EFFECT OF STABILIZING TREATMENT ON PRECIPITATION BEHAVIOR OF ALLOY 706

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Abstract

Ni-Fe-base superalloy 706 has recently been used for high temperature services. A stabilizing treatment between solution-annealing and age-hardening treatments has been proposed for this alloy to improve its creep rupture life. However, the relationship between stabilizing treatment and precipitation behavior has not been well understood. The precipitation behavior of Alloy 706 was investigated and related with creep rupture properties. Samples taken from a gas turbine disk forging were solution-treated at 980°C for 3h and stabilizing-treated in a range of 780 to 900°C for 1.5 h, followed by the double-aging at 720°C for 8h and at 620°C for 8h. Precipitation behavior of these samples was examined by TEM, and creep rupture tests were conducted at three conditions with varying temperature and applied stress.

Fine γ' - γ'' co-precipitates having the core of γ' being overlaid with γ'' on its top and/or bottom and large γ' - γ'' co-precipitate having the core of γ' being completely covered with γ'' were identified in the grain matrix together with large γ' and fine γ'' phases that have been found to precipitate in Alloy 706. η was identified at the grain boundary and found to be accompanied with a serrated grain boundary and denuded zone. Such precipitation behavior was significantly affected by stabilizing temperature, especially below 840°C, and so was creep rupture property accordingly. It is concluded that the best creep rupture properties are obtained when an optimum combination is established between intra-granular fine γ'/γ'' co-precipitates, intra-granular large γ'/γ'' co-precipitates, and the inter-granular η phase.

Introduction

Ni-Fe-base superalloys are age-hardened by the precipitation of coherent γ' and/or γ'' in the austenitic matrix γ (1). Alloy 706 is a relatively

new material and was developed from Alloy 718 a representative wrought superalloy. Compared with Alloy 718, Alloy 706 has a chemical composition of no molybdenum, reduced niobium, aluminum, chromium, nickel and carbon, and increased titanium and iron. This excellent balance of chemical composition results in superior characteristics to Alloy 718 in segregation tendency, hot workability and machinability (2-4). Therefore, Alloy 706 is suitable for large forgings and has been used for high temperature services (5).

A stabilizing treatment between solution-annealing and age-hardening treatments has been proposed for Alloy 706 to improve its creep rupture life (6). The improvement in creep properties is attributed to the precipitation at grain boundary during the stabilizing treatment (2-4, 7-9). We previously reported elsewhere that creep rupture properties of Alloy 706 were significantly affected by stabilizing treatment temperature (10). However, the relationship between stabilizing treatment and precipitation behavior has not been well understood. The present study is concerned with the stabilizing treatment in an effort to correlate creep rupture properties to the morphology of the precipitates that form during the heat treatment.

Procedure

Material

The experimental material was taken from a forged gas turbine disk manufactured from a vacuum induction melted (VIM) and electro slag remelted (ESR) ingot that was diffusion treated and subsequently forged. The material was sectioned mechanically into samples of suitable sizes for the following experiments. The alloy composition used in this study are given in Table I.

Table I Chemical Composition of Alloy 706

												mass %
Ni	Fe	Cr	Al	Ti	Nb	B	C	N	Si	Mn	P	S
42.0	37.1	15.65	0.26	1.54	2.96	0.0034	0.008	0.0046	0.05	0.02	< 0.003	< 0.0005

Figure 1 : Heat treatment program and conditions.

Heat Treatment

Heat treatment conditions are shown in Figure 1. The samples were solution-treated at 980°C for 3h and then stabilizing-treated in a range of 750 to 900°C for 1.5 h. Subsequently they were double-aged at 720°C for 8h and at 620°C for 8h. Alloy 706 is usually reheated to the stabilizing temperature after solution annealing (6). In this study, the stabilizing treatment was conducted in the cooling stage from the solution treatment without cooling the material to the room temperature from the point view of industrial advantage.

Microscopy

These samples were examined by scanning electron microscopy (SEM) and transmission electron microscopy (TEM) for their precipitation behavior. Thin film method was used for TEM sample preparation, and final thinning was achieved by electro-polishing. A 200kV TEM was used with micro-beam technique in both electron diffraction and energy dispersive X-ray spectroscopy (EDS), with the probe diameter being minimum 1nm.

Creep Rupture Test

Creep tests were conducted at three conditions : 600°C / 686.5 MPa, 600°C / 745.3 MPa and 650°C / 686.5 MPa. The diameter of specimens was 6mm and the gauge length was 30mm. In order to ensure the uniformity of temperature, the specimens were held for 24h at the test temperatures before loading.

