High Temperature Oxidation and Thermal Shock Properties of $La_2Zr_2O_7$ Thermal Barrier Coatings Deposited on Nickel-Based Superalloy by Laser-Cladding

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Abstract: In order to reduce the difficulty and cost of manufacturing and improve the high temperature oxidation and thermal shock properties of nickel-based superalloy, a thin $La_2Zr_2O_7$-thermal barrier coating without bond coat was successfully prepared by laser-cladding using $La_2Zr_2O_7$ powders on a nickel-based superalloy substrate. Scanning electron microscopy (SEM) and X-ray diffraction (XRD) methods were used to characterize the microstructure of the coating. The high temperature oxidation and thermal shock properties of the coating were evaluated by the air isothermal oxidation method at 1100 °C for 110 h and thermal cycling method at 25–1100 °C, respectively. The results show that the coating is mainly composed of $La_2Zr_2O_7$-phase. The oxidation weight gain rate of the coating is about two-thirds of that of the substrate, and the first crack thermal shock lifetime of the coating is about 1.67 times of that of the substrate. The oxidation products of the coating are mainly $Fe_2O_3$, $Cr_2O_3$, $NiCr_2O_4$, $Nb_2O_5$ and $La_2Zr_2O_7$. The existence of $La_2Zr_2O_7$ phase in the coating is the main reason for the improvement of its oxidation resistance at 1100 °C and its thermal shock resistance at 25–1100 °C.

Keywords: laser-cladding; $La_2Zr_2O_7$-thermal barrier coating; Ni-based superalloy; high temperature oxidation; thermal shock

1. Introduction

With the development of modern industrial technology, nickel-based superalloys are widely used in aerospace, petrochemical and energy industries [1]. GH4169 is a commonly used precipitation strengthening nickel-based superalloy, which is resistant to high temperature oxidation, corrosion and radiation [2]. However, when its service temperature exceeds 1000 °C, the antioxidation properties of GH4169 at high temperature decline sharply, and a thermal barrier coating is usually required on its surface.

At present, the thermal barrier coating ceramic materials are Al2O3, SiO2, yttria-stabilized zirconia (YSZ) and so on. Although the common YSZ ceramic materials can meet the thermophysical properties and phase stability requirements of the thermal barrier coating at around 1000 °C, YSZ is unable to meet the needs of the development of aeroengine, due to its easy phase transition above 1170 °C [3]. On the other hand, a new ceramic material for thermal barrier coating, $La_2Zr_2O_7$ (Lanthanum zirconate, abbreviations LZ), has attracted great attention due to its high melting point
(2574 K), low thermal conductivity (1.6 W/(m-K)), low density (6.05 g/cm³), low thermal expansion coefficient (9.1 × 10⁻⁶ K⁻¹), no phase transition between room temperature and melting point, and no oxygen penetration [4]. For example, Doleker et al. [5] found that the high temperature oxidation at 1000 °C and thermal shock at room temperature ~ 1150 °C of the LZ/YSZ double ceramic layer were better than that of the single layer YSZ coating when the bond coat was all CoNiCrAlY. Satpathy et al. [6] found that LZ and YSZ had good long-term physical compatibility and better thermal insulation after the preparation of nanometer LZ/YSZ double ceramic layer, by testing the durability of an aircraft engine. Wang et al. [7] found that thermal spraying of n-LZ/YSZ double ceramic coating improved the thermal insulation effect by about 35% compared with n-YSZ single coating. The thermal shock property at 1000 °C was twice as high as that of the n-YSZ coating. The oxidation resistance of two-phase ceramic layer was better than that of single-phase ceramic layer at any temperature. When oxidized at 1200 °C for 400 h, the weight of the dual-phase ceramic layer did not change significantly. Bobzin et al. [8] prepared YSZ, LZ and LZ/YSZ double ceramic layers by using electron beam—physical vapor deposition (EB-PVD). After oxidation at 1300 °C for 25 h, they found that the LZ was prone to fall off, while YSZ had no mixed oxides compared with LZ/YSZ.

