DEVELOPMENT OF Ni-Cr-Fe-W-Al SUPERALLOY FOR ADVANCED ULTRA-SUPERCritical FOSSIL POWER PLANTS

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Abstract

Significant efforts on development of advanced ultra-supercritical (A-USC) fossil fired power plants with steam conditions of 700 °C and 30 MPa or higher have been made in recent years. The most important consideration is the development of materials for components with working temperature as high as 750 °C. This paper presents (1) the design methodology that was used to define the composition of a Ni-Cr-Fe-W-Al superalloy, (2) microstructure-mechanical property relationship that were established in this work and (3) the results of elevated temperature tensile and stress-rupture testing that demonstrate the capacity of the alloy. Based on the thermodynamic calculation, a Ni-Cr-Fe-W-Al alloy, with the nominal composition of 20 Cr, 6 W, 1.0 Mo, 5 Fe, 1.2-2.3Al, 0.5-1.8 Ti, 1.0 Nb in wt. %, has been designed and selected for the experimental evaluation. It was found that increasing the carbon content (in wt.%) from 0.008 to 0.073 increases the total volume fraction of inter- and intra-granular carbides and modifies the intergranular carbide morphology from script-like and discrete to particle-like and semi-continuous. The carbon addition also improves the mechanical strength and the elongation at 750 °C. The stress-rupture properties show the best combination of rupture life and elongation in samples with carbon content 0.034 wt.%. Stress-rupture properties have been examined at 700-850 °C and the results in a Larson-Miller plot show that Ni-Cr-Fe-W-Al alloy exhibits stress-rupture strength of about 220 MPa for 700 °C/10⁵ h and 112 MPa for 750 °C/10⁵ h which is satisfied for the application of superheater/reheater tubing.

Introduction

Advanced ultra-supercritical (A-USC) technology with steam conditions of 700 °C and 35 MPa or higher has been developed to enhance the efficiency of fossil power plants [1-3]. The most important consideration is the selection of materials for components which work at temperatures up to 750 °C. The requirements of materials include stress rupture strength, corrosion resistance, weldability and workability for fabrication into different components [4]. Ferritic or austenitic heat-resistant steels [3,5] for ultra-supercritical (USC) power plants that operate at 560-620 °C will not withstand the higher operation conditions of A-USC. New nickel- or nickel-iron-based superalloys, therefore, need to be developed for components such as super-heater/re-heater tubing, rotors and blades.

The THERMIE/AD 700 project in Europe and the 760-USC project in USA have been carried out for a decade. Alloy 617 and CCA 617 are selected as superheater or reheater tubing materials for A-USC in Europe [6-7]. Inconel 740 and Inconel 740H were designed based on Alloy 263 and are candidate materials for superheater or reheater tubing in the USA [8-10]. Fe-Ni-based alloys, HR6W [11], were developed in Japan for tubing or piping.

The development programs of Ni-based alloy for A-USC power plants in China started from 2010. The representative new-designed materials are GH984G for super-heater/re-heater tubing [12-14]. Based on the relationship between composition and the creep strength, corrosion properties and phase stability, a Ni-Cr-W-Al superalloy [15], GH125, with high aluminum (Al) content was also proposed and evaluated. This alloy possesses excellent oxidation resistance and is workable to produce large piping or small dimensional tubing. Both superalloys possess a unique combination of high temperature strengths and corrosion resistance below 750 °C. Aiming at the higher operating temperature of 750 °C, the design of a new affordable nickel-based superalloy was performed using the PHACOMP method and Thermo-Calc simulation technology. In this paper, the proposed alloy, Ni-Cr-Fe-W-Al alloy, was evaluated for the potential applications in advanced USC power plants. Phase precipitation and phase stability during prolonged exposure were examined by means of tensile tests, optical microscopy (OM), scanning electron microscopy (SEM), transmission electron microscopy (TEM), and thermodynamic calculations. The relationship between heat treatments and mechanical properties is also presented.