Results

SEM Observation

SEM micrographs of Alloy 706 stabilized at various temperatures and aged are shown in Figure 2. No precipitate was seen inside the grains or at the grain boundary for the samples stabilized at 900 and 870°C as for the un-stabilized one. On the contrary, many precipitates were observed when the stabilizing temperature was below 840°C. Especially cellular precipitates that lay parallel to each other were observed clearly at the grain boundary.

Intra-granular Precipitate

In order to identify these precipitates that can not by SEM, TEM observation was conducted. It is reported that the intra-granular precipitate is either γ' (2,3,7,8) or γ'' (9,10) and that they form simultaneously (4,11,12). Therefore, TEM observation was directed to the grain interior.

TEM image of Alloy 706 stabilized at 810°C and aged is shown in Figure 3, where all types of precipitates identified in this study are seen. The precipitates of various shapes and sizes exist inside the grain. The spots arising from long-range ordering were clearly observed in a selected area

Figure 2 : SEM micrographs of Alloy 706 aged following by the stabilizing treatment at various temperatures : (a) unstabilized, (b) 900°C, (c) 870°C, (d) 840°C, (e) 810°C and (f) 780°C.

Figure 3 : TEM micrograph and selected area diffraction of Alloy 706 stabilized at 810°C and aged.

Figure 4 : High resolution image of the cuboidal γ' - γ'' co-precipitate in Alloy 706 stabilized at 810°C and aged.

Figure 5 : Micro beam diffraction patterns at the location shown in Figure 4.

diffraction pattern given in Figure 3, indicating the presence of γ' and/or γ'' . Therefore, high resolution observation was made together with micro-beam techniques in order to identify each precipitate.

As a result, four types of precipitates were identified in the grain interior. The relatively large precipitates as indicated by arrow A were identified γ' , their size being several hundred nanometers. The fine precipitates as indicated by arrow B were identified γ'' , their size being several nanometers. The precipitates as indicated by arrows C and D were identified

two types of γ' - γ'' co-precipitates which had not yet been reported with Alloy 706.

A high resolution image, micro-beam electron diffraction patterns and micro-beam EDS spectra are shown in Figure 4, 5 and 6, respectively, of the co-precipitates as indicated by arrow C. They indicate that this large cuboidal co-precipitate has the core of Ti rich γ' being completely covered with the Nb rich γ'' thin skin, referred to by R.Cozar and A.Pineau as co-precipitate of "compact morphology" in the modified 718 alloys (13-

Figure 6 : Micro beam EDS spectra at the locations shown in Figure 4.

Figure 7 : Schematic diagram of the cuboidal γ' - γ'' co-precipitate in Alloy 706

20). The coherency between γ , γ' and γ'' is maintained as schematically illustrated in Figure 7. It is reported that this co-precipitate is obtained at a higher (Ti + Al) / Nb ratio than in regular Alloy 718. In fact, this ratio is greater of Alloy 706 than of Alloy 718. However, the chemical composition of Alloy 706 is out of the co-precipitate range of the S-R diagram for Alloy 718 (13,14). The co-precipitate range may be shifted for Alloy 706. Further study is needed in this respect.

Figure 8 : High resolution image of the overlaid γ' - γ'' co-precipitate in Alloy 706 stabilized at 810°C and aged.

Figure 9 : Micro beam diffraction patterns at the locations shown in Figure 8.

Figure 10 : Schematic diagram of the overlaid γ' - γ'' co-precipitate in Alloy 706.

TEM information of the co-precipitates as indicated by arrow D are shown in Figure 8 and 9, respectively. Although it is too small to determine precisely its shape and inner structure, it appears to be either a disk or an ellipsoid. From both figures, this fine precipitate has the core of γ' being overlaid with γ'' on its top and/or bottom, referred to by R.Coazar and A.Pineau as co-precipitate of "non-compact morphology", again (13-20). The coherency between γ , γ' and γ'' is maintained as schematically illustrated in Figure 10.

Figure 11 : TEM micrograph and selected area diffraction pattern of grain boundary in Alloy 706 stabilized at 810°C and aged.

Figure 12 : EDS spectra at (a) η , (b) denuded zone and (c) the matrix.

Inter-granular Precipitate

Figure 11 shows TEM image of the cellular precipitates at the grain boundary of Alloy 706 stabilized at 810°C and aged. These phases were identified η from the results of micro-beam electron diffraction and micro-beam EDS. These precipitates have a specific orientation relationship with the γ matrix : $[011]_{\eta} // [2\bar{1}\bar{1}0]_{\gamma}$ and $\{11\bar{1}\}_{\eta} // \{0001\}_{\gamma}$. This relationship is consistent with the study reported by other (9), indicating a semi-coherency between η and γ . The cellular η appears parallel to

each other in order to meet this orientation relationship.