It is well-known that the main practical methods for preparing thermal barrier coatings are plasma spraying (PS) and EB-PVD. The former has the advantages of a simple, economical and practical, good thermal insulation effect, but poor stress tolerance and corrosion resistance. The latter can obtain a coating with better aerodynamic and high temperature properties, but the equipment is expensive, complicated and inefficient. To solve the problems of poor oxidation resistance and short coating lifetime caused by high porosity and crack of plasma spraying coatings, the preparation of thermal barrier coatings by laser re-melting or laser-cladding has been studied. A large number of research results [9–19] in the world show that the laser re-melting of plasma spraying thermal barrier coatings can obtain dense columnar structures of epitaxial growth that are not available in plasma spraying coatings, thus improving the strain tolerance and thermal shock properties of the coatings. Laser-cladding can automatically stratify the composition and columnar structure of the gradient thermal barrier coatings, thus improving the high temperature oxidation and thermal shock properties of the coatings. Through the optimization of the laser process parameters and the reasonable design of the composition and properties of the coating system, the thermal barrier coating properties are better than that of plasma spraying and close to that of EB-PVD. In the process of preparing thermal barrier coating by laser-cladding, there are some reports about the use of bond coat [17–19] and not using bond coat [16,20–23]. Among them, the bond coat is mainly MCoCrAlY (M=Ni, Co, Ni–Co alloy), which mainly plays a bonding role and alleviates the difference of thermal expansion coefficient between the ceramic layer and substrate. However, when the thermal barrier coating temperature exceeds 1150 °C, the MCoCrAlY bond coat will oxidize rapidly. As the oxide film is gradually thickened, there will be cracks between the ceramic layer and the bond coat, or even falling off. The ceramic layer without bond coat mainly uses pure ceramic powder [20] or ceramic-based mixed powder [16,21–23]. Obviously, the thermal barrier coating with a bond coat must be prearranged with a bond coat, and then the ceramic layer can be prepared by laser-cladding. The preparation process is complex, and the advantage is that thick ceramic thermal barrier coating can be prepared. Of course, the thermal barrier coating without a bond coat can directly use laser-cladding to prepare the ceramic coating. The preparation process is simple, and the disadvantage is that the thin crack-free and no pores ceramic coating can only be prepared [20].

To our best knowledge, there are no literature reports on the preparation of LZ thermal barrier coating by laser-cladding, but there are a lot of literature reports on the preparation of LZ thermal barrier coating by PS and EB-PVD methods [24–26]. In order to use laser-cladding to prepare thin LZ thermal barrier coating (good thermal stability; long-term service temperature can exceed 1200 °C), this paper wants to try the laser-cladding without bond coat to prepare thin LZ coating, to reduce the preparation process and reduce the manufacturing cost.

In this paper, a thin La₂Zr₂O₇ thermal barrier coating without bond coat was prepared on the surface of GH4169 superalloy by laser preset cladding technology, and its high temperature oxidation and thermal shock properties at 1100 °C and 25–1100 °C were studied, respectively. The results show
that the thin La₂Zr₂O₇ thermal barrier coating without bond coat has better high-temperature oxidation and thermal shock properties than GH4169 superalloy.

2. Materials and Methods

The laser cladding of La₂Zr₂O₇ (JCPDS 01-073-0444) powder (Figure 1) was carried out on a GH4169 nickel-based superalloy. The chemical composition of the used GH4169 superalloy is given in Table 1. The sample size used in the laser-cladding was 100 mm × 50 mm × 8 mm. The powder had a particle size of 37~75 μm and purity of 99.5%. The La₂Zr₂O₇ powder was preset on the surface of the GH4169 superalloy using 4% polyvinyl alcohol solution. The thickness of the preset layer was about 0.2 mm. The laser-cladding experiment was finished by using a LDF8000-60 type semiconductor laser-cladding system (Augsburg, Germany) (Figure 2). The preliminarily optimized laser-cladding parameters were as follows: laser power was 3500 W, laser scanning speed was 10 mm/s, laser spot size was 5 mm × 5 mm, and laser spot overlap rate was 30%. Figure 3 shows the macroscopic morphology of the sample after laser-cladding.

