Effect of Trace Element Hf on the Microstructure of Nickel-Based Powder Metallurgy Superalloy FGH97 Postprint

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Abstract

The morphology, chemical composition, and content of the g'phase and MC-type carbides in FGH97 powder superalloys with five Hf contents were investigated using scanning electron microscopy (SEM) and physicochemical phase analysis. The results indicate that Hf promotes the precipitation of both the g' and MC phases and alters their chemical compositions. While Hf has minimal effect on the size and morphology of the MC phase, it significantly influences those of the g' phase, inducing morphological instability that leads to splitting of cubic g' precipitates and accelerating the transition to a stable cubic preferred morphology. In FGH97 alloy, Hf addition can modify the critical splitting size Dc of the g' phase by changing the lattice misfit d. A relationship between Dc and Hf content w(Hf) was established: Dc=315.4+640.2w(Hf)-358.2[w(Hf)]2. As Hf content increases, |d| gradually decreases while Dc increases. When the g' phase grows to the critical size, it splits from a cubic morphology into an octet of small cubic sub-particles.

Full Text

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Abstract

Microelement Hf added in Ni-based powder metallurgy (PM) superalloy can modify microstructure and improve mechanical properties, such as stress-rupture life, creep resistance and crack growth resistance, and also benefit to eliminate notch sensitivity. So systematically studying the effect of microelement Hf on PM superalloy microstructure will help to comprehend its corresponding mechanism. The effects of microelement Hf on the morphologies, chemical compositions and content of γ' phase and MC carbide in FGH97 PM superalloy were investigated by means of SEM and physicochemical phase analysis. The results showed that Hf facilitated the precipitations of γ' phase and MC carbide, and changed chemical compositions of γ' phase and MC carbide. The effect of Hf on the size and morphology of MC carbide was not obvious, while Hf greatly affected the size and morphology of γ' phase and accelerated the splitting of γ' phase from one instable cubic γ' particle to stable octet of cubes. As Hf affected the lattice misfit of γ '/γ phase (δ), modifying Hf content changed the critical splitting size of γ' phase (Dc). The relationship between Dc and Hf content (w(Hf)) was found to be Dc=315.4 + 640.2w(Hf) - 358.2[w(Hf)]^2. With Hf content increased, the absolute value of δ decreased and Dc increased. Cubic γ' particle split into an octet of cubes when γ' phase grew up to the critical splitting size.

KEY WORDS powder metallurgy superalloy, FGH97, Hf, γ'phase morphology stability, MC carbide

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1. Introduction

The addition of microelement Hf to nickel-based powder metallurgy superalloys can improve mechanical properties such as stress-rupture life, creep resistance, and crack growth resistance by modifying the microstructure, and also helps eliminate notch sensitivity [**?**]. Hf promotes the precipitation of γ' phase and MC-type carbides, enters into these phases to form Hf-containing γ' and MC carbides, and changes their chemical compositions while increasing their lattice constants [**?**, **?**].

Previous studies have shown that Hf addition changes the morphology of γ' phase in nickel-based powder metallurgy superalloys. For example, in IN100 superalloy, Hf promotes γ' phase growth—compared with the alloy containing 0.40% Hf (mass fraction, the same below), the blocky γ' phase becomes coarser in the alloy with 1.05% Hf, providing less strengthening effect [?]. In NASA IIB-11 superalloy, Hf addition promotes γ' phase precipitation in a network morphology [?]. Reference [?] reported that adding 0.25%~1.7% Hf to Astroloy superalloy significantly affects γ' phase morphology. With increasing Hf content, numerous fan-shaped γ' phase arrangements precipitate from the alloy, which can be explained by one or more γ' phases nucleating at grain boundaries and subsequently growing into the matrix. Elements continuously diffuse from the matrix to the γ' phase, promoting branching of γ' phase and resulting in radial growth that eventually forms fan-shaped arrangements. Studies [?, ?, ?] have shown that adding appropriate amounts of Hf to nickel-based powder metallurgy superalloys makes MC-type carbides distribute dispersedly. Thus, Hf addition leads to different γ' phase morphologies in different nickel-based powder metallurgy superalloys. Additionally, research [?] has demonstrated that under elastic strain fields, individual cubic γ' phase in nickel-based superalloys can split into doublet of plates and octet of cubes, where the γ' phase size does not increase but instead transforms into smaller cubic γ' phases.

