Preparation of IC21 Spherical Powders by PREP Process

Qingsiang Wang*, Zhu Zhen and Shujin Liang
Sino-Euro Materials Technologies of Xi’an Co., Ltd., Xi’an 710018, China.
Email: wangqx2010@163.com

Abstract. The IC21 spherical powders with main content of Ni3Al were successfully manufactured by the high speed plasma rotating electrode process (HS-PREP). The powders particle size distribution fitted the mixed spraying model well. The chemical contents changes after melting were detected. The microstructure of the IC21 powders was formed by cellular crystal on the surface and dendrite inside, which was a typical PREP powder. The morphologies and properties of the irregular powders were also analyzed which indicated that the composition segregation and oxides inclusion of the electrode were the main reason for the formation. However, its proportion was less than 0.5%, which would not affect the additive manufacturing. The fundamental powder particle size distribution data for different rotating speeds was measured. The morphology and properties result show that the PREP could support qualified IC21 spherical powders with significant powder yields.

Keywords. Particle size distribution; IC21; Superalloy; Atomization.

1. Introduction
Ni3Al-based superalloys are developed based on the typical Ni-base superalloys in 1980. Compared with the traditional Ni-base alloy, the Ni3Al-based superalloy has lower density and better high-temperature properties with the higher content of Al 7.5-8.0 wt.%, which has been used extensively in aerospace, gas turbine and other higher temperature oxidation filed [1-5].

The Mo-rich Ni3Al single crystal superalloy of IC21 contained Re element was expanded from the IC6SX alloy which has been applied in some advanced engines for aerospace [6-7]. The SC structure results in the reducing of the grain-boundary strengthening elements of B, Zr and Hf [2, 8]. It has been reported that IC21 has a better high-temperature properties than that of the IC6SX alloy [9].

With development of the additive manufacturing (AM), the using of superalloy powders becomes more and more universal [10-12]. The gas atomization (GA) and centrifugal atomization (CA) are the main commercial atomization methods for superalloy powders, such as electrode induction melting gas atomization (EIGA) and plasma rotating electrode process [13-15].

Compared with GA method, the PREP powders show a lower level of porosity, which can not escape during rapid melting and solidification [16]. Besides, there is no clear research result of the particle size distribution (PSD) control of GA method, which is important for atomization cost control. Moreover, the accurate PSD model proposed by our research group, which can be used to predict a random size range powder yield for PREP, has been reported recently. It fitted the results well under the conditions that the rotating speeds ranging from 14000-20000 r/min [17]. However, the last research are only focused on nickel-based alloy such as EP741NP and Inconel718, and the intermetallic compound alloys like Ti3Al, Ni3Al and Nb3Sn which have been used in the AM application for aviation blades and superconductivity are not vericated. The research status shows that supplying nickel-based spherical powders by PREP is more preferred and cost-effective. Therefore, in
order to enlarge the AM applications for IC21, the manufacturing of PREP IC21 powders is of significance.

2. Experiments and Principle

The IC21 powders were atomized and received by PREP. The atomization powers were set to 50-60 kW when working. In order to reduce the increase of gas elements in the chamber, the vacuum degree of the atomization chamber is controlled to be lower than 5×10⁻³ Pa maintained for at least an hour, and then a non-transferred plasma torch as the heat source with working gas atmosphere of Ar/He mixture was used. The electrode diameter was 75 mm and the safe rotating speed for it was less than 24000 rpm. The powders were atomized in different rotating speed, and then the powders were sieved immediately and a comparison was done between the tested value and the predicted values. The physical factors of IC21 were calculated by JMatPro 7, for ρ 8.22 g/cm³, σ 1.83 N/m, μ 7.21 mPa·s.

The powders and the electrode should be sampled to analyze the chemical changes after the HS-PREP. The as-received powders should be also well protected to make optical microscopy (Olympus GX51 optoical microscope), scanning electron microscope (SEM) to analyze the powder quality (JSM-6700F, JEOL, Japan). The energy dispersive spectrometer (EDS) was used for the elemental analysis. Electron Backscatter Diffraction (EBSD) analysis was performed on the as-polished samples in a SEM system equipped with an EBSD detector which is used to analyze the cross section of the powder to obtain the grain and grain boundary morphology. The properties such as fluidity and apparent density with those powders were also measured with ASTM B855 standard. Laser particle size test was also done by Mastersize 2000 with ASTM B822 standard.