As shown in Figure 11, the precipitation of η resulted in the formation of the serrated grain boundary and denuded-zone around it. Micro-beam EDS found a leanness of Niobium and Titanium in this zone as shown in Figure 12. The denuded zone was obscure after 840°C stabilization, but it became wider and more distinct as the stabilizing temperature decreased. At 780°C, its width was greater than 100nm as shown in Figure 13.

Figure 13 : TEM micrograph near the grain boundary of Alloy 706 aged after stabilizing at (a) 810°C and (b) 780°C.

It is reported that there is not only η , but also δ at the grain boundary at Alloy 706 (7,9,12). However, no precipitate was identified δ for more than a hundred precipitates at grain boundary in this study. Only a few precipitates were identified γ' in the samples stabilized at 840 and 810 °C. This is thought that η forms through the transformation of $\gamma \rightarrow \gamma' \rightarrow \eta$ as in A286 (1), leaving γ' as an intermediate phase. The grain boundary appears to become serrated as the η phase grows.

Precipitation Behavior and Stabilizing Temperature

In order to clarify at which stage of the whole heat treatment such precipitation as described above occurs, TEM studies were carried out for the samples before and after the aging treatment. The relatively large γ' and cuboidal $\gamma' - \gamma''$ co-precipitate were found to form in the stabilizing treatment at 840, 810 and 780°C. The precipitation of η and the accompanying phenomena were also found to occur in the same stabilizing treatment. On the contrary, the fine γ'' and overlaid $\gamma' - \gamma''$ co-precipitate formed during the double-aging treatment. But, when stabilized at 780°C, these fine precipitates were rarely observed even after aging. It is extremely difficult to determine the amount of these fine precipitates, especially the co-precipitate. From Figure 14, however, the amount of the

fine precipitates formed at the aging treatment are greater as the stabilizing temperature higher. It is concluded that the cuboidal co-precipitate is dominant when stabilized at 780°C whereas the fine precipitates are when the stabilizing temperature is higher than 810°C.

The results obtained in this study has led to three groups of stabilizing temperatures in terms of the precipitation behavior ; 900 and 870°C (Group A), 840 and 810°C (Group B), and 780°C (Group C). The precipitation behavior of Group A is virtually the same as in the case where the stabilizing treatment is discarded. That is, the fine γ'' and overlaid $\gamma' - \gamma''$ co-precipitate arise inside the grain without any precipitation at the grain boundary. In the case of Group B, the fine precipitates are still dominant whereas the large cuboidal $\gamma' - \gamma''$ co-precipitate is also present inside the grain. At the same time, the η phase grows at the grain boundary, resulting in the grain boundary serration and the denuded zone that is still limited and narrow with this group. The large cuboidal co-precipitate is dominant in Group C, and the denuded zone becomes very wide. The precipitation behavior described here is summarized in Table II.

Creep Rupture Property and Stabilized Temperature

The creep strain vs. time curves for three test conditions are shown in Figure 15, 16 and 17 ; 600°C/686.5MPa, 600°C/745.3MPa and 650°C/686.5MPa, respectively. The creep rupture properties can be grouped into three classes ; here again Group A (900 and 870°C), Group B (840 and 810°C) and Group C (780°C). The creep rupture property does not appear to be affected by the stabilizing treatment for Group A. However, it was significantly affected when stabilizing temperature is below 840 °C. The creep rupture property of Group B are markedly improved in creep rupture life and creep rupture elongation. On the contrary, it was much degraded in the Group C.

Figure 14 : Change in vickers hardness with the stabilizing treatment of Alloy 706.

Table II Summary Of Precipitation Behavior For Alloy 706 Stabilized At Various Temperatures (○ : pronounced △ : observable × : absent)

stabilizing temperature	large γ'	fine γ''	fine overlayed $\gamma' - \gamma''$	large cuboidal $\gamma' - \gamma''$	η	denuded zone
Unstabilized	×	○	○	×	×	×
900℃	×	○	○	×	×	×
870℃	×	○	○	×	×	×
840℃	○	○	○	△	○	△
810℃	△	○	○	△	○	△
780℃	△	△	△	○	○	○

Figure 15 : Creep rupture curves of Alloy 706 tested at 600 °C/686.5MPa.

Figure 16 : Creep rupture curves of Alloy 706 tested at 600 °C/745.3MPa.

Figure 17 : Creep rupture curves of Alloy 706 tested at 650 °C/745.3MPa.

Figure 18 : Change in the minimum creep rate of Alloy 706 with stabilizing temperature.