Excessive Hf addition provides little benefit for improving the comprehensive mechanical properties of alloys [?]. In currently used nickel-based powder metallurgy superalloys containing Hf, such as N18, RR1000, EP741NP, and FGH97, the Hf content is controlled below 0.8% [?, ?]. Therefore, this work investigates the effects of Hf content on the chemical composition, morphology, size, and content of γ'phase and MC-type carbides in FGH97 nickel-based powder metallurgy superalloy, which helps understand the relationship between microstructure and properties in Hf-containing powder metallurgy superalloys.

2. Experimental

Five FGH97 nickel-based powder metallurgy superalloys with different Hf contents were selected for this study. The FGH97 alloy contains solid solution strengthening elements Co, Cr, W, and Mo, as well as γ' phase and MC-type carbide forming elements Al, Ti, Nb, Zr, and Hf. The main chemical composition of FGH97 alloy (mass fraction, %) is: C 0.04, Co 15.75, Cr 9.0, W 5.55, Mo 3.85, Al 5.05, Ti 1.8, Nb 2.6, Hf 0~0.89, trace B and Zr, and Ni balance. The five Hf contents (mass fraction, %) used in this work were 0, 0.16%, 0.30%, 0.58%, and 0.89%. Alloy powders were prepared by plasma rotating electrode process with particle sizes of 50~150 m, and consolidated by hot isostatic pressing (HIP) at 1200 °C. The consolidated samples were solution treated at 1200 °C for 4 h followed by air cooling, then subjected to a three-step aging treatment with final aging at 700 °C for 15~20 h.

The chemical composition and content of γ' phase and MC-type carbides were determined by physicochemical phase analysis. The morphology of carbides was observed using a JSM-6480LV scanning electron microscope (SEM), and carbide particle sizes were measured using an image analyzer by counting 10 fields at 500× magnification. The morphology of γ' phase was observed using JSM-6480LV SEM and SUPRA 55 field emission gun SEM (FEG-SEM). SEM samples were prepared by electrolytic polishing followed by electrolytic etching. The electrolytic polishing was performed in a solution of 20% H_2SO_4 + 80% CH_3OH (volume fraction) at 30 V for 15~20 s. The electrolytic etching was conducted in a solution of 85 mL H_3PO_4 + 5 mL H_2SO_4 + 8 g CrO_3 at 5 V for 3~6 s. The γ' phase size was measured using Image-Pro Plus 6.0 software. The lattice constant of γ' phase and the γ '/γ misfit in bulk alloy samples were measured using a D/max 2500H X-ray diffractometer (XRD). The lattice constant of extracted γ' phase powder was measured using a TTR3 XRD with Cu target (Cu Kα_1 wavelength = 0.15406 nm). The measurement method is described in reference [**?**].

3. Results

The experimental results show that the five FGH97 alloys with different Hf contents consist of a γ matrix, γ' phase, MC-type carbides, and trace amounts of M_6C-type carbides and M_3B_2-type borides, with γ' phase and MC-type carbides being the main precipitates. Table 1 presents the physicochemical phase analysis results of phase contents in FGH97 alloys with different Hf contents. As shown in Table 1, with increasing Hf content in the alloy, the MC-type carbide content increases and the γ' phase content also slightly increases. The γ' phase content accounts for about 62%, MC-type carbides do not exceed 0.34%, and the total amount of M_6C-type carbides and M_3B_2-type borides does not exceed 0.21%. Thus, no new phases were found in FGH97 alloys with different Hf contents. From Hf-free to 0.89% Hf-containing FGH97 alloys, the grain shape is relatively regular with little change in size, ranging from 30~40 m.

3.1 Morphology and Composition of γ' Phase In the five FGH97 alloys with different Hf contents, γ' phase distributes both within grains and at grain boundaries, exhibiting three morphologies: large-sized grain boundary γ' phase precipitated from the γ solid solution during cooling (termed grain boundary γ' phase); intragranular square γ' phase precipitated from supersaturated γ solid solution during cooling (termed secondary γ' phase); and fine γ' phase precipitated from supersaturated γ solid solution during aging (termed tertiary γ' phase). Figure 1 [Figure 1: see original paper] shows the morphology of γ' phase in FGH97 alloy with 0.30% Hf, where grain boundary γ' phase and secondary γ' phase are blocky (Fig. 1a) and tertiary γ' phase is granular (Fig. 1b).

