EFFECTS OF ALUMINUM, TITANIUM AND NIOBIUM ON THE TIME - TEMPERATURE - PRECIPITATION BEHAVIOR OF ALLOY 706

Takashi Shibata, Yukoh Shudo, and Yuichi Yoshino

Technology Research Center, The Japan Steel Works, Ltd.,
1-3 Takanodai, Yotsukaido, Chiba 284, Japan

Abstract

Ni-Fe-base superalloy 706 has been used for high temperature services. The time - temperature - precipitation (TTP) diagram is essential in the design of heat treatments for any precipitation strengthened superalloy. The TTP diagrams have been already presented for Alloy 706. However, effects of aluminum, titanium and niobium, important substitutional elements of γ' and γ'' precipitates, on the TTP behavior are not clear in the literature.

In this study, the TTP and the time - temperature - hardness (TTH) diagrams are presented for experimental alloys containing only one or two of Ti, Nb and Al, in a temperature range of 600 - 900°C. The observation by optical microscopy, scanning electron microscopy and transmission electron microscopy revealed that γ' , γ'' , $\gamma'-\gamma''$ co-precipitates and η form in alloys containing Ti.

Among the three elements, Ti plays the most important role in the precipitation strengthening behavior of Alloy 706. Furthermore, neither Al nor Nb can demonstrate their effects without Ti addition. Nb promotes γ'' formation and prevents η formation. Al enhances the formation of stable $\gamma'-\gamma''$ co-precipitates, more effectively in the co-existence of Ti and Nb.

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, it 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 the 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).

The time - temperature - precipitation (TTP) diagram is one of the essential tools for designing the heat treatment of precipitation strengthened

superalloy. Especially for Alloy 706, complicated heat treatments are used to draw its full ability (6). In fact, its mechanical properties are greatly affected by the precipitation at the heat treatment (7-11). The TTP diagrams of Alloy 706 have already been presented (2,3), and updated recently (12).

Alloy 718 has been investigated thoroughly on its TTP behavior, which has led to many compositional modifications (13-22). However, effects of aluminum, titanium and niobium, which are all important substitutional elements in the precipitation of γ' and γ'' , on the TTP behavior of Alloy 706 are not clear in the literature. In this study, the TTP diagrams are presented for six experimental 706 alloys, in order to clarify the role of Al, Ti and Nb in the TTP behavior.

Procedure

Material

Six heats of experimental alloys were melted in a 50 kg vacuum induction melting (VIM) furnace. The chemical composition of these six alloys is listed in Table I. Alloy 706 contains Al, Ti and Nb, but these experimental alloys contain only one or two of these elements. Nickel and chromium contents were nearly constant in all the alloys as shown in Table I, with iron being the balance. All the ingots were diffusion treated and subsequently forged to the billets with a cross section of 30' x 120' mm². The billets were sectioned mechanically into samples of suitable sizes. For comparison, a commercial Alloy 706 forging, a large turbine disk, was also used as a sample.

Heat Treatment

The condition of solution treatment for each heat was determined by preliminary experiments so as to fully dissolve precipitates formed in the forging process and to obtain a mean grain size of ASTM #3-4. After the solution treatment, samples were isothermally heat treated in a temperature range of 600 - 900°C for up to 100 h. In this study, the heating rate to the solution and aging temperatures was 50°C/h as shown in Figure 1, simulating a large forging.

Table I Chemical Composition of Experimental Alloys

Heat	Ni	Fe	Cr	Al	Ti	Nb	C	N	O	B	Si	Mn	P	S
No.1	43.36	39.23	16.43	0.34	0.01	0.05	< 0.003	0.0033	0.0020	< 0.005	0.035	0.010	< 0.003	0.0008
No.2	43.75	37.74	16.23	0.04	1.68	0.05	0.003	0.0012	0.0025	< 0.005	0.035	0.010	< 0.003	0.0010
No.3	43.96	36.89	15.95	0.05	0.01	2.56	< 0.003	0.0043	0.0145	< 0.005	0.040	0.010	< 0.003	0.0009
No.4	43.54	37.56	16.29	0.30	1.71	0.05	< 0.003	0.0014	0.0018	< 0.005	0.025	0.010	< 0.003	0.0006
No.5	43.62	35.05	16.13	0.05	1.75	2.82	< 0.003	0.0026	0.0025	< 0.005	0.045	0.010	< 0.003	0.0009
No.6	43.76	36.55	16.30	0.30	0.01	2.54	0.003	0.0025	0.0010	< 0.005	0.050	0.010	< 0.003	0.0008
706	43.64	34.81	16.27	0.25	1.78	2.87	< 0.003	0.0024	0.0019	< 0.005	0.010	0.010	< 0.003	0.0011

Figure 1 : Heat treatment program and conditions.