Alloy Design

Phase stability is important for the long-term application of new-designed nickel-based alloys. Phase diagram modeling using Thermo-Calc software and database TTNi8 was carried out to evaluate the phase precipitation and the effects of Cr, W, Fe, Co, Al and Ti additions on the thermal stability and weldability. Optimization of the alloy chemistry and its correlation with elevated temperature strength was based on some important factors as follows:

- W and Mo addition for the solution solid strengthening and the precipitation of carbides.
- Al, Ti and Nb addition for γ' precipitation strengthening.
- Fe addition and decreased Co content for lowering the cost.
- Volume fraction of γ' and the weldability of the designed alloys.
- Precipitation of titanium or niobium carbides and its morphology control.
- B and C addition for grain boundary strengthening.

The addition of Cr is more than 18 wt.% to increase the hot corrosion resistance [16] at temperature up to 700-750 °C in A-USC power plants. It was recommended that Cr content should be as high as 25-30 wt.%. However, as shown in Figure 1, the co-existence of Cr and W in the new designed Ni-Cr-Fe-W-Al alloy restricts the Cr content to be less than 22.5 wt. %. It was predicted that higher Cr levels are likely to precipitate topologically closed packed (TCP) phases (such as P, α and sigma), which are considered to have detrimental effects on mechanical properties.

The amount of Al and Ti in Ni-Cr-Fe-W-Al alloy also shows some effects on the brittle TCP phase precipitation. With the decreasing Al and Al/Ti ratio, the contents of Cr and W in the alloy could be increased without the precipitation of TCP phases, but the increment of Cr addition is more than that of W. As selected for the experimental research in the following section, the contents of Cr and W were set as 20 and 5 wt.% to eliminate the precipitation of detrimental W or Cr-rich TCP phases.

The strengthening effects of γ' are determined by Al and Ti addition. The increasing addition of Al and Ti induce high volume content of γ' -Ni₃(Al, Ti) phases. But the welds of nickel-base superalloys with high γ' volume fraction show an increasing tendency for strain-age cracking (SAC) during aging treatments. The amounts of Al and Ti in nickel-base superalloys which are free from strain-age-cracking after welding, therefore, are restricted to the region shown in Figure 2. As for traditional superalloys, the Al/Ti ratio was controlled to increase the high temperature tensile strength. For Ni-Cr-Fe-W-Al alloy, the thermodynamic calculation results show that η -Ni₃Ti precipitates rather than γ' -Ni₃(Al, Ti) in alloys with the decreasing Al/Ti ratio. For the sake of strengthening effects of γ' and eliminating the η precipitation and strain-age-cracking susceptibility of new-designed alloys, Al and Ti contents were chosen in the range of 1.2-2.3 wt.% and 0.5-1.8 wt.%, respectively. The content of γ' in Ni-Cr-Fe-W-Al alloy was predicted to be 20%.

The influence of Fe and Co on precipitation and phase stability was studied using thermodynamic calculations and the results are illustrated in Figure 3. It was shown that the co-addition of Co and Fe is likely to precipitate TCP phases according to the New PHACOMP method, which are described below. For these evaluations, the Fe content is set in the range of 4.0-5.0 wt.% without Co addition in Ni-Cr-Fe-W-Al alloy. The calculation of the number of electron vacancies (N_v) and the energy levels of the d orbital of element M (M_d numbers) for Ni-Cr-Fe-W-Al alloy

were performed. The calculation of $\bar{N}_v$ and $\bar{M}_d$ are expressed in Equations (1)^[17] and (2)^[18].

$$\bar{N}_v = \sum_{i=1}^n N_{vi} X_i \quad (1)$$

$$\bar{M}_d = \sum_{i=1}^n M_{di} X_i \leq \bar{M}_d^{Cr} \quad (2)$$

$$\bar{M}_d^{Cr} = 1.44 - 0.009 \sum_{i=1}^n A_i X_i \quad (3)$$

The mole fraction of a component (i) in the γ matrix is calculated by Thermo-Calc software. Alloys are taken to be safe with low tendency for TCP precipitation if $\bar{N}_v < 2.35$ and $\bar{M}_d < 0.921$.