The experimental results indicate that trace Hf addition to FGH97 alloy does not change the morphology of grain boundary γ' phase and tertiary γ' phase, but significantly affects the morphology of secondary γ' phase. Figure 2 [Figure 2: see original paper] shows SEM images of secondary γ' phase morphologies in FGH97 alloys with different Hf contents. In Hf-free and 0.16% Hf-containing alloys, secondary γ' phase is mainly cubic (Figs. 2a and b). With increasing Hf addition, secondary γ' phase grows and splits. In FGH97 alloy with 0.30% Hf, secondary γ' phase is mainly octet of small cubes and butterfly-shaped (Fig. 2c). In the alloy with 0.58% Hf, secondary γ' phase is mainly cubic and octet of small cubes (Fig. 2d). In the alloy with 0.89% Hf, secondary γ' phase is mainly cubic (Fig. 2e).

Table 2 gives the γ' phase contents in FGH97 alloys with different Hf contents. With increasing Hf addition, the γ' phase content slightly increases from 61.9% in Hf-free alloy to 62.7% in 0.89% Hf-containing alloy. Grain boundary γ' phase accounts for less than 5%, secondary γ' phase accounts for more than 50%, and tertiary γ' phase accounts for less than 7%, with little change in the proportions among the three types of γ' phase. When Hf is added to FGH97 alloy, the γ' phase becomes $(Ni,Co)_3(Al,Ti,Nb,Hf)$ containing mainly Ni, Co, Al, Ti, Nb, and Hf, where Hf substitutes for Al while other elements show little change. Figure 3 [Figure 3: see original paper] shows the Al and Hf contents in γ' phase of FGH97 alloys with different Hf contents. With increasing Hf content in the alloy, the Hf content in γ' phase gradually increases while the Al content gradually decreases, indicating increased substitution of Al by Hf. At Hf contents of 0, 0.16%, 0.30%, 0.58%, and 0.89%, the chemical formulas of γ' phase are $(Ni_{0\cdot852}Co_{0\cdot148})_3(Al_{0\cdot783}Ti_{0\cdot129}Nb_{0\cdot088})$, $(Ni_{0\cdot854}Co_{0\cdot146})_3(Al_{0\cdot781}Ti_{0\cdot129}Nb_{0\cdot088}Hf_{0\cdot002})$, $(Ni_{0\cdot855}Co_{0\cdot145})_3(Al_{0\cdot778}Ti_{0\cdot129}Nb_{0\cdot088}Hf_{0\cdot005})$, $(Ni_{0\cdot856}Co_{0\cdot144})_3(Al_{0\cdot773}Ti_{0\cdot129}Nb_{0\cdot088}Hf_{0\cdot010})$, and $(Ni_{0\cdot857}Co_{0\cdot143})_3(Al_{0\cdot767}Ti_{0\cdot129}Nb_{0\cdot088}Hf_{0\cdot016})$, respectively. The amounts of Al substituted by Hf in γ' phase are 0, 0.2%, 0.5%, 1.0%, and 1.6%, respectively.

Table 3 gives the average sizes of γ' phase in FGH97 alloys with different Hf contents. With increasing Hf content, the size of tertiary γ' phase shows little change, with an average size of 14~18 nm. The sizes of grain boundary γ' phase and secondary γ' phase first increase and then gradually decrease, with grain boundary γ' phase averaging 820~1450 nm and secondary γ' phase averaging 276~511 nm. The alloy with 0.30% Hf shows the largest grain boundary γ' phase and secondary γ' phase sizes at 1450 nm and 551 nm, respectively. The secondary γ' phase sizes in all alloys follow a normal distribution. Since the atomic radius of Hf is larger than that of Al, the lattice constant of γ' phase increases after Hf addition. XRD analysis of bulk alloy samples and extracted γ' phase powder shows that the lattice constant of γ' phase in bulk samples increases from 0.35928 nm in Hf-free alloy to 0.35953 nm in 0.89% Hf-containing alloy, while that of powder γ' phase increases from 0.35890 nm to 0.35922 nm. In bulk alloy samples, the γ' phase lattice constant is smaller than that of the γ matrix phase, forming a negative misfit. Consequently, the γ' phase is subjected to tensile stress from the γ matrix phase, which increases the atomic spacing and lattice constant of γ' phase. When γ' phase is extracted from the alloy, this tensile stress disappears and the γ' phase becomes unconstrained, resulting in a smaller lattice constant for powder γ' phase compared to that in bulk samples.