![XRD patterns of La₂Zr₂O₇ powder](image1.png)

**Figure 1.** XRD patterns of La₂Zr₂O₇ powder.

| Element | Cr  | Ni  | Nb  | Al  | Co  | Ti  | Fe   |
|---------|-----|-----|-----|-----|-----|-----|------|
| %       | 18.8| 52.7| 5.3 | 0.5 | 0.02| 0.9 | Bal. |

**Table 1.** Chemical composition of the experimental GH4169 alloy.
The different phases of the coating were determined with the X-ray diffraction (XRD) technique using CuKα radiation at 40 kV and 40 mA (X’Pert PRO, Almelo, Netherlands, start position 2θ = 20.0066°, end position 2θ = 89.9856°, step size 2θ = 0.0130°, scan type was continuous, divergence slit size was 0.4354°). The microstructure of the cross-section coating etched with an aqua regia was examined by a Quanta 650 scanning electron microscope (SEM, FEI, Hillsboro, USA), with energy-dispersive X-ray spectroscopy (EDS, FEI, Hillsboro, USA).

The high temperature oxidation and thermal shock properties were tested according to Chinese aviation industry standard HB5258-2000 “Test method for the determination of oxidation resistance in steel and high temperature alloys” and Chinese aviation industry standard HB7269-96 “Quality inspection of thermal barrier coatings by thermal spraying”, respectively. The test temperature of the high temperature oxidation was 1100 °C, and the test time was 2, 4, 8, 12, 16, 20, 30, 40, 50, 60, 70, 80, 90, 100 and 110 h, respectively. The detailed experimental process is as follows:

1. A digital vernier caliper is used to measure the size of the coating and substrate samples and calculate the surface area $S_0$ of each sample.
2. Washing, ultrasonic, drying alumina crucible.
3. The dried crucible was placed in the M1230 type high temperature furnace and heated to 1150 °C for 30 min, then taken out and cooled to room temperature for weighing, and the crucible was burned to constant weight. Mass of the crucible was measured using an electronic analytical balance (Sartorius BS110, Goettingen, Germany) with an accuracy of 0.1 mg.
4. After each sample is put into the crucible, its overall mass $W_i$ is weighed.
5. The crucible containing the sample was placed in a high temperature furnace, which had been heated to 1100 °C for holding time.
6. The crucible with the sample was taken out and cooled to room temperature and weighed. The crucible mass $W_i$ with the sample was recorded.
7. The mass difference $\Delta W_i$ ($\Delta W_i = W_i - W_0$) of each sample before and after oxidation together with the crucible was taken as the oxidation weight gain mass of the sample.
8. Calculate the $\Delta W_i / S_0$ value.
9. Repeat the above steps until all samples are completed.
10. The $\Delta W_i / S_0$ vs. t curves of all samples were drawn as the isothermal oxidation kinetics curves of different samples at 1100 °C.

It should be pointed out that the sizes of the coating and the substrate samples were 8 mm × 8 mm × 1.3 mm and 8 mm × 8 mm × 8.7 mm, respectively. The heating rate for high temperature oxidation in the box-type resistance furnace was 10 °C/min. According to the requirements of HB5258-2000 standard, we have opened a hole of 12 mm in the door of the box-type resistance furnace, to make enough air enter the furnace chamber and maintain the oxidation atmosphere in the furnace chamber.
The thermal shock property was tested according to the following method: First, the sample (the coating or the substrate sample) was put into an electric furnace at 1100 °C and kept at this temperature for 15 min. Then, it was taken out and quickly cooled in the water at 25 °C, thus completing a thermal shock test. Repeat the process until a crack appears on the surface of the sample. At this point, the number of thermal shocks are denoted as the first crack thermal shock lifetime of the sample.