From the distribution coefficient of elements between γ' phase and γ matrix, Ti, Al, Nb, and Ta mainly distribute in γ' phase with Mo, Cr and about half W and Fe dissolved in the matrix. The phase stability is then determined by the content by Cr, W and Fe as shown in Figure 1 and 3. The relationship between $\bar{N}_v$ or $\bar{M}_d$ and boron (B) or carbon (C) contents is shown in Figure 4. Based on Figure 4, the contents of C in Ni-Cr-Fe-W-Al should be above 0.005 wt.%. As known in nickel-base alloys, carbon has significant influence on carbide evolution and the related mechanical properties. Considering for the variation of carbon content in commercial superalloys as shown by Guo^[19], experimental research has been carried out to optimize the carbon content in Ni-Cr-Fe-W-Al alloy and the results will be present in the following section.

Boron (B) is also present in superalloy to increase the grain boundary strength. The content of B in wrought nickel-base alloys is usually less than 0.006 wt.%^[19]. The B content in this investigation was selected as 0.005 wt.%.

Figure 1. Use of phase diagram modeling to predict the effects of W and Cr on the precipitation of P, α and sigma phase. The proposed Ni-Cr-Fe-W-Al alloy lies in the γ' space that is outlined with bold lines.

Figure 2. Calculated the desired γ' weight percent at 750 °C of a baseline alloy (in wt.%) with variation of Al and Ti. The proposed alloys outlined in the diagram (*) should be of good weldability.

Figure 3. Calculated phase diagram above 700 °C of model alloys (in wt.%) with variation of Fe and Co content. The proposed alloys lie in the γ' space.

Figure 4. Carbon content and Al/Ti ratio on the Nv and Md values of Ni-20Cr-5Fe-5W-1.0Mo-0.8Nb model alloy, calculated using Equations (1) and (2).

Optimization of Heat Treatments

Nominal chemistry of Ni-Cr-Fe-W-Al alloy, determined according the thermodynamic calculations as shown above, is presented in Table I. A cast ingot with weight of 25 kg was vacuum-induction melted. The chemical composition of ingots shown in Table I was analyzed using spark emission spectroscopy and carbon-sulfur analyzer. After soaking at 1150 °C for 2 hours, the ingot was forged into billets of 35 mm diameter. The billets were heat treated at 1150 °C for 1 hour and hot rolled to 16 mm diameter bars. Samples for microstructure examination, heat treatment and mechanical testing were cut from the bars.

Heat treatments for superalloys are performed to control the grain size and produce better size distribution of γ' precipitates which give optimum stress rupture property [20]. The influence of heat treatment on microstructural evolution and mechanical properties at room temperature and elevated temperature of Ni-Cr-Fe-W-Al, with chemical composition of 20.0% Cr, 5.0% Fe, 5.8% W, 1.2% Mo, 1.2% Al, 1.8%Ti, 0.8% Nb, 0.025% C and 0.005% B, was investigated. Specimens were annealed at 1020, 1050, 1080, 1100, 1150 °C for 10-180 minutes and quenched in water. The average grain sizes of solution-annealed samples were calculated using the lineal intercept method. The relationship between average grain size, the temperature and soaking time of solution-annealing (SA) was present in Figure 5.

Figure 5. Variations of average grain size (in μm) after different solution annealing treatment.

As shown in Figure 5, grains coarsened largely with the annealing time range of 10-60 minutes and the grain growth was relatively stable with time increasing up to 120-180 minutes. Compared with the holding time, SA temperature showed more influence on the grain growth than holding time at certain temperature. The average grain size at 1150 °C for 60 min was 168 μm , which is almost triple of that at 1020 °C for 60 min. After aging treatment at 760 °C, M_{23}C_6 carbide decorated grain boundaries and spherical-

shaped γ' particles formed in the matrix. The morphology and distribution of carbides and γ' varied little with the solution temperature. However, the stress-rupture life under conditions of 750 °C and 320 MPa increased with the increasing solution temperature as shown in Figure 6. The positive effects of high temperature annealing could be related with the coarse grain size, which would reduce the crack formation and propagation stress-rupture testing at 750°C (about $0.65T_m$).

Figure 6. Stress-rupture life and ductility of Ni-Cr-Fe-W-Al alloy as a function of solution annealing temperature.

The creep strain to failure (elongation) and reduction of area were improved with the increasing solution temperature in the range of 1020-1080 °C and then tended to keep invariant. Based on the experimental results, the solution annealing parameters for Ni-Cr-Fe-W-Al alloy is recommended to be 1100 °C for 60 minutes followed by water quenching.

