THERMAL STABILITY STUDY ON A NEW NI-CR-CO-MO-NB-TI-AL SUPERALLOY

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Abstract

A new precipitation-hardenable Ni-Cr-Co-Mo-Nb-Ti-Al superalloy for advanced ultra-supercritical boiler tubes is under development at Special Metals Corporation. This paper presents the results of a microstructural stability and corrosion resistance study on this new superalloy. The precipitates found in the alloy after aging at 704, 725 and 760 °C are γ' , η , $M_{23}C_6$, a minor amount of G phase and the stable carbide MC. The coarsening of γ' precipitates in the alloy follows a cube rate law: $\bar{r}^3 \propto t$. The η phase has been found to develop a Widmanstätten pattern structure following long exposure at elevated temperatures. The factors associated with structural instability of the alloy include the coarsening of γ' , the formation of η and G phase. This alloy maintains good microstructural stability during prolonged aging at 704 and 725 °C. However, the stability may warrant improvement if the alloy is to be used at 760 °C. The hot corrosion that occurs at 700 °C consists of two stages. The initial stage is controlled by a sulfidation mechanism and acidic fluxing mechanism serves the later stage. The presence of water vapor in air can accelerate oxidation of the alloy.

Introduction

The energy crisis and environmental restrictions have been exacerbated in recent years. This has prompted utilities to increase pressure and temperature of their pulverized coal-fired boilers so as to improve thermal efficiency and reduce SO_x , NO_x and CO_2 emissions. Today's boilers with efficiencies around 45% typically operate at a 30 MPa steam pressure and 600 °C steam temperature. Typical superheater tubing, which are commonly employed, are austenitic stainless steels, such as TP304H, TP347H, Super304, and the Tempaloy series alloys, etc. Recent ultra-supercritical steam conditions up to 375 bar and 700 °C, are being planned by both the European THERMIE project and the German MARCKO project, will enhance the efficiencies of coal-fired boilers to about 50%. The superheater and reheater materials will therefore be required to have high creep rupture strength ($\geq 100 \text{ MPa}/10^5 \text{ h}$) at a temperature of about 750 °C, together with high corrosion resistance ($\leq 2 \text{ mm}$ cross-section loss in $2 \times 10^5 \text{ h}$). For long-term service at these high pressures and temperatures, neither solid solution austenitic heat-resisting steel nor a currently available nickel-base superalloy can fulfill these requirements for stress rupture strength and corrosion resistance [1–3].

NIMONIC^{*} alloy 263 is a wrought Ni-Cr-Co base superalloy that has found application in gas turbines because of its stable microstructure, attractive creep strength and good oxidation resistance. On the basis of NIMONIC alloy 263, a new Ni-Cr-Co-Mo-Nb-Ti-Al superalloy, has been designed to meet these new

stringent targets. The content of Cr and Mo in the new alloy has been adjusted for peak sulfidation resistance, while the strengthening element Nb has been added for additional high temperature strength as well. The new alloy requires the stress rupture strength no less than $100 \text{ MPa}/10^5 \text{ h}$ at 750 °C. However, the expected life is very long and the properties of the alloy can be greatly influenced by the degradation of microstructure. Additionally, severe corrosion problems may result from fireside attack to be envisaged for tubular components due to highly aggressive ash deposits that contain alkaline metals and sulfur from the coal. The objective of the present investigation is to examine the microstructure evolution during long-term aging at elevated temperatures and to study corrosion resistance of this new superalloy in laboratory-simulated pulverized coal-fired boiler environments and oxidation behavior of the alloy in air with water vapor. The structure stability and the possible corrosion mechanisms of the alloy are also discussed

Experimental Procedure

The chemical compositions of 3 heats new superalloy employed in this investigation are shown in Table 1. The alloy was vacuum induction melted, and then vacuum arc remelted. The ingot was homogenized at 1204 °C for 16 h and subsequently hot worked to 15 mm bar at temperature no less than 1050 °C. The bar was solution-annealed at 1150 °C for 30 min and water quenched.