The surface morphologies of the oxidized specimens were observed using a scanning microscope (Quanta 650, FEI, Hillsboro, USA) with an energy spectrum.

3. Results and Discussion

3.1. Microstructure

Figure 4 shows the scanning electron microscopy morphology of the cross-section coating. When we adopted the measurement method in reference [27], the coating thickness was about 13–18 μm. It can be seen from Figure 4 that the outermost layer of the coating is relatively dense, but the density of the lower part of the coating needs to be improved (this should be achieved by further optimization of laser-cladding parameters), and the interface between the coating and the substrate is good except for a few cracks. This may be due to the large difference in the thermal expansion coefficient between La2Zr2O7 and GH4169 (18.7 × 10^-9/K) and the rapid heating and cooling of the laser-cladding process. In Figure 4, energy-dispersive spectroscopy (EDS)’s results at area A show only La, Zr and O element, and the atomic percentages of the three elements are 15.4%, 18.3% and 66.3%, respectively. According to the XRD calibration results in Figure 5, it can be determined that the coating is indeed La2Zr2O7 phase.

![Figure 4. SEM image of the laser-clad La2Zr2O7 coating.](image)

Figure 4 presents the XRD patterns of the coating prepared by laser-cladding. The results show that the phases are La2Zr2O7 (JCPDS 00-017-0450) and FeNi (JCPDS 00-018-0646) in the laser-clad coating. The La2Zr2O7 phase should come from the laser melting and solidification of the La2Zr2O7 powder, and the FeNi phase should come from the GH4169 substrate (Figure 6). For the La2Zr2O7 phase, according to the diagram of La2O3-ZrO2 [28], the La2Zr2O7 with pyrochlore structure exists in a rather large range temperature from melting point 2300 °C to room temperature. Therefore, when the La2Zr2O7 powder is heated and melted by the laser, the La2Zr2O7 phase does not decompose. When the laser is removed, the melted La2Zr2O7 powder solidifies into the La2Zr2O7 phase. For the FeNi phase, this may be related to the presence of a small number of pores in the lower part of the thin coating (Figure 4) that cause the X-ray to penetrate the coating to the substrate.
In addition, the ratios \( I_{222}/I_{440} \) and \( I_{222}/I_{622} \) of the peak height intensity of crystal planes (222) (at \( 2\theta = 28.59^\circ \)), (440) (at \( 2\theta = 47.56^\circ \)) and (622) (at \( 2\theta = 56.44^\circ \)) in Figure 1 are 2.03 and 2.68, respectively, while the ratios \( I_{222}/I_{440} \) and \( I_{222}/I_{622} \) of crystal plane (222) (at \( 2\theta = 28.66^\circ \)), (440) (at \( 2\theta = 47.69^\circ \)) and (622) (at \( 2\theta = 56.52^\circ \)) in Figure 5 are 1.10 and 1.48, respectively. This may be related to the preferential growth of the crystal planes (440) and (622) in La\(_2\)Zr\(_2\)O\(_7\) phase, during the solidification of the laser-cladding. This phenomenon of preferential facet growth has been widely reported in the literature [29]. Different exposed crystal faces have different oxygen adsorption energies, resulting in different interactions between oxygen and LZ [30], which further affects the antioxidation property of the LZ coating at high temperature.