3.2 Morphology and Composition of MC-Type Carbides MC-type carbides exhibit a granular morphology and are dispersedly distributed within grains and at grain boundaries, with larger sizes at grain boundaries. With increasing Hf addition to FGH97 alloy, the MC-type carbide size shows little change, with an average size of 0.878~1.064 m. Figure 4 [Figure 4: see original paper] shows SEM images of MC-type carbide morphology in FGH97 alloy with 0.30% Hf.

The addition of Hf to FGH97 alloy forms composite MC-type carbides (Nb,Ti,Hf)C containing mainly Nb, Ti, and Hf. Figure 5 [Figure 5: see original paper] shows the relationship between MC-type carbide content and the contents of Nb, Ti, and Hf in MC-type carbides versus Hf content in FGH97 alloy. With increasing Hf addition, the total amount of carbide-forming elements Nb, Ti, and Hf increases, leading to increased MC-type carbide content from 0.264% in Hf-free alloy to 0.338% in 0.89% Hf-containing alloy. Figure 6 [Figure 6: see original paper] shows the changes of Nb, Ti, and Hf contents in MC-type carbides with Hf content in the alloy. With increasing Hf content, the Hf content in MC-type carbides gradually increases while Nb and Ti contents gradually decrease, indicating substitution of Nb and Ti by Hf. Moreover, with increasing Hf content, more Ti and Nb are substituted in MC-type carbides at a roughly 1:1 ratio, independent of Hf content in the alloy, as shown in Table 4 . At Hf contents of 0, 0.16%, 0.30%, 0.58%, and 0.89%, the simplified chemical formulas of MC-type carbides are $(Nb_{0\cdot664}Ti_{0\cdot336})C$, $(Nb_{0\cdot654}Ti_{0\cdot323}Hf_{0\cdot023})C$, $(Nb_{0\cdot642}Ti_{0\cdot308}Hf_{0\cdot050})C$, $(Nb_{0\cdot619}Ti_{0\cdot280}Hf_{0\cdot101})C$, and $(Nb_{0\cdot574}Ti_{0\cdot253}Hf_{0\cdot173})C$, respectively. Since the atomic radius of Hf is larger than those of Nb and Ti, the lattice constant of MC-type carbides slightly increases after Hf addition. XRD results of extracted carbide powder show that the lattice constant of MC-type carbides increases from 0.442 nm in Hf-free alloy to 0.447 nm in 0.89% Hf-containing alloy.

4. Discussion

The above experimental results show that at low Hf content in FGH97 alloy, γ' phase appears as regularly arranged cubic particles. With increasing Hf content, cubic γ' phase splits, indicating that Hf promotes the growth and splitting of cubic γ' phase. The cubic γ' phase splits into an octet of small cubes, enabling γ' phase to more quickly achieve a stable cubic preferred morphology [**?**].

Elastic strain energy theory determines precipitation characteristics and preferred morphology based on the principle of minimizing the sum of elastic strain energy and interfacial energy. The preferred morphology of γ' phase is determined by the minimum sum of elastic strain energy and interfacial energy. However, when elastic stress fields of γ' phase particles overlap, elastic interaction occurs between particles. Studies [**?**] have shown that elastic interaction between γ' phase particles not only affects their arrangement but also influences the morphology of individual γ' particles, with elastic interaction playing a dominant role in γ' phase morphology. The splitting process of coherent γ' phase is an energy reduction process. During splitting, the interfacial energy of γ' phase increases, but the elastic interaction energy between split γ' particles can overcome this increase in surface energy, thereby reducing the total system energy. Therefore, elastic interaction energy is the driving force for γ' phase splitting. The total energy E of a coherent individual γ' particle can be expressed as [?]:

E = E + E + E

where E is the elastic strain energy caused by γ/γ' misfit, E is the interfacial energy of γ' phase, and E is the elastic interaction energy between γ' particles. E is negative and proportional to the absolute value of misfit $|\delta|$, meaning E originates from γ/γ' misfit δ, i.e., from the overlap of lattice misfit stress fields.

Microscopic elastic theory calculations [?] show that when cubic γ' particles are small, the total energy of cubic γ' phase is lower than that of octet of small cubes, making cubic γ' phase stable. As γ' particle size increases, the total energy of octet of small cubes becomes lower than that of cubic γ' phase, making γ' morphology unstable and causing splitting into octet of small cubes. Clearly, the morphological stability of γ' phase depends on the magnitude of elastic interaction energy relative to surface energy.