The PREP was used for producing spherical powders by the step as melting, atomization and solidification. The schematic diagram of a typical PREP atomizer can be seen in figure 1. In atomization, the rotating electrode was fed into the chamber and touched the flames elected from the plasma torch placed in another direction. The end of the electrode, heated by the high-temperature flames, would be molten immediately and formed a thin liquid film by the influence of spinning. The boundary of the liquid film would form some protrusions and become a huge liquid drop, fly away from the boundary when the centrifugal force is powerful enough against the droplets’ surface tension which is the direct drop formation (DDF). With the development of the atomization power (liquid flow or centrifugal effect), the particle-separation would evolve into the ligament disintegration (LD), the particle formed by the strings is usually smaller than the DDF. If the atomization power keeps going, the atomization model would become the film disintegration (FD). The differences are of the DDF, LD and FD are shown in figure 2.

![Figure 1. A sketch map of the PREP atomizer.](image-url)
Figure 2. The elemental 3 models for PREP, direct drop formation (DDF), ligament disintegration (LD) and film disintegration (FD). [17]

The most important physical factors for the CA are liquid density ($\rho$), melting pool diameter ($D$), volume melting rate ($Q$), metal liquid ($\gamma$) surface tension, viscosity ($\mu$) and the speed of the molten pool ($\omega$). The drop diameter formed by the DDF is shown in equation (1) [17].

$$d = \frac{1}{\omega} \sqrt{\frac{12\gamma}{\rho D}}$$

The commercial PREP atomization model is the mixture of the LD and DDF [17]. Thus, the LD powders fraction, $\varepsilon_{LD}$, in the final received powders can be considered as equation (2) [17]. The $Q_1$ and $Q_2$ are the critical melting rate of DDF-LD and the fully developed LD [17].

$$\varepsilon_{LD} \approx \frac{Q - Q_1}{Q_2 - Q_1}$$

$$\left(\frac{Q_1 \rho}{\mu D}\right) \left(\frac{\alpha \rho D^2}{\mu} \right)^{0.95} = 1.52$$

$$\left(\frac{Q_2 \rho}{\mu D}\right) \left(\frac{\alpha \rho D^2}{\mu} \right)^{0.63} = 0.46$$

The diameter for LD particles can be calculated by equation (5) [15-17].

$$d_{LD} = 2.0D \sqrt{\frac{\gamma}{\rho \alpha \rho^2 D^3}}$$

The PSD can be calculated as a Rosin-Rammlar distribution shown in equation (6) to (7) [17].

$$F(d)=1-\exp(\ln(0.5)\cdot\left(\frac{d}{d_{50}}\right)^n)$$

$$F(a, b) = (1 - \varepsilon_{LD})(F_{DDF}(b) - F_{DDF}(a)) + \varepsilon_{LD}(F_{LD}(b) - F_{LD}(a))$$
The shape factor of the PREP RR distribution peaks is about 5. Before the PSD model, the classical view often regards the PREP PSD as a unimodal caused by the DDF, so the single-DDF model result can be calculated as $\varepsilon_{LD}=0$.

3. Results and Discussions

3.1. PSD Comparing between Tested Value and Simulations

The PSD data calculated from mixed model, single-DDF model and the sieving experiments for different rotating speeds was shown in figure 3 and figure 4. The shape factors for the used RR distributions for both the mixed model and single DDF model are 5 (n=5). The percentage of $<45 \, \mu m$ for 22000 rpm IC21 was about 30.18 wt.%, the mixed model result was 24.82 wt.% and the single DDF result was 3.41 wt.%. For 16000 rpm, the tested $<45 \, \mu m$ percentage was 7.23 wt.% and the mixed model calculation result was 4.92 wt.%, while the DDF model result was 0.70 wt.%. The other size ranges’ data had similar results. It is indicated that the mixed model matched the tested value well, but the single-DDF model had distinct differences compared with the real values. The reason was that the in higher speed (>20000rpm), the rotating power was strongly increased and the main atomization had been developed from the DDF into DDF-LD mixture, and the LD particle diameter was always smaller than the DDF particle as shown in equation (5) and equation (1), thus, the PSD would be bimodal. Therefore, using the classical view of single DDF model would bring more errors.

![Figure 3](image)

**Figure 3.** HS-PREP IC21 PSD data of testing, mixed model calculation and single DDF model of RR distribution with a shape factor of 5, with 22000 rpm rotating speed and 75 mm electrode diameter.

The good fitting relationship between mixed model and the tested values showed that the real atomization system for the IC21 was also a mixture of the LD and DDF. Thus, it was not accurate for evaluating the PREP IC21 PSD under the classical view that the PSD should be unimodal. Another evidence was that when the rotating speed decreased from 22000 to 16000 rpm, the simulated PSDs from the mixed model and the single DDF assumption became more similar than the high-speed results shown in figure 4. The reason was that higher speed often made the centrifugal power stronger and increased the LD fraction of the mixture, so the gap between the PSD model (LD-DDF mixture) and single DDF model became larger.
Figure 4. IC21 PSD data of testing, mixed model calculation and single DDF model of RR distribution with a shape factor of 5, with 16000 rpm rotating speed and 75 mm electrode diameter.