Table 1. Chemical compositions of 3 heats new alloy (wt%):

Heat	C	Cr	Co	Nb	Ti	Al	Mo
1	0.034	24.31	19.63	1.83	1.58	0.75	0.52
2	0.06	24.97	19.80	2.01	1.69	0.87	0.58
3	0.032	22.96	19.27	1.87	1.63	0.72	0.51

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Heat	Fe	Si	Mn	Zr	S	P	Ni
1	0.75	0.45	0.27	0.017	0.0022	0.003	Bal
2	0.71	0.47	0.30	0.366	0.0018	0.013	Bal
3	1.01	0.40	0.28	0.011	0.0022	0.002	Bal

The specimens of Heat 1 after solution annealing were aged at 704, 725 and 760 °C for 500, 1000, 2000 and 4000 h, respectively. The phase identification of these specimens was conducted on scanning electron microscope (SEM) and transmission electron microscope (TEM). Specimens for SEM examination were prepared by electrolytic polishing with a solution of 80% CH_3OH + 20% H_2SO_4 and electrolytic etching with a solution of 170 ml H_3PO_4 + 15 g CrO_3 + 10 ml H_2SO_4 after mechanical grinding to grit 800 paper. The specimens for TEM examination were ground to a thickness about 60 to 80 μm and then electropolished in a solution containing 10% $HClO_4$, 25% CH_3CH_2OH and 65% C_4H_9OH at room temperature.

* NIMONIC and INCONEL are trade marks of the Special Metals Corporation group of companies

The chemical compositions and weight fractions of the precipitates were ascertained through physical and chemical phase analyses. The γ' precipitates were electrolytically extracted in a water solution containing 1% $(\text{NH}_4)_2\text{SO}_4$ and 1% $\text{C}_6\text{H}_8\text{O}_7 \cdot \text{H}_2\text{O}$ at 0–5 °C, and the mean radius of γ' precipitates was determined by using X-ray diffractometer with Kratky small angle scattering goniometer (SAXS).

The pulverized coal-fired boiler environment was simulated as coal ash plus flue gas. All corrosion test specimens of Heat 2, coated with 5% Na_2SO_4 + 5% K_2SO_4 + 90% $\text{Fe}_2\text{O}_3/\text{Al}_2\text{O}_3/\text{SiO}_2$ in 1:1:1 ratio, were exposed in a furnace with flowing gas of N_2 + 15% CO_2 + 3.5% O_2 + 0.25% SO_2 . The weight of coal ash on the specimens' surface was about 10 mg cm^{-2} . The coating procedure was repeated for about every 500 h without cleaning the samples and the flow rate of pre-mixed flue gas was 200 ml min^{-1} during corrosion. Platinum foil was applied as a catalyst for the reaction: $2\text{SO}_2 + \text{O}_2 \rightarrow 2\text{SO}_3$. The specimens were exposed at 700 °C for 116, 500, 1984 and 5008 h, respectively. Additionally, the oxidation test on the samples of Heat 3 was performed in a flow of air with 10% water vapor at 750 °C. After corrosion tests, the specimens were analyzed by using XRD and SEM with EDX.

Results and Discussion

Basic Structure Analyses

As a starting point for structure study, the phase identification in this new alloy was firstly carried out by thermodynamic phase computation and then experimental phase determination for comparison.

Figure 1. Phase diagram simulated by Thermo-Calc

Thermodynamic calculation was carried out to predict the phase stability and phase fractions in the alloy using Thermo-Calc software, version M, accompanied with 14-element Ni-database. The calculated phase diagram of the alloy under equilibrium condition is shown in Figure 1, in which all the predicted equilibrium phases and their weight fractions at each temperature are given. Thermodynamic calculation (Figure 1) reveals that the equilibrium phases above 700 °C include γ , γ' , η , MC and M_{23}C_6 . The liquidus, solidus, η and γ' solvus temperatures of the alloy are about 1375, 1303, 1076 and 812 °C, respectively. The predicted solidification temperature range (72 °C) of this alloy is in good agreement with the experimental value (74 °C).