Discussion

As described, the classification of precipitation behavior agrees well with the classification of creep rupture properties, indicating a strong connection between them. Therefore, the results of the present study are discussed here in accordance with the classification of stabilizing temperature.

Group A ; stabilized at 900 and 870°C

The precipitation behavior is virtually the same as for the heat treatment program without stabilizing treatment. Therefore, creep rupture properties are not affected by the stabilizing treatment.

Group B ; stabilized at 840 and 810°C

Creep rupture properties are markedly improved. This improvement is contributed by the precipitations in the grain matrix and at the grain boundary.

The contribution of the precipitates in the matrix is depicted in Figure 18 that shows the minimum creep rate replotted from Figure 15, 16 and 17. The minimum creep rate is the smallest in the stabilizing temperature range for Group B. In this stabilizing temperature range, relatively large cuboidal γ' - γ'' co-precipitate is found to co-exist with the fine overlaid co-precipitates. It is reported that the cuboidal co-precipitates are more stable than single phase precipitates and are able to improve high temperature properties of Alloy 718 (13-20). The co-precipitates

Figure 19 : The relative duration of tertiary creep rupture life for Alloy 706 stabilized at different temperatures.

should have the same effect in Alloy 706. The co-existed condition with large precipitates and fine ones may also contribute to the reinforcement of grain interior.

The contribution of the precipitation at the grain boundary is seen in the relative duration of tertiary creep to the whole creep life shown in Figure 19 that is replotted from Figure 15, 16 and 17. The relative tertiary creep duration is the greatest in the stabilizing temperature range of Group B. As seen in Table II, this improvement is mainly due to the reinforcement of grain boundary which is caused by the pinning of grain boundary by η , grain boundary serration, and indistinct denuded zone. Firstly, precipitates at grain boundary prevent effectively the grain boundary sliding. In Alloy 706, η phase has semi-coherency with the matrix and therefore effectively pins the grain boundary. Secondly, the grain boundary serration also prevents the grain boundary sliding effectively (21,22). That is, the geometrical change of grain boundary is considered to extend the tertiary creep duration. Thirdly, the indistinct denuded zone is considered to be retard effectively crack propagation as reported with Alloy 718 (23). In fact, this was supported by SEM micrographs of fracture surfaces shown in Figure 20. The fracture surface of Group B specimens consists of many micro-dimples in contrast to the smooth fracture surface of Group A specimens, although grain boundary fracture occurs in both groups.

Group C ; stabilized at 780°C

Creep rupture properties are extremely degraded in creep rupture life. However, creep rupture elongation is very large. The minimum creep

Figure 20 : SEM fractographs of ruptured Alloy 706 (a) unstabilized and (b) stabilized at 810°C.

rate is far larger than those of the other groups as seen in Figure 19. The relative tertiary creep duration is smaller than that of Group B as seen in Figure 20. These facts mean that there are two reasons for the degradation of creep properties.

As seen in Table II, the large cuboidal co-precipitate is dominant inside the grain in this stabilized temperature range. In general, the smaller the precipitates, the more effective they are in precipitation hardening and the more stable they are for heat. Therefore, the degradation of creep properties is attributed to the large precipitates dominant in the matrix. The wide denuded zone around η is another characteristic of the precipitation in this temperature range. It causes readily grain boundary sliding whereby overshadowing the beneficial effect of η precipitation.

Conclusions

Intensive TEM study and creep rupture tests were conducted in order to characterize the precipitates and to relate them to creep rupture properties for Ni-Fe-base superalloy Alloy 706 stabilized at various temperatures. Conclusions are summarized as follows.

(1) The precipitation behavior of Alloy 706 stabilized at 900, 870°C is practically the same as in the case where the stabilizing treatment is discarded. That is, both fine γ'' and overlaid $\gamma' - \gamma''$ co-precipitate form in the grain matrix at the double-aging treatment, and no precipitation occurs at the grain boundary. Therefore, creep rupture properties is not affected by the stabilizing treatment.

(2) When stabilized at 840 and 810°C, the fine precipitates are still dominant inside a grain while large cuboidal $\gamma' - \gamma''$ co-precipitate is present together with them. At the same time, η phase precipitates at the grain boundary, causing serrated grain boundaries and narrow denuded zone around η . The best creep rupture properties are obtained with this complex stage of precipitation.

(3) In the case of Alloy 706 stabilized at 780°C, large cuboidal co-precipitate is dominant inside the grain, and the denuded zone is very wide, leading to extremely degraded creep rupture properties.

It can be concluded that the desirable creep rupture properties are obtained when the best combination is achieved for the fine overlaid γ' / γ'' co-precipitates, large cuboidal γ' / γ'' co-precipitates, and η phase.

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