Evaluations of Precipitation Behavior

The heat treated samples were subjected to optical microscopy, scanning electron microscopy (SEM) and transmission electron microscopy (TEM) for their precipitation behavior. The sample preparation and observation conditions are described elsewhere. Hardness was measured by a Vickers hardness tester, in order to produce the time - temperature - hardness (TTH) diagram.

Result and Discussion

Solution Treatment Condition

The conditions of solution treatments were investigated in a range of 850 - 1050 °C and 0.5 - 5h. Figure 2 shows the relationship between Vickers hardness and the test temperature for the six experimental alloys aged for 2h. Hardness of all the alloys decreased rapidly over the temperature range from 900 °C to 950 °C, and tailed off at about 120 Hv when temperature exceeds 950 °C. It indicates that γ' and/or γ'' formed during the forging process are fully dissolved above 950 °C. The dissolution temperature was practically the same for all the experimental alloys, suggesting the solvus temperature of these precipitates being unaffected by their chemical compositions. This is consistent with the early work (7).

In order to be sure if the grain boundary precipitate such as η and δ is dissolved, all of the solution treated samples were subjected to optical microscopy and SEM. The microscopic observations revealed no precipitate either in the grain or at the grain boundary in any of the alloys tested, as shown in Figure 3 as an example. Carbide and/or nitride have been reported to appear occasionally at the grain boundary (2-4, 7-10, 12). However they were not seen in this study due possibility to the relatively low carbon and nitrogen contents of these alloys.

When solution-treated at 980 °C for 2h, the grain size of all the alloys tested was within the range of ASTM #3 to 4. The grain grew rapidly to ASTM #1-2 above 1000 °C, regardless of alloy composition. Therefore, the solution treatment was done at 980 °C for 2h for all the alloys.

TTH Behavior of Ti-Free Alloy

Hardness of alloys Nos.1, 3 and 6 changed little within the limit of this experiment. The strengthening element is Al for No.1, Nb and Al for No.3 and Nb for No.6, respectively. None of the alloys contain titanium. Neither 0.3% Al nor 2.5% Nb nor the combination of both is sufficient to produce noticeable age hardening, indicating that the Ti-free alloys are not hardenable. This is in part consistent with an early work on Nb containing Ni based alloy (23). Thus, Ti plays the most important role in the precipitation strengthening of Alloy 706. From this point of view, the following study was conducted with Ti-containing alloys, namely Nos.2, 4, 5 and commercial Alloy 706.

Figure 2 : Change in vickers hardness with the solution treatment of experimental alloys

Figure 3 : SEM micrographs of experimental alloys solution -treated at 980°C for 2h ;
(a) alloy No.1, (b) No.2, (c) alloy No.3, (d) No.4, (e) No.5 and (f) No.6.

TTH Diagram of Ti-Containing Alloy

The alloys containing Ti were all age-hardenable, especially at the temperatures between 700 - 800°C, indicating the formation of γ' and/or γ'' phases. The TTH diagrams of three experimental alloys, Nos.2, 4 and 5, and Alloy 706 are shown in Figure 4. The highest hardness was about 400 Hv in No.5 and Alloy 706, but about 300 Hv in Nos.2 and 4. The higher hardness is attributed to the Nb content of those alloys, suggesting a synergistic effect between Nb and Ti.

The age hardening was fast at temperatures about 800°C, but the highest hardness was achieved below 700°C in the Ti-containing alloys as seen in Figure 4. Fast over-aging prevents hardness from exceeding 300 Hv at 800°C. The over-aging is associated with the transformation of γ' to η as in A-286 or γ'' to δ as in Alloy 718 (1). The softening occurs at 800°C a little more extensively in alloys Nos.2 and 4 than the remainder. Likewise, No.5 appears slightly more sensitive to the over-aging than Alloy 706.

The TTH diagram of Alloy 706 is similar to the one in the previous report (12). However, the "nose" temperature of the diagram is higher in this study. This is thought to be due to the precipitation of γ' and/or γ'' during the heating stage of the heat treatment that simulated slow heating of large ingots.