Microstructural features of Ni-Cr-Fe-W-Al alloy after SA and aging treatment are shown in Figure 7. Aging treatment is carried out at 760 °C for 16 hours with quenching in air. It is noted that the grain size of Ni-Cr-Fe-W-Al alloy after SA is approximately 92 μm as shown in Figure 7 a. After aging treatment, γ' phase formed and distributed homogeneously in the γ matrix and its average diameter was about 20nm according to the SEM and TEM analysis as shown in Figure 7 c and e, respectively. M_{23}C_6 carbide particles precipitated at grain boundaries as shown in Figure 7 b and d. The EDS analysis indicates that the metal cluster (M) in M_{23}C_6 was mainly composed of Cr, Mo, W with some Ni and Fe. The distribution of intergranular M_{23}C_6 is not uniform because of the low carbon content compared with heat-resistant nickel-base superalloys [19]. The following section will discuss the influence of carbon content on carbide distribution and mechanical properties of Ni-Cr-Fe-W-Al alloy.

Table I Chemistries of designed Ni-Cr-Fe-W-Al alloy (wt.%)

	Cr	Fe	W	Mo	Al	Ti	Nb	C	B
Nominal	18.0-22.5	4.0-5.5	4.5-6.5	1.0	1.2-2.3	0.5-1.8	0.8	0.010-0.080	0.003-0.006
Experiment	20.0	5.0	5.8	1.2	1.2	1.8	0.8	0.008	0.005

Figure 7. Microstructure of Ni-Cr-Fe-W-Al alloy: (a) OM image of grain size, (b) SEM images of $M_{23}C_6$ at grain boundaries in as-aged sample, (c) SEM image of γ' , (d) TEM image of $M_{23}C_6$ and the related SAED, (e) γ' morphology.

Carbon Effects on Carbide Morphology and Mechanical Properties

Three cast ingots with weight of 10 kg were vacuum-induction melted and their chemical compositions were shown in Table II. After soaking at 1150 °C for 2 hours, the ingots were forged into billets of 35 mm diameter. The billets were heat treated at 1150 °C for 1 hour and hot rolled to bars of 16 mm diameter. Samples with compositions in Table I and II were solution annealed at 1100 °C for 60min followed by water quench and aged at 760 °C for 16 hours with quenching in air. Then the relationship between carbon content and carbide evolution, tensile and stress-rupture properties were investigated.

Carbon and chromium, titanium and other carbide-forming alloying elements form intergranular or intragranular carbides in nickel-base alloys. The carbide morphology in Ni-Cr-Fe-W-Al alloy after heat treatment at 1100 °C for 60 min and 760 °C for 16 hours is presented in Figure 8. The intergranular carbides exhibit script-like morphology and their distribution is inhomogeneous in the specimen with 0.008 wt.% carbon as shown in Figure 8 (a). No intragranular carbides were found. As the carbon content increases to 0.025 or 0.034 wt.%, the morphology of intergranular carbides changes, to become semi-continuous and particle-like and there are some blocky intragranular carbides as shown in Figure 8 (b). In specimens with 0.073 wt.% carbon, blocky carbides were distributed at grain boundaries and in the matrix, the number of carbides increase obviously compared with specimens in Figure 8 (a)-(c). The morphology of intergranular carbides, however, were the same as those in Figure 8 (b) and (c). The composition of blocky carbides in the sample with 0.073% carbon was analyzed by SEM/EDS. The metal cluster, M, was mainly composed of 53.4 Nb, 11.7 Ti, 5.5 W (in wt.%). The result showed that this type carbide should be Nb and Ti-rich MC or (Nb,Ti)C.

The tensile properties tested at room temperature and 750°C are listed in Table III and Table IV, respectively. They show an improvement in tensile properties associate with the carbon addition. The yield stress (YS) and ultimate tensile strength (UTS) at 750°C increase from 633 MPa and 859 MPa to 731 MPa and 897 MPa. Furthermore, the elongation of high temperature tensile sample is drastically improved from 12% to 48%. The stress-rupture tests showed that the samples with 0.035 wt.% and 0.073 wt.% carbon have longer rupture life than the low carbon content samples. Stress-rupture ductility shows an improvement with carbon addition which is the same as tensile tests.

