C by varying the oxidation level ranging from 0 to 120 h. The weight gain decreases with the decrease of SDAS and the composition of the oxide layers were Cr$_2$O$_3$, accompanying with Fe-Nb oxides. Meanwhile, with the decrease of grain size, the oxidation products become smaller and the oxidation layer becomes more compact and uniform, which helps to improve the high temperature oxidation resistance of Inconel alloy.

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Data availability statement

All data that support the findings of this study are included within the article (and any supplementary files).

Declarations

We declare that we have no financial and personal relationships with other people or organizations that can inappropriately influence our work, and there are no professional or other personal interests of any nature or kind in any product, service and/or company that could be construed as influencing the position presented in the review of the manuscript, entitled by ‘Grain refinement, High Temperature Oxidation Resistance and Oxidation Kinetics of nano-TiO$_2$ added Inconel 718 Alloy deposits’.

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