Identification of Precipitates

As an example, SEM micrographs of alloys Nos.2, 4, 5 and Alloy 706 aged at 730°C for 10h and at 830°C for 10h are shown in Figure 5. No precipitate was seen inside the grain despite the hardness increase in these samples. However, many cellular precipitates were observed at the grain boundary, except for No.5 and Alloy 706 aged at 730°C for 10h.

TEM images and selected area diffraction patterns inside the grains of alloys Nos.2 and 4 aged at 730°C for 100h are shown in Figure 6. The spherical precipitates were clearly observed in the grain interior. The micro-beam EDS revealed that the precipitates in No.2 consisted of Ni and Ti, and those in No.4 contained Ni, Ti and Al. The ratio of Ni to (Ti+Al) was nearly 3:1 for all the precipitates analysed. The intra-granular precipitates were identified γ' phase having FCC structure.

In the case of alloy No.5 and commercial Alloy 706, precipitates of different shape were observed. Figure 7 shows TEM micrograph, selected area diffraction pattern and micro beam diffraction patterns of alloy No. 5 aged at 730°C for 10h. The disk shaped precipitates were observed inside the grain, appearing the same as γ'' reported on Alloy 706 (4) and on Alloy 718 (13-22). The diffraction patterns, prove that they are γ'' phase. The precipitate designated C has a diffraction pattern of γ' , but it may be a γ'' disk that is viewed from its $\langle 001 \rangle$ direction. The precipitates in No.5 contained Ni, Nb and Ti, with the ratio of Ni to (Nb+Ti) being nearly 3:1.

Figure 6 : TEM micrographs and selected area diffraction patterns of experimental alloys aged at 730°C for 100h ; (a) alloy No.2 and (b) No.4

Figure 7 : TEM micrograph, selected area diffraction pattern and micro-beam diffraction patterns of experimental alloy No.5 aged at 730°C for 10h.

A TEM micrograph, selected area diffraction pattern and micro beam diffraction pattern are shown in Figure 8 of Alloy 706 aged at 730°C for 10h. Non-spherical precipitates were observed, but no-disk shaped γ'' . From the diffraction patterns, the non-spherical precipitates are the co-precipitate having the core of γ' phase being overlayed with γ'' phase on its top and/or bottom, which is referred to as "non-compact morphology" (13-22). The co-precipitate is expressed here $\gamma'-\gamma''$. The results of micro-beam EDS revealed that the γ' phase contained Ni, Ti, Nb and Al, and γ'' phase Ni, Nb and Ti, and that the ratio of Ni to (Ti+Nb+Al) were nearly 3:1 for both γ' and γ'' phases. These co-precipitates were also found in alloy No.5.

The inter-granular precipitates as seen in Figure 5 were identified as η phase. Figure 9 shows TEM image and selected area diffraction pattern at the grain boundary of alloys No.4 aged at 730°C for 10h. The η phase consisted of Ni and Ti in alloys Nos.2 and 4, while it consisted of Ni, Nb and Ti in alloy No.5 and Alloy 706. However, the ratio of Ni to (Ti+Nb) were maintained nearly 3:1 for all the alloys tested here. The η phase contained no aluminum because it has little solubility for Al (1). The selected area diffraction pattern indicates that the η phase has a specific orientation relationship with the γ matrix, as $[011]_{\eta} // [2\bar{1}0]_{\gamma}$ and $\{1\bar{1}\bar{1}\}_{\eta} // \{0001\}_{\gamma}$. This relationship is consistent with other work (9). The η phase appears parallel to each other as seen in Figure 5 in order to meet this orientation relationship.

Figure 8 : TEM micrograph, selected area diffraction pattern and micro-beam diffraction patterns of Alloy 706 aged at 730°C for 10h.

Figure 9 : TEM micrograph and selected area diffraction pattern near the grain boundary of experimental alloy No.2 aged at 730°C for 10h.

TTP Diagram

As described above, four types of precipitates were identified in the alloys containing Ti. γ' and η were found in alloys Nos.2 and 4. In addition to them, γ'' and $\gamma'-\gamma''$ co-precipitate were found in alloy No.5 and Alloy 706. The TTP diagrams of the four alloys are shown in Figure 10. The regions of γ' , γ'' and $\gamma'-\gamma''$ agreed well with the TTH diagram.