Figure 8. SEM images showing the carbide morphology in Ni-Cr-Fe-W-Al alloy with carbon content (a) 0.008, (b) 0.025, (c) 0.034 and (d) 0.073 (in wt.%).

Table II Chemistries of designed Ni-Cr-Fe-W-Al alloy with verified carbon content (wt.%)

Cr	Fe	W	Mo	Al	Ti	Nb	C	B
20.0	5.0	5.8	1.2	1.2	1.8	0.8	0.025	0.005
20.0	5.0	6.0	1.3	1.2	1.8	0.8	0.034	0.005
20.0	5.0	6.2	1.2	1.2	1.8	0.8	0.073	0.004

Table III Tensile and stress-rupture test results at room temperature

Carbon content, wt.%	YS, MPa	UTS, MPa	Elongation, %	Reduction of area, %
0.008	738	1141	37	41
0.025	735	1200	30	29
0.034	766	1213	34	35
0.073	790	1232	30	38

Table IV Tensile and stress-rupture test results at 750 °C

Carbon content, wt.%	U.T.S., MPa	Y.S., MPa	Elongation, %	Rupture life at 300 MPa, h	Elongation of stress-rupture sample, %
0.008	632.6	858.7	12	630	9
0.025	694.8	893.5	41	660	12
0.034	699.2	895.3	43	849	29
0.073	731.2	896.8	48	736	40

Phase Stability and Stress-rupture performance of Ni-Cr-Fe-W-Al Alloy at elevated temperatures

The alloy maintained acceptable room and elevated temperature ductility (>15 %) following thermal exposures of up to 3000 hours at temperatures between 700 and 800 °C, which indicates that Ni-Cr-Fe-W-Al alloy possesses good microstructural stability after a long time exposure. The phase stability of Ni-Cr-Fe-W-Al alloy, the chemical composition of which was shown in Table I, was investigated after prolonged aging at 760 and 800 °C. The SEM images are shown in Figures 9. Discrete $M_{23}C_6$ carbides were observed at grain boundaries and the carbide morphology varied little among various exposure conditions. The

investigation of phase stability confirms the absence of TCP phases in the new designed Ni-Cr-Fe-W-Al alloy.

Stress rupture properties of Ni-Cr-Fe-W-Al alloy were determined at 700-850 °C and the test results are shown in Figure 10 in terms of the Larson-Miller Parameter (LMP). Short-term stress-rupture tests illustrate that Ni-Cr-Fe-W-Al alloy exhibits stress-rupture strength of about 220 MPa at 700 °C and 112 MPa at 750 °C for a life of 10^5 hours, which is acceptable for service application at 700-750 °C. Long-term creep tests are carried out at 700-750 °C and the proposed longest rupture life will be approximately 20000-35000 hours.

Figure 9. SEM microstructure of Ni-Cr-Fe-W-Al alloy after exposure at (a) 760 °C for 2000 hours and (b) 800 °C for 3000h.

Figure 10. Stress-rupture test results of Ni-Cr-Fe-W-Al alloy.

Conclusions

A nickel-based alloy for superheater/reheater tubing in A-USC power plants has been designed, and evaluated in terms of critical mechanical properties and stability of microstructure. The Ni-Cr-Fe-W-Al alloy has the nominal composition of 20 Cr, 6 W, 1.0 Mo, 5 Fe, 1.2-2.3Al, 0.5-1.8 Ti, 1.0 Nb, 0.0045 B, 0.008-0.073 C in wt. %. The phase stability and mechanical properties were evaluated by thermodynamic calculation and experiments. The influence of microstructural evolution on the mechanical properties has been examined using heat treatment experiments. The carbon addition improves the mechanical strength and the elongation at 750 °C. Stress-rupture tests at 750 °C and 300 MPa shows that the best combination of rupture life and elongation was produced in the alloy with 0.034 wt.% carbon. Stress-rupture properties have been examined at 700-850 °C and the results shown in terms of the Larson-Miller Parameter indicates that the Ni-Cr-Fe-W-Al alloy exhibits stress-rupture strength of about 220MPa at 700 °C and about 112 MPa at 750 °C for a creep rupture life of 10^5 hours.