Figure 5 shows the powder size distribution curve with the rotating speed from 10000 rpm to 22000 rpm. It is indicated that the yield distribution curve of powders obtained by PREP follows a double logarithmic normal distribution. When the rotating speed was higher than 20000 rpm, the average size of the powders was about 55-65 μm, and most of the powders are distributed in the range of 10-180 μm. Moreover, about 90% of the particle size is less than 106 μm, and the yield of powders less than 53 μm is 43%. This is smaller than the powder prepared by electrode induction melting gas atomization (EIGA) as a whole, while the D10 data is larger than EIGA, which indicated that in the 0-15 μm range, EIGA had more advantages [18]. However, when the rotating speed was 16000 rpm, the average particle size of the powder is about 90-106 μm, and most of the powders are distributed in the range of 45-180 μm. Moreover, about 90% of the particle size is more than 53 μm, and the yield of powders more than 53 μm is 85%. When the rotating speed was further reduced to 10000 rpm, a large amount of coarse powder would be obtained which can not satisfy the additive manufacturing for selective laser melting (SLM) and electron beam melting (EBM).

3.2. Chemical Contents of Electrode and Powders
The chemical contents of both electrode and as-received powders were shown in table 1. It is indicated that after the rapid melting-atomization-solidification steps, the contents of the fundamental element still matched the requirement of the IC21. The results showed that the HS-PREP could support applicable IC21 powders without the obvious elements contents changes and burning loss of Al. It should also be mentioned that oxygen and nitrogen in the received powders significantly increased after HS-PREP, the probable reason was that the residual air polluted the powders, which was a common phenomenon for any atomization methods. For the record, the elements such as O and N still keep qualified after HS-PREP.
Table 1. The chemical contents of IC21 standard, electrode and powders.

| Elements (wt.%) | Al   | Mo   | Ta   | Cr   | Re   | Y    | N    | O    | H    |
|----------------|------|------|------|------|------|------|------|------|------|
| Standard       | 7.6~8.3 | 9~13 | 2.4~4 | 1.5~2.5 | 1~2 | <0.01 | < | 0.003 | 0.01 | <0.001 |
| Electrode      | 8.05 | 10.33 | 3.41 | 1.85 | 1.24 | <0.01 | 0.001 | 0.001 | <0.001 |
| Powders        | 7.94 | 10.15 | 3.33 | 1.58 | 1.25 | <0.01 | 0.002 | 0.005 | 0.001 |

3.3. Microstructure the HS-PREP IC21 Powders

It is well known that the elements of chromium, molybdenum and tantalum are listed as Al-substituting elements in NiAl and act as strengthener in the IC21 superalloy [19]. Figure 6 shows the XRD patterns of the HS-PREP IC21 spherical powders which indicated that the nickel monoaluminide was obtained as the main phase with peaks of (110) (200) (211). Moreover, the chromium/molybdenum/tantalum based solid solution crystallizing in the bcc system with the same peaks of (110) (200) (211) was also formed. However, it is very difficult to quantitatively assess the contents of phase components of IC21 spherical powders according to the XRD patterns. This is because the NiAl and Cr/Mo/Ta phases had close lattice parameters in the cubic crystal system. Furthermore, the lattice parameter of the bcc phase was 0.2877 nm by calculated with the XRD data. Compared with the reference value (0.2887 nm) for equiatomic nickel monoaluminide, it is significantly reduced because of the decreased aluminum content and replacement of some atoms in the NiAl lattice with Cr, Mo and Ta atoms.

Figure 6. XRD patterns of HS-PREP IC21 spherical powders.

The OM, SEM and EDS results of the HS-PREP IC21 powders and cross section were shown in figure 7. It can be indicated that the shape of the HS-PREP IC21 powder was almost spherical. The surface of the powders was full of developed dendrites (figure 7(b)) and the interdendritic precipitates were found inside the powders as seen in figure 7(c) and 7(d) which was almost the same as Inconel718 alloy [20]. The secondary dendritic arm spacing (SDAS) of the HS-PREP IC21 powders was about 2-5 μm, owing to the fast cooling speed. The melt droplets contact with the He/Ar atmosphere medium being sputtered to result in rapid crystallization at rates of 104-106 K/s due to the small particle size, while the spherical shape is retained. The microstructure is consisted of the major and continuous γ(Ni based solid solution) phase, with less volume fraction of dendrites of β(NiAl) phase formed as a consequence of microsegregation [21]. The γ(Ni3Al) phase was also found while the proportion of quantity was very small. The EDS detection of the IC21 powders was shown in figure 7(e,f). It can be seen that the EDS element content was very similar with the IC21 requirement which indicated that the HS-PREP IC21 powders had no obvious micro segregations. Combined with the chemical analysis, the HS-PREP IC21 powders had very homogeneous composition ranging from macro-size to micro-size, which was useful to support isotropic homogeneity.
EBSD was used to analyze the cross section of the powder to obtain the grain and grain boundary morphology which could get the grain size distribution inside the powders. The result of the IC21 powders in size range between 45-53 μm was shown in figure 8. It can be seen that there were many different sized grains inside the IC21 powder with the average particle size of 50 μm. The shape of the grains was irregular and generally jagged. The average grain size was 7.5 μm, with the largest grain size reaching 17 μm.

