Effect of Three Heat Treatments on High Temperature Oxidation Properties of GH4169 Alloy Produced by SLM Additive Technique

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Abstract. In this paper, GH4169 nickel-based superalloy molded samples produced by Selective Laser Melting (SLM) were subjected to aging treatment and solution and aging treatment to study the high temperature oxidation behavior under different heat treatments. It is found that the high temperature oxidation products of GH4169 samples produced by SLM is mainly Cr2O3. The alloy sample under heat treatment has a higher high temperature oxidation rate. The oxide film of GH4169 alloy sample treated by solution and aging treatment has a high forming speed, and the surface of the oxide film is continuous and dense, and the quality is the best, and the protection effect on the alloy matrix is the best.

1. Introduction
GH4169 is a nickel-based superalloy with excellent comprehensive mechanical properties. It is widely used in the manufacture of important parts in aerospace, petrochemical and other fields [1]. It is an important basic alloy material, and its mechanical properties have been extensively studied [2, 3]. Since high-temperature nickel-based alloys have sufficient oxidation resistance at the service temperature (<700°C), there are few studies on their high temperature oxidation problems. However, the GH4169 alloy has many oxidizable elements such as Nb, Mo and Fe and a spot of Al, the alloy parts therefore may be oxidized on the surface during hot working or high temperature service, and excessively thick oxidation may be formed in severe cases, which in turn affects the normal and safe use of parts, and even leads to scrap [4].

In addition, therefore, the application of SLM rapid prototyping technology to produce complex solid superalloy parts with excellent performance can solve the problem of low forming efficiency of parts due to various factors in the traditional manufacturing process. Therefore, this study has a great theoretical and practical significance to study on the high temperature oxidation performance of GH4169 alloy manufactured by SLM and the influence of different heat treatments on its high temperature oxidation performance. The main research contents of this topic are as follows:
(1) Study the results of alloys under different heat treatments after heating and oxidizing experiment, and analyze the law of oxidation mass gain;
(2) Study the surface morphology and phase composition of the oxide film after isothermal temperature oxidation, analyze the oxidation process, and summarize the effect of heat treatment on the high temperature oxidation performance of GH4169 alloy and its mechanism.

2. Experimental procedures

2.1. Experimental Materials
The alloy powder was prepared into GH4169 alloy samples by a EOSINT-M280 selective laser melt forming system. In the SLM process, the laser power is 300W, the laser diameter is 0.1mm, the scanning speed is 1200mm/s, the scanning distance is 0.12mm, and the thickness of each layer is 0.03mm. Its chemical composition is shown in Table 1.

| C  | Si | B  | Mn | Cr   | Ni | Mo | Al | Nb | Ti | Cu | Co | Fe   |
|----|----|----|----|------|----|----|----|----|----|----|----|------|
| 0.03| 0.05| 0.003| 0.03| 19.01| 52.30| 3.06| 0.57| 5.07| 1.00| 0.02| 0.02| Bal. |

2.2. Heat Treatment
According to the TTT curve of the alloy and the conventional heat treatment system, three different heat treatment processes were developed in this experiment.

| Number | Heating Treatment | Name |
|--------|-------------------|------|
| A      | 720°C×3h, 50°C/h FC to 620°C×3h, AC | DA   |
| B      | 950°C×1h, AC+720°C×3h, 50°C/h FC to 620°C×3h, AC | ST   |
| C      | 1050°C×1h, AC+720°C×3h, 50°C/h FC to 620°C×3h, AC | GST  |
| D      | Untreated         | AS   |

The heat treatment experiment of the GH4169 alloy sample was carried out in GWL-1400 electric furnace at a heating rate of about 300°C/h. The samples’ number, heat treatment and its name are shown in Table 2.

2.3. High Temperature Oxidation Experiment
The polished and cleaned samples were oxidized for 48h in a GWL-1400 box-type electric furnace at 850°C. Another set of samples is placed in a differential scanning calorimetry (DSC) to perform a heating and oxidizing experiment. The experimental atmosphere is pure oxygen, the oxidation temperature is gradually increased from 25°C to 1200°C, the heating rate is 0.25°C/s, and the total heating time is 4700 s.

The oxidation resistance of the GH4169 alloy is analyzed by the percentage of oxidation mass gain of samples. To calculate the percentage increase in weight of high temperature oxidation samples, refer to the following formula:

\[ P^+ = \frac{W_t - W_0}{W_0} \times 100\% \]  

(1)

Where: \( P^+ \) is the percentage of oxidation mass gain of the sample; \( W_t \) is the mass of the sample after the oxidation experiment (mg); \( W_0 \) is the mass (mg) of the sample before the oxidation experiment.
2.4. **Characterization Analysis**

The metallographic structure is observed using an optical microscope (OM). The phase composition of the alloy sample and its oxidized oxide film is analyzed by Rigaku Ultima IV X-ray diffractometer (XRD). The scanning range is 2θ=20-80°. The FEI Nova Nano SEM 450 scanning electron microscope is used to observe and analyze the morphology of the surface oxide film of the alloy samples under different heat treatments.

![XRD patterns of GH4169 alloy samples under different heat treatments](image)

**Figure 1.** XRD patterns of GH4169 alloy samples under different heat treatments

3. **Results and discussion**

3.1. **Unoxidized Phase**

Figure 1 shows that the diffraction peak of the matrix phase can be monitored under all conditions. The γ' phase and the γ'' phase are the two main strengthening phases of the GH4169 alloy, but the two strengthening phases are co-precipitated with the γ matrix phase, so the diffraction peaks of the γ' phase and the γ'' phase are covered up by γ phase, which results in the inability to observe individual diffraction peaks of the γ' phase and the γ'' phase from the diffraction pattern. In addition, since the volume fraction of the σ phase and the carbide phase in the alloy are small, it is difficult to detect the diffraction peaks of them. These results are basically consistent with the findings of Song et al [5].