References

1. R. Viswanathan, and J. Nutting, "Materials for Ultrasupercritical Coal Power Plants-Boiler Materials," *Journal of Materials Engineering and Performance*, 10 (2001), 81-95.
2. B. Jorgen, K. Sven, and R. Blum, "High-efficiency Coal-fired Power Plants Development and Perspectives," *Energy*, 31(2006), 1437-1445.
3. R. Viswanathan, and J. Nutting, ed., *Advanced Heat Resistant Steels for Power Generation* (London: IOM Communications Ltd., 1999), 349.
4. R. Viswanathan, and J. Nutting, ed., *Advanced Heat Resistant Steels for Power Generation* (London: IOM Communications Ltd., 1999), 33.
5. R. Viswanathan, J. Sarver, and J.M. Tanzosh, "Boiler Materials for Ultra-supercritical Coal Power Plants-Steamside Oxidation," *Journal of Materials Engineering and Performance*, 15 (2006), 255-274.
6. D. Allen et al., "Creep Rupture and Ductility of As-manufactured and Service-aged Nickel Alloy IN617 Materials and Welds," *Materials at High Temperatures*, 21 (2004), 55-60.
7. N. Rogalev et al., "A Survey of State-of-the-art Development of Coal-fired Steam Turbine Power Plant Based on Advanced Ultrasupercritical Steam Technology," *Contemporary Engineering Sciences*, 7(2014), 1807.
8. B.A. Baker. "A New Alloy Designed for Superheater Tubing in Coal-Fired Ultra Supercritical Boilers," *Superalloys 718, 625, 706 and Derivatives 2005*, ed. E.A. Loria (The Minerals, Metals & Materials Society, 2005), 601-612.
9. J.P. Shingledecker, N.D. Evens, G.M. Pharr, "Influence of Composition and Grain Size on Creep-Rupture Behavior of Inconel Alloy 740," *Materials Science and Engineering A*, 578 (2013), 277-286.
10. J.C. Zhao, V. Ravikumar, and A.M. Beltran, "Phase Precipitation and Phase Stability in Nimonic 263," *Metallurgical and Materials Transactions A*, 32 (2001), 1271-1282.
11. T. Tokairin et al., "Investigation on Long-term Creep Rupture Properties and Microstructure Stability of Fe-Ni Based Alloy Ni-23Cr-7W at 700 oC," *Materials Science and Engineering A*, 565 (2013), 285-291.
12. M-L. Mei et al., "Influence of Ti/Al Ratios on γ' Coarsening Behavior and Tensile Properties of GH984G Alloy during Long-term Thermal Exposure," *Acta Metallurgica Sinica*, 50 (2014), 1260-1268.
13. J. T. Guo, and X. K. Du, "A Superheater Tube Superalloy GH2984 with Excellent Properties," *Acta Metallurgica Sinica (In Chinese)*, 41 (2005), 1221-1227.
14. T.T. Wang et al., "Stability of Microstructure and Mechanical Properties of GH984G Alloy during Long-term Thermal Exposure," *Materials Science Forum*, 747-748 (2013), 647-653.

15. Y.C. Ma et al., "High-temperature Oxidation Behavior of A Ni-Cr-W-Al Alloy," *Journal of Materials Science and Technology*, 27(2011), 841-845.
16. S.N. Zhang, private communication with authors, 5 December 1998.
17. L.R. Woodyatt, C.T. Sims, and H.J. Beattie, "Prediction of Sigma-type Phase Occurrence from Compositions in Austenitic Superalloys," *Transactions AIME*, 236 (1966), 519.
18. M. Morinaga, N. Yukawa and H. Ezaki, "Solid Solubilities in Nickel-metal-based fcc Alloys," *Philosophy Magazine A*, 51(1985), 247.
19. Jiangting Guo, *Materials Science and Engineering for Superalloys* (Beijing, Science Press, 2008), 23-71.
20. G.E. Fuchs, "Solution Heat Treatment Response of A Third Generation Single Crystal Ni-base Superalloy," *Materials Science and Engineering A*, 300(2001), 52-60.