Moreover, compared with Figure 1, the peak positions of crystal planes (222), (440) and (622) in Figure 5 are shifted to the right. That is, these peak positions are correspondingly moved from 28.59\(^\circ\), 47.56\(^\circ\) and 56.44\(^\circ\) in Figure 1, to 28.66\(^\circ\), 47.69\(^\circ\) and 56.52\(^\circ\) in Figure 5, respectively. According to the Bragg diffraction formula \( 2\sin\theta = n\lambda \), the increase of incident angle \( \theta \) leads to the decrease of the crystal plane spacing \( d \) value, which further leads to the decrease of the lattice constant. In fact, the lattice constant of La\(_2\)Zr\(_2\)O\(_7\) phase of the cubic crystal structure in Figure 1 is \( a = b = c = 1.0808 \) nm, and in Figure 5 is \( a = b = c = 1.07930 \) nm. This may be related to the doping of different alloying elements, such as Ni, Cr, Fe, Nb, etc. from the GH4169 substrate into the La\(_2\)Zr\(_2\)O\(_7\) phase during the laser-cladding process. Since the ionic radii of Ni\(^{2+}\) (0.072 nm), Cr\(^{3+}\) (0.069 nm), Fe\(^{3+}\) (0.064 nm) and Nb\(^{5+}\) (0.070 nm) are all smaller than that of La\(^{3+}\) (0.106 nm) in La\(_2\)Zr\(_2\)O\(_7\) phase; the lattice constant of the La\(_2\)Zr\(_2\)O\(_7\) phase can be reduced when these alloying ions partially replace La\(^{3+}\) to form a substitution solid solution. Literature [28] also confirmed the existence of this phenomenon.
As can be seen from Figure 6, the GH4169 substrate is mainly composed of FeNi (JCPDS 00-003-1209), AlNi3 (JCPDS 00-009-0997), Cr3C2 (JCPDS 00-036-1482) and Ni3Nb (JCPDS 00-023-1274) phases. This is consistent with the results reported in the literature [31].

3.2. High Temperature Oxidation Properties

Figure 7 shows the oxidation weight gain rate of different samples at 1100 °C for different times. It can be seen from Figure 7 that the oxidation weight gain rate of the La2Zr2O7 coating is smaller than that of the GH4169 substrate. This indicates that the La2Zr2O7 coating can protect the GH4169 substrate from oxidation. The reason is that both the oxygen vacancy mobility and the oxygen ion conductivity of La2Zr2O7 are very low [32], and La2Zr2O7 is a ceramic material with extremely low oxygen permeability, which is basically no oxygen permeability material [4, 33]. In addition, the oxidation weight gain rate of the La2Zr2O7 coating is about two-thirds of that of the GH4169 substrate at 1100 °C for 110 h.

![Figure 7. Oxidation weight gain rate of different samples at 1100 °C for different times.](image)

Figures 8 and 9 show the XRD patterns of different samples after high temperature oxidation at 1100 °C for 110 h, respectively. As can be seen from Figure 8, after the oxidation at 1100 °C for 110 h, NiO (JCPDS 01-078-0643), Cr2O3 (JCPDS 01-082-1484), Nb2O5 (JCPDS 00-015-0166), NiCr2O4 (JCPDS 01-075-0198), Fe2O3 (JCPDS 01-076-1821) oxides were formed on the surface of the GH4169 substrate. This is consistent with the results reported in the literature [27]. During the oxidation process of the GH4169 substrate, dense Cr2O3 film, dense Al2O3 film and loose Nb2O5 film were firstly formed on the surface of the substrate. Although the dense Cr2O3 and Al2O3 oxide film can prevent the diffusion of oxygen element, the oxygen element can continue to diffuse into the interior, due to the loose Nb2O5 oxide film. Therefore, when the oxidation continues, NiO, Fe2O3 and NiCr2O4 oxides are formed [34]. It can be seen from Figure 9 that after the oxidation at 1100 °C for 110 h, in addition to maintaining part La2Zr2O7 (JCPDS 01-073-0444) phase, oxides such as Cr2O3 (JCPDS 00-038-1479), Nb2O5 (JCPDS 00-015-0166), NiCr2O4 (JCPDS 00-004-0763) and Fe2O3 (JCPDS 01-076-1821) were formed on the coating surface. Among them, the last four oxides should come from the oxidation of the GH4169 substrate. There are three possible reasons for the five oxides: First, the thermal stability of La2Zr2O7 phase is high, and it will not decompose at 1100 °C, so the La2Zr2O7 phase will persist in the coating. Second, there are a small number of pores and cracks in the coating (Figure 4). Third, the La2Zr2O7 coating demonstrates cracking or layered peeling, due to the difference of thermal expansion coefficient between the La2Zr2O7 ceramic layer and the GH4169 substrate. During the long oxidation process at high temperature, oxygen will diffuse to the GH4169 substrate through the pores and cracks, and then cause partial oxidation of the GH4169 substrate and form the Cr2O3, Nb2O5, NiCr2O4 and Fe2O3.
Figure 8. XRD patterns of the GH4169 substrate after high temperature oxidation at 1100 °C for 110 h.