γ'' and $\gamma'-\gamma''$ are seen only in Nb-containing alloys, suggesting that the γ'' formation requires both Ti and Nb. These precipitates are the cause of the greater hardness of the Nb-bearing alloys, described earlier with respect to their TTH diagrams. That is, the γ'' phase reinforces the matrix more effectively than the γ' phase (1).

The region of η precipitation grows wider as aging time increases in all the alloys. In fact, the η phase was found to shoot out from the grain boundary as the aging time increased at about 800°C. The γ' , γ'' , $\gamma'-\gamma''$ all transform eventually to η when aged for long time at high temperatures in all the alloys tested. However, the region of η precipitation is much wider in the Nb-free alloys than in the Nb-containing alloys, suggesting that γ' transforms to η more readily than γ'' and $\gamma'-\gamma''$. That is, the Nb-containing alloys are thought to be more stable at high temperatures. This is supported by the aging response previously described of Figure 4. Thus, Nb not only reinforces the matrix by the γ'' precipitation, but also enhances the high temperature stability by delaying the transformation from the intra-granular precipitates to the grain boundary η phase.

The TTP behavior of alloy No.5 and Alloy 706 is more complicated than those of No.2 and No.4, especially at the temperatures between 700 - 800 °C. Figure 11 demonstrates how the precipitate morphology develops with aging, when Alloy 706 is aged at 730°C. γ' phase appears faintly at 0.1h, which is characterized by the ordering spots in the diffraction pattern. As the exposure time increases, the $\gamma'-\gamma''$ begins to form replacing the γ' phase, and the γ'' phase becomes predominant. It should be noted that the size of the $\gamma'-\gamma''$ co-precipitate in Alloy 706 aged at 730°C for 10h is much smaller than that of γ'' in alloy No.5 aged at the same condition. This suggests that the stability of the $\gamma'-\gamma''$ is greater than that of γ'' at high temperatures, as previously reported for Alloy 718 (13-22).

Figure 10 : TTP diagrams of experimental alloys containing Ti : (a) alloy No.2, (b) No.4, (c) No.5 and (d) Alloy 706.

Figure 11 : TEM micrographs and selected area diffraction patterns of Alloy 706 aged at 730 °C for (a) 0.1h, (b) 1h, (c) 10h and (d) 100h.

The TTP diagrams of alloy No.5 and Alloy 706 are somewhat different, although those of alloys No.2 and No.4 are very similar. The difference between alloy No.5 and Alloy 706 is characterized especially by the region of $\gamma' - \gamma$. The precipitation occurs in these alloys pass in the same sequence $\gamma' \rightarrow \gamma' - \gamma \rightarrow \gamma$, but the region of $\gamma' - \gamma$ is fairly wider in Alloy 706 than in alloy No.5. It indicates that the Alloy 706 has better thermal stability than alloy No.5. Such difference reflects a synergetic effect among Al, Nb and Ti. Therefore, the effect of Al addition is considered to form the stable $\gamma' - \gamma$.

The solubility for Al in γ is extremely low whereas that for Nb in γ' is very high, hence a low Al content favors the γ formation whereas high Al content the γ' phase (4). This effect is seen in Figure 10. The dominant $\gamma' - \gamma$ co-precipitation should be explained by the same effect of Al addition. Moreover, the same effect is expected in the transformation to η , since η has little solubility for Al (1). Further study is needed to shed more light on the stability of the precipitates as influenced by the chemical composition.

Conclusions

In order to help design the modification of Alloy 706, the isothermal TTP and TTH diagrams of experimental alloys and commercial Alloy 706 are presented. γ' , γ , $\gamma' - \gamma$ co-precipitates and η were found in the alloys containing Ti.

Ti plays the most important role in the precipitation strengthening of Alloy 706. Al and Nb do not serve as a hardening agent without Ti. Nb is needed for the strengthening through the γ formation and the prevention of η formation. Al is useful for the formation of stable $\gamma' - \gamma$ co-precipitates, and is effective when Ti and Nb are both present.