Figure 2. SEM images of Heat 1 aged at 704 °C for 500 (a), 1000 (b), 2000 (c) and 4000 h (d)

Figure 3. SEM images of Heat 1 aged at 725 °C for 500 (a), 1000 (b), 2000 (c) and 4000 h (d)

Figure 4. SEM images of Heat 1 aged at 760 °C for 500 (a), 1000 (b), 2000 (c) and 4000 h (d)

This new alloy is based on Ni-25Cr-20Co with Mo for solid solution strengthening and with Nb, Ti and Al for γ' precipitation strengthening. Phase analyses results indicate that the weight fractions of γ' , MC, $M_{23}C_6$ and G phase in the sample of Heat 1 as standard heat-treatment (1150°C/30 min/WQ+800 °C/16 h/AC) are 12.980%, 0.183%, 0.115% and 0.054%, respectively. The lattice parameter (a_0) of γ -matrix is in the range of 3.59~3.60 Å and the lattice mismatch degree of γ' - γ is about 0.70%.

Microstructure Evolution at Long Time Aging

SEM images of the samples of Heat 1 aged at 704 °C for 500, 1000, 2000 and 4000 h are shown in Figure 2. The morphology and distribution of precipitates in all samples are quite similar. Ultra fine γ' precipitates distribute in the grains, which contributes the main strengthening effect for the new alloy. The larger

particles (MC) distribute in matrix at random. The grain boundary precipitates can be obviously observed after long time aging at 704°C. The detailed phase analyses indicate that the major carbides are MC and $M_{23}C_6$. The MC and $M_{23}C_6$ are (Nb,Ti)C- and $Cr_{23}C_6$ -type carbide, respectively. The MC carbide forms from the liquid and it is stable for long time aging at high temperatures. $M_{23}C_6$ mainly forms at grain boundaries and have no significant variation with prolonged aging time.

Figure 3 shows SEM images of the samples aged at 725 °C for 500, 1000, 2000 and 4000 h. The morphology and distribution of precipitated phases in these samples are very similar to that of the samples aged at 704 °C. However, after aging for 4000 h at 725 °C,

Figure 5. TEM morphologies of γ' precipitates of Heat 1 aged at 704 °C ((a) and (b)), 725 °C ((c) and (d)) and 760 °C ((e) and (f)) for 1000 h and 4000 h

a small quantity of needle-like and blocky precipitates has formed mainly nearby grain boundaries.

Figure 4 shows SEM images of the samples aged at 760 °C for 500, 1000, 2000 and 4000 h. The γ' precipitates can be seen clearly because of their growth at higher aging temperature. The significant structure change is η -phase formation. After 500 h aging, only small amount of η phase forms in the matrix and nearby the grain boundaries. The quantity and size of η precipitates rapidly increase with aging time. Till 4000 h, not only η phase initiates from grain boundaries but also a significant amount of η phase forms in the grains as Widmanstätten pattern structure. In addition, there are γ' -free zones surrounding η plates. It indicates that the η phase forms at the expense of γ' phase. The average chemical composition of η precipitates analyzed by EDX is (in wt.%): Ni 61.0, Cr 6.0, Co 10.0, Ti 12.3, Nb 7.3, Al 2.5. This stable hexagonal close-packed η phase is $(\text{Ni,Cr,Co})_3(\text{Ti,Nb})$ and can also dissolve a small amount of Al.

Attention should be paid that larger blocky particles have been formed at grain boundaries (Figure 4). This grain boundary phase is identified later as G phase.