Figure 9. XRD patterns of the coating after high temperature oxidation at 1100 °C for 110 h.

Figure 10 as with Figure 11, Figure 10 shows the surface and cross-section morphologies of different samples after high temperature oxidation at 1100 °C for 110 h, respectively. Tables 2 and 3 are the EDS’s.

Figure 10. Surface and cross-section morphologies of the oxidized substrate at 1100°C for 110 h, (a) Surface morphology; (b) Cross-section morphology.

Combined with the XRD (Figures 8 and 9) and EDS’s results (Tables 2 and 3) of the different oxidized samples, it can be seen that the oxidation products of the GH4169 substrate after oxidation
mainly include NiO, Cr₂O₃, Nb₂O₅, NiCr₂O₄ and FeO₃ phases, and the thickness of the oxide layer is about 40-45 μm (Figure 10b). The oxidation products of the coating after oxidation mainly include La₂Zr₂O₇, Cr₂O₃, Nb₂O₅, NiCr₂O₄ and FeO₃ phases, and the thickness of the oxide layer is about 18 ~ 30 μm (Figure 11b).

![Figure 11. Surface and cross-section morphologies of the oxidized coating at 1100°C for 110 h; (a) Surface morphology; (b) Cross-section morphology.](image)

| Element | O | Ni | Nb | Cr | Fe | Ti | Co | Al |
|---------|---|----|----|----|----|----|----|----|
| Spot1   | 38.7 | 32.8 | 16.0 | 7.4 | 5.1 | 0 | 0 | 0 |
| Spot2   | 55.1 | 31.8 | 9.8 | 1.9 | 1.4 | 0 | 0 | 0 |
| Spot3   | 52.1 | 32.9 | 8.5 | 4.4 | 2.1 | 0 | 0 | 0 |
| Spot4   | 30.9 | 21.7 | 8.4 | 30.7 | 7.4 | 0.9 | 0 | 0 |
| Spot5   | 53.7 | 34.2 | 7.9 | 2.9 | 1.3 | 0 | 0 | 0 |
| Area B  | 62.1 | 18.2 | 6.9 | 1.8 | 6.3 | 0.8 | 0.3 | 3.6 |
| Area C  | 0 | 22.9 | 25.0 | 33.9 | 12.4 | 2.6 | 0.1 | 3.1 |

| Element | O | Zr | La | Ni | Nb | Cr | Ti | Fe | Al | Co |
|---------|---|----|----|----|----|----|----|----|----|----|
| Spot1   | 65.9 | 2.1 | 0.3 | 1.6 | 11.9 | 15.9 | 1.1 | 1.3 | 0 | 0 |
| Spot2   | 57.2 | 1.8 | 1.0 | 5.8 | 18.7 | 12.1 | 0 | 3.0 | 0.4 | 0 |
| Spot3   | 63.7 | 1.7 | 0.1 | 3.5 | 1.6 | 22.6 | 0.3 | 6.5 | 0 | 0 |
| Spot4   | 66.8 | 1.6 | 0.2 | 1.7 | 9.6 | 12.5 | 2.7 | 3.4 | 1.5 | 0 |
| Spot5   | 72.0 | 1.5 | 0.1 | 4.5 | 10.0 | 7.9 | 1.7 | 2.3 | 0 | 0 |
| Area D  | 49.1 | 10.8 | 0.4 | 15.4 | 4.2 | 3.6 | 1.0 | 6.7 | 8.6 | 0.2 |
| Area E  | 0 | 0 | 56.9 | 7.2 | 15.8 | 0.5 | 17.7 | 1.8 | 0.1 |