References

1. E.E.Brown and D.R.Muzyka, "Nickel-Iron Alloys", Superalloys II, ed., C.T.Sims, N.S.Stoloff, and W.C.Hagel (New York, John Wiley & Sons, 1987), 165-188.
2. H.L.Eiselstein, "Properties of Inconel Alloy 706", ASM Technical Report, No.C 70-9.5 (1970), 1-21.
3. H.L.Eiselstein, "Properties of a Fabricable, High Strength Superalloy", Metals Engineering Quarterly, November(1971), 20-25.
4. E.L.Raymond and D.A.Wells, "Effects of Aluminum Content and Heat Treatment on Gamma Prime Structure and Yield Strength of Inconel Nickel-Chromium Alloy 706", Superalloys --Processing (Columbus, OH:Metals and Ceramics Information Center, 1972), N1-N21.
5. P.W.Schilke, J.J.Pepe, and R.C.Schwant, "Alloy 706 Metallurgy and Turbine Wheel Application", Superalloys 718, 625, 706 and Various Derivatives, ed., E.A.Loria (Pittsburgh, PA:TMS, 1994), 1-12.
6. Inconel 706 : Undated brochure obtained from The International Nickel Company, (1974).
7. J.H.Moll, G.N.Maniar, and D.R.Muzyka, "The Microstructure of 706, a New Fe-Ni-Base Superalloy", Metallurgical Transactions, 2(1971), 2143-2151.
8. J.H.Moll, G.N.Maniar, and D.R.Muzyka, "Heat Treatment of 706 Alloy for Optimum 1200 σ Stress-Rupture Properties", Metallurgical Transactions, 2(1971), 2153-2160.
9. L.Remy, J.Laniese, and H.Aubert, "Precipitation Behavior and Creep Rupture of 706 Type Alloys", Materials Science and Engineering, 38(1979), 227-239.
10. G.W.Kuhlman et.al., "Microstructure - Mechanical Properties Relationships in Inconel 706 Superalloy", Superalloys 718, 625, 706 and Various Derivatives, ed., E.A.Loria (Pittsburgh, PA:TMS, 1994), 441-449.
11. T.Takahashi et.al., "Effects of Grain Boundary Precipitation on Creep Rupture Properties of Alloy 706 and 718 Turbine Disk Forgings", ibid., 557-565.
12. K.A.Heck, "The Time-Temperature-Transformation Behavior of Alloy 706", ibid., 393-404.
13. R.Coazar and A.Pineau, "Morphology of γ' and γ Precipitates and Thermal Stability of Inconel 718 Type Alloys", Metallurgical Transactions, 4(1973), 47-59.
14. J.P.Collier et.al., "The Effect of Varying Al, Ti, and Nb Content on the Phase Stability of Inconel 718", ibid., 19A(1988), 1657-1666.
15. J.P.Collier, A.O.Selius, and J.K.Tien, "On Developing a Microstructurally and Thermally Stable Iron - Nickel Base Superalloy", Superalloys 1988, ed., D.N.Duhl et.al. (Warrendale, PA: The Metallurgical Society, 1988), 43-52.
16. E.Andrieu, R.Coazar, and A.Pineau, "Effect of Environment and Microstructure on the High Temperature Behavior of Alloy 718", Superalloy 718 - Metallurgy and Applications, ed., E.A.Loria (Pittsburgh, PA:TMS, 1989), 241-256.
17. E.Gou, F.Xu, and E.A.Loria, "Effect of Heat Treatment and Compositional Modification on Strengthening and Thermal Stability of Alloy 718", Superalloys 718, 625 and Various Derivatives, ed., E.A.Loria (Pittsburgh, PA:TMS, 1991), 389-396.
18. E.Gou, F.Xu, and E.A.Loria, "Comparison of γ'/γ Precipitates and Mechanical Properties in Modified 718 Alloys", ibid., 397-408.
19. J.A.Manriquez et.al., "The High Temperature Stability of IN718 Derivative Alloys", Superalloys 1992, ed., S.D.Antolovich et.al. (Warrendale, PA: TMS, 1992), 507-516.
20. E.Andrieu et.al., "Influence of Compositional Modifications on Thermal Stability of Alloy 718", Superalloys 718, 625, 706 and Various Derivatives, ed., E.A.Loria (Pittsburgh, PA:TMS, 1994), 695-710.
21. X.Xie et.al., "Investigation on High Thermal Stability and Creep Resistant Modified Inconel 718 with Combined Precipitation of γ' and γ ", ibid., 711-720.
22. E.Gou, F.Xu, and E.A.Loria, "Further Studies on Thermal Stability of Modified 718 Alloys", ibid., 721-734.
23. I.Kirman, "Precipitation in the Fe-Ni-Cr-Nb System", Journal of the Iron and Steel Institute, December(1969), 1612-1618.