Figure 5 gives the examples of the coarsening of γ' precipitates at 704, 725 and 760 °C for 1000 and 4000 h. It shows the growth of γ' precipitates with increasing aging time and temperature, particularly with temperature increasing. At initial stage of long time aging, the γ' particles are small and spherical. However, γ' particles are somewhat cuboidal with increasing aging time and temperature, which means γ' has a large lattice mismatch with γ -matrix.

The coarsening behavior of γ' particles was examined as a function of temperature from 704 to 760 °C and as a function of ageing time up to 4000 h for the alloy. The relationship between average effective radius of γ' precipitates obtained by SAXS in this alloy with various ageing time at three temperatures are plotted in Figure 6. It is clear that the relationships between effective radius $\bar{r}^3$ and ageing time t at different aging temperatures are linear, suggesting that the coarsening of γ' particles in this new superalloy containing not too high volume fraction of γ' follows typical $\bar{r}^3 \propto t$ kinetics of diffusion-controlled particle growth (LSW Law). It is also an evidence in Figure 6 that the γ' particle coarsens more rapidly as the aging temperature increases.

Results of Phase Analyses on Precipitates

The weight fractions of precipitates in the samples of Heat 1 aged at 704 and 760 °C for 1000 and 2000 h obtained by physical and chemical phase analyses are given in Table 2. The results indicate that the precipitates in the alloy are $\gamma'(+\eta)$, MC, M_{23}C_6 and G phase. Because of the similar electrochemical property, the γ' phase and the η phase could not be differentiated by this method. The weight fraction of γ' precipitates in samples aged at 760 °C is total fractions of γ' and η . The actual fraction of γ' phase in the samples aged at 760 °C is less than that of at 704 °C, because a certain amount of γ' has transformed to η . The fractions of $\gamma'(+\eta)$, MC and M_{23}C_6 have no large changes with increasing time at temperatures 704 and 760 °C. Phase analyses also indicate that the chemical composition of γ' precipitate is $\text{Ni}_3(\text{Ti,Al,Nb})$ and G

phase is $\text{A}_6\text{B}_{16}\text{Si}_7$ -type $(\text{Nb,Ti})_6(\text{Ni,Co})_{16}\text{Si}_7$. It is worth to mention that the fractions of G phase in the samples aged at

Figure 6. Coarsening of γ' precipitates in the alloy

Table 2. Fractions of the precipitates of Heat 1 (wt%)

Heat-treatment	$\gamma'(+\eta)$	MC	M_{23}C_6	G
704°C/1000h	16.629	0.154	0.139	0.046
704°C/2000h	16.835	0.151	0.151	0.063
760°C/1000h	14.364	0.161	0.170	0.336
760°C/2000h	14.633	0.154	0.217	0.471

Figure 7. SEM image of G phase and EDX result in the sample aged at 760 °C for 1000 h

Figure 8. XRD spectra of the extracted phase in the sample aged at 760 °C for 4000 h

Figure 9. Precipitation behavior of η phase in the alloy (725 °C/4000 h (a); 750 °C/900 h (b); 800 °C/100 h (c); 850 °C/50 h (d); 900 °C/16 h (e); 950 °C/26 h (f))

Figure 10. TTT diagram for η in the alloy

760 °C are much higher than those of at 704 °C. Figure 7 shows a large particle of G phase at grain boundary in the sample of the alloy aged at 760 °C for 1000 h and EDX result shows that the atomic fraction of Si in the G phase is about 19.25%. This result closes to the atomic fraction in a typical G phase (24.14%Si). The XRD spectra of the electro-extracted phases of the sample aged at 760 °C for 4000 h is given in Figure 8.