In addition, it can be seen from Figure 7 and Table 3 that the oxidation mechanism of the La₂Zr₂O₇ coating and the substrate is basically the same. The difference is that the La₂Zr₂O₇ coating may first generate stress in the coating, due to the difference of thermal expansion coefficient between the La₂Zr₂O₇ ceramic layer and the GH4169 substrate in the thermal cycling process, which is called thermal mismatch stress, and then leads to the coating cracking or layered peeling. Once the La₂Zr₂O₇ coating appears cracking or layered peeling, the external oxygen will spread to the surface of the GH4169 substrate and undergo the same oxidation reaction as the GH4169 substrate. This indicates that the thin La₂Zr₂O₇ coating without bond coat prepared by laser-cladding can delay the oxidation reaction time of the GH4169 substrate to a certain extent, thus improving the oxidation resistance of the GH4169 substrate at high temperature. Of course, if a bond coat is present, the oxygen diffused from the outside will first react with the bond coat alloy, by oxidizing to form the thermal growth oxide (TGO) layer. Once the thickness of TGO layer increases to a certain amount, it will also crack due to stress mismatch, resulting in layer cracking or peeling [35]. Subsequently, the GH4169 substrate will also undergo oxidation reaction. From the high temperature oxidation process without bond coat and with bond coat, it can be seen that the coating with bond coat delays the oxidation of
the GH4169 substrate longer than the coating without bond coat. However, the preparation process of the bond coat is an independent process, such as the plasma spraying process, which undoubtedly increases the manufacturing difficulty and cost. If the requirement of the coating lifetime is not very long, such as the thermal insulation layer for launching satellites and missile warheads, the manufacturing method of the coating without bond coat can be considered. This is also the significance of this study.

Moreover, Figure 7 is actually the oxidation kinetics curve of the GH4169 substrate and laser-clad \( \text{La}_2\text{Zr}_2\text{O}_7 \) coating, oxidizing 0–110 h at 1100 °C. According to Wagner theory [36], when the metal is oxidized at high temperature, it is possible to protect the metal only when a complete dense oxide film with good adhesion to the metal substrate is formed [37]. According to the theory, under ideal conditions, the relationship between the thickening of the oxide film and the oxidation time is parabolic:

\[
\triangle W^2 = Kt
\]

Oxidation weight gain is usually used to replace the increase in oxide film thickness. In formula (1), \( \triangle W \) stands for oxidation weight gain, \( K \) stands for oxidation rate constant and \( t \) stands for oxidation time. However, in practice, the premise of formula (1) is usually unsatisfied, and the following modified formula is usually required:

\[
\triangle W = Kt^n
\]

In order to facilitate fitting, deformation is adopted in the calculation formula [38]:

\[
\ln t = n \ln \triangle W - \ln K
\]

The oxidation kinetics curves of the GH4169 substrate and the coating were fitted according to the formula (3) based on the data of Figure 7, and the \( n \) and \( K \) values were obtained, respectively (Table 4). As can be seen from Table 4, the \( n \) and \( K \) values of the coating are 1.53 and 0.47, respectively. The \( n \) and \( K \) values of the GH4169 substrate are 1.31 and 0.48, respectively. According to the judgment that "the larger the oxidation index is, the smaller the oxidation rate constant is, the denser the oxide film is, and the better the oxidation resistance at high-temperature is", the high temperature oxidation resistance of the coating is better than that of the GH4169 substrate. This is consistent with the experimental results (Figure 7).