The misfit δ was measured by XRD, and the critical splitting size Dc (the size of large cubic γ' particles at the onset of splitting) and average γ' particle size Da were measured using Image-Pro Plus 6.0 software, as shown in Table 5 . Based on Table 5, the relationship between Dc and Hf content w(Hf) is plotted in Figure 7 [Figure 7: see original paper]. The relationship between Dc and w(Hf) can be expressed as:

$\mathrm{Dc} = 315.4 + 640.2\mathrm{w(Hf)} - 358.2[\mathrm{w(Hf)}]^2$

Table 5 and Figure 7 show that with increasing Hf content in the alloy, $|\delta|$ gradually decreases while Dc gradually increases. When γ' particle size exceeds Dc, γ' particles split from cubic to octet of small cubes, leading to changes in γ' phase size.

Reference [?] pointed out that γ' phase splits when growing to a certain critical size and derived an expression for the critical size for splitting from cubic to octet of small cubes:

$\mathrm{Dc} = 50\mathrm{r}_0$

where $\mathrm{r}_0 = \sigma/\mathrm{E}_1$ is the characteristic length of the material, with σ being the specific surface energy of γ' phase and E_1 being a material constant given by $\mathrm{E}_1 = -0.5\mathrm{b}^2\Delta\delta^2/[\mathrm{c}_{11}(2\mathrm{c}_{11}-\Delta)]$, where $\mathrm{b} = \mathrm{c}_{11} + 2\mathrm{c}_{12}$, $\Delta = \mathrm{c}_{11} - \mathrm{c}_{12} - 2\mathrm{c}_{44}$, b is the bulk modulus of γ' phase, Δ is the anisotropy factor of γ' phase, and c_{11}, c_{12}, and c_{44} are elastic constants of γ' phase in different crystal directions.

Assuming that small Hf additions to FGH97 alloy have negligible effects on σ and other parameters and only affect δ, the relationship between Dc and δ can be derived from equation (3):

$Dc = K/|\delta|$

where $K = -\sigma c_{11}(2c_{11}-\Delta)/(0.5b^2\Delta)$. Equation (4) shows that the smaller $|\delta|$ is, the larger Dc becomes, confirming that the measured trend of Dc in Table 5 is correct.

Hf addition to FGH97 alloy promotes the growth of cubic γ' phase. In Hf-free and 0.16% Hf-containing FGH97 alloys, most γ' particles have not reached the critical size, so they remain cubic without splitting (Figs. 2a and b). With further Hf addition, γ' particle size continues to increase. When Hf content reaches 0.30%, γ' particles grow to the critical size and cubic γ' particles begin to split into the low-energy preferred morphology of octet of small cubes (Fig. 2c). As seen in Fig. 2c, many γ' particles appear to consist of 4 cubes, but FEG-SEM observation clearly reveals they are composed of 8 small cubes [?]. When Hf content reaches 0.89%, γ' particle size far exceeds the critical splitting size, and most γ' particles have completed splitting, becoming cubic with smaller sizes (Fig. 2d).

5. Conclusions

1. The main precipitates in FGH97 alloys with different Hf contents are γ' phase and MC-type carbides, with small amounts of M_6C-type carbides and M_3B_2-type borides.
2. Hf addition to FGH97 alloy partially enters γ' phase, occupying Al sublattice sites and substituting for Al atoms, changing the γ' phase composition to $(Ni,Co)_3(Al,Ti,Nb,Hf)$. Partial Hf also enters MC-type carbides, substituting for Ti and Nb atoms and changing the MC-type carbide composition to (Nb,Ti,Hf)C. With increasing Hf content in the alloy, γ' phase content slightly increases and MC-type carbide content increases.
3. Hf addition to FGH97 alloy does not affect the size and morphology of MC-type carbides but strongly influences the size and morphology of γ' phase. Hf entering γ' phase changes the distribution of elastic interaction energy during γ' growth, promoting the splitting of cubic γ' phase into octet of small cubes and enabling γ' phase to more quickly achieve a stable cubic preferred morphology.
4. Hf addition to FGH97 alloy changes the critical splitting size Dc of γ' phase by modifying the misfit δ. The relationship between Dc and Hf content w(Hf) is $Dc = 315.4 + 640.2w(Hf) - 358.2[w(Hf)]^2$. With increasing Hf content, the absolute value of misfit $|\delta|$ gradually decreases and Dc increases. When γ' particles grow to the critical size, they split from cubic to octet of small cubes.

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Note: Figure translations are in progress. See original paper for figures.