TTT-diagram of η Formation

Figure 9a, b, c, d, e and f show the SEM images of the samples of Heat 1 aged at 725 °C for 4000 h, 750 °C for 900 h, 800 °C for 100 h, 850 °C for 50 h, 900 °C for 16 h and 950 °C for 26 h, respectively. In these samples, a small amount of η phases formed at grain boundary and/or in matrix. In addition, the η phase has

not formed in the sample aged at 1000 °C for 140 h. However, the experiment is difficult to find out when the η phase really started to form. According to the results shown in Figure 9, the TTT-diagram for η phase formation can be given approximately (Figure 10). Though no exact results at temperatures above 950 °C, the trend of TTT-diagram is also given in accordance to the thermodynamics calculation, which indicates the highest stable temperature of η phase is about 1087 °C. According to Figure 9, it is likely that the η phase forms in the temperature range of 700~1087 °C. The peak value of precipitating speed of η phase is about 900 °C.

Coal Ash/Flue Gas Corrosion Resistance

Surface morphologies of the samples of Heat 2 after coal ash/flue gas corrosion tests at 700 °C for 116, 500, 1984 and 5008 h are shown in Figure 11. The particles of corrosion products are very small and the grinding traces can be seen on the surface of samples, as shown in Figure 11a and b. This result indicates that the oxide scale is very thin. With an increase in time, the size of oxide particles and the thickness of oxide scale increase. EDX analyses show that there is no large difference in chemical compositions of corrosion products of the samples corroded for different times at 700 °C. The corrosion products are rich in Cr and O and with a small amount of Al, Fe, Si, Ti and Co.

Cross-section images of the samples after corrosion at 700 °C for 116, 500, 1984 and 5008 h are presented in Figure 12. The samples exhibit broad, frontal attack with finger-like intrusions and isolated internal sulfide. The thickness of the scale increases with time and more internal sulfides can be found. As shown in Figure 12a, b and c, the oxide layers are compact, dense and adherent to the surface of the sample after corrosion for 116, 500 and 1984 h. However, after exposure for 5008 h, a layered structure forms (Figure 12d). The outer layer is loose and porous and the inner layer is still compact and also has a good adherence to the matrix.

Figure 13 reveals X-ray mapping of the elements in the sample exposed at 700 °C for 5008 h. The outer loose layer is rich in Co, Cr, Ni, Fe, O and with a small amount of Al. A large amount of Cr and O as well as a trace amount of Al and Ti concentrate in the inner oxide layer. It should be noted that aluminum oxide distributes in the innermost of the oxide scale. Sulfur not only distributes at the scale/matrix interface but also concentrates in the internal penetrates. The internal penetrates are also enriched in Cr and Ti(Nb). X-ray mapping also shows severe Cr-depletion in the internal penetration zone. For example, the fraction of Cr in Cr-depletion zone is only about 7.4wt% and the fraction of Ni and Co has increased to about 66.1wt% and 24.5wt%, respectively. The scales formed on the samples after corrosion tests for 500 and 1984 h are similar to the inner layer of that for 5008 h.

Figure 14 gives an example of XRD results of the samples after corrosion tests for 116 and 5008 h. In combination of X-ray mapping with X-ray diffraction results, the oxides in outer loose layer are identified as CoCr_2O_4 , $\text{Fe}(\text{Cr,Al})_2\text{O}_4$ and NiCr_2O_4 spinels. The black particles in the outer layer are SiO_2 , which come from the coal ash. The inner layer of oxide scale is mainly composed of Cr_2O_3 with a small amount of Al_2O_3 and TiO_2 . The internal sulfides are identified as CrS, Ti- and Nb-sulfide.