**Table 4.** Oxidation rate constant \( K \) and oxidation index \( n \) of the coating and substrate.

| Samples              | Oxidation Index \( n \) | Oxidation Rate constant \( K \) |
|----------------------|-------------------------|---------------------------------|
| \( \text{La}_2\text{Zr}_2\text{O}_7 \) coating | 1.53                    | 0.47                            |
| GH4169 substrate     | 1.31                    | 0.48                            |

### 3.3. Thermal Shock Properties

According to Chinese aviation industry standard HB7269-96, we obtained that the first crack lifetime of the coating and the substrate samples were 100 and 60, respectively. This indicates that the thermal shock property of the coating is better than that of the substrate, and the first crack lifetime of the coating is 1.67 times that of the substrate. This may be related to the low thermal expansion coefficient of \( \text{La}_2\text{Zr}_2\text{O}_7 \) phase in the coating and the high thermal expansion coefficient of the substrate. According to the thermal stress formula, \( \sigma = \alpha \times \Delta T \), the thermal stress \( \sigma \) is small under the same temperature difference \( \Delta T \) because the coefficient \( \alpha \) of thermal expansion of \( \text{La}_2\text{Zr}_2\text{O}_7 \) phase in the coating is small. On the contrary, the thermal stress is greater.

Figure 12a and Figure 12b are macroscopic photos of the coating and substrate after 100 and 60 thermal shocks, respectively. It can be seen from Figure 12 that the first crack width of the coating is larger than that of the substrate. This may be related to the fact that the fracture toughness of the \( \text{La}_2\text{Zr}_2\text{O}_7 \) coating is lower than that of the GH4169 substrate. The lower the fracture toughness value of the \( \text{La}_2\text{Zr}_2\text{O}_7 \) coating, the faster the crack propagation, the larger the crack opening and the wider
the crack width. On the contrary, the higher the fracture toughness value of the GH4169 substrate, the slower the crack propagation, the smaller the crack opening and the smaller the crack width.

Figure 12. Macroscopic photos of different samples after first crack thermal shock; (a) Coating; (b) Substrate.

It should be pointed out that if the laser-cladding method is used to prepare the thin LZ thermal barrier coating with a bond coat, the coating resistance to high temperature oxidation and thermal shock properties should be better than the coating without bond coat, but the former is more expensive to manufacture. In addition, the use of a bond coat is an essential step in the preparation of a thick LZ thermal barrier coating with excellent properties by laser-cladding. Finally, in order to obtain the thin LZ coating without cracks and pores, the laser-cladding parameters in this paper need to be further optimized.

4. Conclusions

In order to reduce the difficulty and cost of manufacturing and improve the high temperature oxidation and thermal shock properties of nickel-based superalloy, a thin La2Zr2O7 coating without bond coat was successfully prepared on GH4169 substrate by laser-cladding based on pure La2Zr2O7 powder. The thin La2Zr2O7 coating is mainly composed of the La2Zr2O7 phase. The high temperature oxidation property of the thin La2Zr2O7 coating at 1100 °C for 110 h and the thermal shock property at 25-1100 °C are superior to that of the GH4169 substrate. The difference of the thermal expansion coefficient between La2Zr2O7 and GH4169 has an important effect on the high temperature oxidation and thermal shock properties of the thin La2Zr2O7 coating. The preparation method of the thin La2Zr2O7 coating without the bond coat provided in this paper is suitable for a situation where the requirement of the coating lifetime is not long, such as the thermal barrier coating for launching satellite and missile warhead, which can reduce the manufacturing difficulty and cost. In addition, in order to obtain the thin La2Zr2O7 coating without cracks and pores, the laser-cladding parameters in this paper need to be further optimized.

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