However, some irregular particles less than 0.5% were also found during the preparation process. The EDS detection of the irregular particles was shown in figure 9 and table 2. It can be seen that the EDS element content was different with the IC21 requirement which indicated that the black irregular particles were the composition segregation and oxides inclusion found in the raw material of electrode. It is proved that the melting time in the PREP was too short to cause a change in composition.

![Figure 7](image_url)

**Figure 7.** Images of HS-PREP IC21 spherical powders: (a) ×50, (b) ×1000. (c) OM image of cross section, (d) the interdendritic precipitates, (e) and (f) EDS results of the HS-PREP IC21 spherical powders.
Figure 8. Orientation distribution map of IC21 powders in size range between 45-53 μm.

Figure 9. The EDS results of the HS-PREP IC21 irregular powders.

Table 2. The EDS results of the HS-PREP IC21 irregular powders.

| Sample | Elements | Ni  | Al  | Cr  | Mo  | Ta  | Re  | O   | N   |
|--------|----------|-----|-----|-----|-----|-----|-----|-----|-----|
|        | EDS Mass wt.% | 92.36 | 4.13 | 1.64 | 1.87 | /   | /   | /   | /   |
|        | EDS Atom at.%  | 88.52 | 8.61 | 1.77 | 1.1  | /   | /   | /   | /   |
|        | EDS Mass wt.% | 70.6 | 11.45 | 2.01 | 9.99 | 2.33 | 0.2 | 2.55 | 0.87 |
| 005    | EDS Atom at.%  | 59.98 | 21.17 | 1.93 | 5.2  | 0.64 | 0.05 | 7.95 | 3.08 |
|        | Error %       | 0.8  | 0.12 | 0.33 | 0.3  | 0.43 | 0.47 | /   | /   |

In order to analyze the cause of the formation of irregular powder, the photo and structure diagram of the molten pool after solidification were done as shown in figure 10. It can be seen from figure 10 that the solidified molten pool is mainly composed of three parts, coarse grain area, fine grain area and passageway. During powder preparation, the temperature curve is shown in figure 10(b). It gradually decreased from the core to the edge of the molten pool. The composition segregation and oxides inclusion were mainly found in the core of the electrode which was the defects due to melting. During the powder preparation process, due to the difference in melting point temperature, the defect points of the rod in the core were more easily thrown out directly under the action of centrifugal force and maintain the original shape, forming irregular particles. Meanwhile, ormal droplets will be ejected along the flow channel, forming regular spherical particles. Therefore, improving the uniformity of the composition of the structure and increasing the vacuum degree during the smelting process can reduce irregular particles during the powder preparation process.
Figure 10. The photo (a) and structure diagram (b) of the molten pool after solidification.

3.4. Properties of IC21 Powders

The fluidity, apparent density and tap density were also measured for different size of the IC21 powders as seen in table 3. All the properties between two kinds of powders were almost similar. The result also indicated that all the powders had good fluidity which was usefull for the SLM and adverse for the EBM in the process of additive manufacturing.

Table 3. The properties of IC21 powders.

| Properies         | 0-53 μm | 53-106 μm |
|-------------------|---------|-----------|
| Fluidity (s/50g)  | 14.47   | 14.92     |
| Apparent density (g/cm³) | 4.72   | 4.76     |
| Tap Density (g/cm³)  | 5.24   | 5.21     |

4. Conclusion

The HS-PREP could manufacture high quality IC21 spherical powders without obvious irregular particles or micro/macro segregations. The particle size distribution of the HS-PREP IC21 powders showed a good fitting relationship with the mixed model (DDF-LD mixture).

The weight percentages of any size range for the HS-PREP IC21 powders could be well calculated and the fitting effects of the mixed model were more accurate than the classical view of the single DDF assumption for PREP.

The chemical contents changes after melting were detected with less gas element increment. The morphologies and properties of the HS-PREP IC21 powders were also analyzed which indicated that the composition segregation and oxides inclusion of the electrode were the main reason for the irregular powders ormation.

Acknowledgments

This work was financially supported by the National Key Research and Development Program Funded Projects (2018YFB1106400).

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