Figure 11. Surface morphologies of the samples of Heat 2 after corrosion at 700 °C for 116 (a), 500 (b), 1984 (c) and 5008 h (d)

Figure 12. Cross-section images of the samples of Heat 2 after corrosion at 700 °C for 116 (a), 500 (b), 1984 (c) and 5008 h (d)

Figure 13. X-ray mappings of some elements of in the sample of Heat 2 after corrosion at 700 °C for 5008 h

Figure 14. X-ray diffraction spectra of the sample of Heat 2 after corrosion at 700 °C for 116 and 5008 h

Corrosion Mechanism under Coal Ash/Flue Gas Environment

(Na,K)₃Fe(SO₄)₃ has been identified as the primary compound in the corrosive deposits on superheater tubes in coal-fired boilers which contributes to accelerated corrosion rates. The melting point of (Na,K)₃Fe(SO₄)₃ is about 560 °C. In this study, the partial pressure of SO₃ is at the order of 10⁻³ atm and Fe₂(SO₄)₃, NiSO₄

and CoSO_4 are expected to be stable in contact with the 0.25% SO_2 -gas at 700 °C. The melting points of Na_2SO_4 - CoSO_4 and Na_2SO_4 - CoSO_4 eutectic are 565 °C and 671 °C, respectively. In gas environments containing SO_3 partial pressure on the order of 10^{-3} atm, no corrosion by basic fluxing and acidic fluxing of neither Al_2O_3 nor Cr_2O_3 should occur due to the positive gradient of the solubility at the scale/salt interface in acidic liquid salt [4].

Due to the existence of the sulfates on the surface of samples and the formation of the low melting point eutectics, the scales are expected to suffer accelerated attack by molten sulfates at 700 °C. However, according to cross section morphology and structure analyses on the scale, the severe corrosion has not occurred until 1984 h. After that, the serious attack by molten sulfates has occurred and the loose outer scale, accompanied by a compact inner scale, has formed with increasing time.

The overall reaction that occurs at 700 °C can be divided into following two stages: an initial stage and a propagation stage.

At the initial stage of corrosion, Cr_2O_3 scale forms rapidly on the surface of the alloy due to high Cr content in the alloy with the internal oxidation reaction of some small amount elements such as Al and Ti taking place simultaneously. Although the sulfates on the surface of the alloy are in molten state, the fluxing of Cr_2O_3 can not occur and the oxide effectively protects the matrix from being attacked by molten salts. The deposits on the surface of alloy tend to lower the activity of oxygen and raise the activity of sulfur beneath the deposits. Various states of the sulfur, including S, S^{2-} , SO_2 , etc, diffuse inward through the cracks to the scale/metal interface and stable CrS, Ti- and Nb-sulfide form. With an increase in time, the previously formed sulfides will be oxidized and generate S, some of which can then migrate further inward to form additional sulfide. Thus, both the pervious Cr_2O_3 layer and internal sulfides grow. The scale/alloy interface also migrates inward.

With the increase of Cr-depletion and the relative higher content of Co and Ni in internal penetration zone, corrosion is gradually progressing to the propagation stage and the acidic fluxing of the scale occurs. Due to the high diffusion rate of Co in the scale, CoO forms on the exterior part of the scale. CoO particles are surrounded by Cr_2O_3 and the solid-state reaction occurs to form CoCr_2O_4 spinel in the outer layer of the scale gradually. Subsequently, CoO and a small amount of NiO form on the surface of the scale. Since the thermodynamic stability of NiSO_4 is much lower than that of CoSO_4 and CoO is better than NiO as the catalyst to stabilize the SO_3 , CoSO_4 is expected to form preferentially. Corrosion induced by molten sulfates enters to the accelerated stage. High SO_3 partial pressure is required to stabilize the low melting point solution of sulfates. The reaction proceeds by the inward migration of SO_3 and outward migration of cobalt. At longer times when the liquid salt is saturated with cobalt, only the cobalt dissolves at the scale/salt interface to form CoO in molten sulfates. In the $\text{Co}^{3+}/\text{Co}^{2+}$ exchange reaction, Co^{3+} may be replaced with Fe^{3+} and then iron oxide will form in molten sulfates [5, 6]. Various oxides form spinels by solid-state reaction.