![Oxidation kinetic curves of GH4169 alloy samples under different heat treatments](image)

**Figure 2.** Oxidation kinetic curves of GH4169 alloy samples under different heat treatments

3.2. **Oxidation Kinetics**

As can be seen from the Figure 2, the oxidation kinetics curves of the four samples showed the same trend as a whole: the oxidation mass gain is not obvious in the temperature range of 25°C-800°C, and the curve showed a relatively flat shape. It shows that GH4169 alloy has excellent high temperature oxidation resistance below 800°C. After 800°C, the alloy undergoes intense oxidation reaction and the weight increases rapidly. This rule accords with the conclusions of C. Wagner and Tomashov [6-8].
AS sample does not show a significant tendency to oxidize before 900°C and shows a rapid increase after 900°C. The DA and ST samples both have small oxidation mass gains and low oxidation rates before 1000°C. But the rates increase significantly after 1000°C, and the percentage of mass gain of the ST sample is higher than that of the DA sample in the same case. Before 1100°C, the general trend of mass gain of GST sample is about the same as the curve of AS sample.

3.3. Oxide Film Analysis

3.3.1. Phases. It can be seen from the Figure. 3 that after isothermal temperature oxidation, the diffraction peaks of γ matrix phase and Cr2O3 are observed in each sample, and the difference in heat treatments also makes the intensities of characteristic peaks of each phase different. A small amount of Fe2O3 is also observed in the oxide film of each oxide film. Besides, a NiCr2O4 spinel phase is observed both in the GST sample and the AS sample.

![Figure 3. XRD patterns of oxide film of GH4169 alloy samples under different heat treatments](image)

In the initial stage of oxidation, the surface of the nickel-based superalloy will react to form a large amount of Cr2O3 oxide layer [9], and the weight of the oxidation product of the alloy increases rapidly. Since Cr rapidly diffuses to the surface of the alloy for oxidation, a depleted area of Cr appears under the oxide layer, which is called depletion of Cr [10-11]. Under the action of the chemical element concentration gradient, Ni element reacts with oxygen to form NiO. At the same time, at a higher temperature, NiO can react with Cr2O3 to form NiCr2O4 spinel phase. The formed Cr2O3 oxide film is uniform and dense, which can prevent further oxidation of the inner alloy matrix, and NiCr2O4 relatively does not have such protection.

Due to the depletion of Cr, Fe element is also diffused to the surface of the alloy by the concentration gradient of chemical elements [12], and reacts with oxygen in the surrounding environment to form Fe2O3. NiO and Cr2O3 can also interact to further form a NiFe2O4 spinel phase.

In this experiment, the oxidation products Cr2O3 are formed in the four samples, and no obvious NiO characteristic peaks and NiCr2O4, NiFe2O4 spinel phase characteristic peaks are observed. It is proposed that the formed oxide film Cr2O3 is continuously dense and the depletion of Cr of matrix surface is not significant, which hinders the formation of NiCr2O4 and NiFe2O4 spinel phases.

3.3.2. Surface Morphology. It can be seen from Fig. 4 that the surface structure of the oxide film of the AS sample is relatively uneven, and the grains of oxidation structure are sparse (Fig. 4a), and a large number of pores and cracks can be observed. The pore size of the oxide film on the surface of the DA sample is reduced, but severe folds occurred (Fig. 4b). Besides, plenty of cracks are found at the edges of the folds (Fig. 4b). The surface oxide films of the ST and GST samples are both dense and uniform, and there are fewer holes and cracks (Fig. 4c, 4d), indicating that the solution treatment can improve
quality of oxide film of GH4169 alloy. Furthermore, as the solution temperature increases, the pores and cracks of oxide film of alloy reduce, making the compactness of oxide film better.

In addition, it can be seen that the surface of the oxide film of the ST and GST samples under solution treatment even shows a distinct continuous clustered rod-like oxidation structure (Fig. 4c, 4d), which are more clear on the surface of the GST oxidized sample (Fig. 4d). It is speculated that the formation position is at grain boundary because the grain boundary can provide the nucleation position and nucleation energy required for the oxide nucleation [13]. The nucleation oxide grows initially perpendicular to the surface of the alloy. Then it follows by re-nucleation at the interface to form new oxides and interconnects to grow between the oxides, ultimately forming a continuous oxide film structure. The oxide firstly develop and grow at the grain boundary, and it is known from the foregoing results that the grain size and boundary size become large after solution treatment, so that the rod-shaped oxide structure is formed at the large grain boundary during the oxidation process and can be observed easily.

![Figure 4. Low magnification morphology of oxide film surface of GH4169 alloy samples under different heat treatments](image)

4. Conclusion

Main conclusions are drawn as follows:

(1) Direct double aging treatment does not affect the grain size change of the alloy. The grains of the sample subjected to the aging and solution treatment are increased, and they significantly increase after solid solution at 1050°C and aging treatment because the σ phase is completely dissolved into the matrix at 1050°C, its limiting effect on grain growth disappears, resulting in grain coarsening and grain boundary flattening.

(2) The three samples treated by heat treatment formed a continuous dense oxide film during oxidation, and the surface defects were not obvious. The surface of the oxide film of GST sample is
smooth, continuous and dense, few cracks existed, and the number of holes is the least. In addition, obvious rod-like oxidation structure is observed in the oxide film morphology both of ST and GST samples. This is because the rod-shaped oxidized structure should be an oxide cluster structure formed at the grain boundary, and can grow rapidly and be clearly observed on the surface of the oxide film of solution-treated alloy with large grain and grain boundary.

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