The experimental results show that nickel-base alloys are in general more resistant to low temperature hot corrosion than cobalt-base alloys. A small increase in Cr level and decrease in Co level will act in a beneficial way to resist coal ash corrosion. The increase in Cr content may result in precipitation of TCP phases,

such as σ phase, which will develop a harmful effect on mechanical properties of the alloy. However, the decrease in Co content not only prevents the formation of σ phase but also benefits to the formation of pure Cr_2O_3 scale and retards the sulfidation and dissolution of cobalt oxide. More evaluations are needed to consider the effect of the increase in Cr level and the decrease in Co level on the overall properties of the alloy.

Oxidation in Air with 10% Water Vapor

The mass change curve for the sample of Heat 3 oxidized at 750°C for 2480 h in air with 10% water vapor is shown in Figure 15. The sample was cycle to room temperature approximately once per week for mass measurement. The oxidation behavior basically follows the parabolic law. The rate of mass gain increases rapidly at initial stage of oxidation (<500 h) and then slows with time. However, mass gain results obtained at same temperature in air without water vapor were much lower. It is apparent that the addition of water vapor does accelerate the oxide growth rate.

Figure 15. Mass change behavior of the samples (Heat 3) oxidized at 750 °C for 2480 h in air with 10% water vapor

The cross-section image of the scale and X-ray mapping of some elements in the scale are shown in Figure 16. The oxide scale is composed of an external oxide layer and an internal penetration zone. The external oxide layer has been found to be not compact and adherent to the surface. The cracks in the scale may be associated with the stress developed in the oxide layer during cooling from high temperature. The oxides formed in the outer scale are rich in Cr, Ti and O. Small amounts of Ni and Co are also found in this region. The oxides formed in this layer are comprised mostly of Cr_2O_3 , with some TiO_2 and a small amount of $(\text{Ni},\text{Co})\text{Cr}_2\text{O}_4$. The internal oxides are rich in Al, Ti and O and identified as Al_2O_3 and TiO_2 .

The influence of water vapor on high temperature oxidation of chromia-forming Fe-Cr and Fe-Cr-Ni alloys has received considerable attention. The possible explanations proposed for water vapor effect can be: (1) increasing the mass transport of oxygen through iron oxide, (2) forming gaseous iron hydroxide leading to increased mass transport of iron through the scale, (3) increasing the diffusion rate of chromium through chromium oxide and (4) causing the vaporization of chromium oxide hydroxide [7]. However, only a few works deal with the influence of water vapor on the oxidation of Ni-Cr alloys. Due to the insufficiency of the experimental results in this study, the detailed

explanation of the effect of water vapor on the oxidation of this superalloy could not be gained. A basic analysis on the oxidation mechanism of this superalloy is proposed in this study.

Figure 16. Cross-section image of the sample after corrosion for 2480 h at 750 °C in air with 10% H₂O and X-ray maps of elements

At the initial oxidation stage, some kinds of oxides, (Ni,Co)O and Cr₂O₃, etc, form on the surface of specimens and the internal oxidation reaction of some elements takes place simultaneously. Because of the high concentration of chromium in the alloy, the continuous Cr₂O₃ film forms quickly on the alloy surface with subsequent growth and the oxidation of nickel and cobalt is inhibited. (Ni,Co)O particles were surrounded with Cr₂O₃ and the solid-state reaction occurs to form (Ni,Co)Cr₂O₄ spinel in the scale gradually and distributes in the external oxide layer. Due to the high stability of Al₂O₃ and TiO₂, Al and Ti can be selectively oxidized at the matrix/oxide interface and internally oxidized in the matrix even though they are at a relatively low concentration. It is likely that water vapor induces the increased transport of Cr ions and also induces the evaporation of chromia.

Conclusions

1. The precipitates observed in a new Ni-Co-Cr-Mo-Nb-Ti-Al superalloy aged at 704, 725 and 760 °C are γ' , η , M₂₃C₆, G phase and stable MC. The γ' , MC, M₂₃C₆ and G phase are mainly composed of Ni₃(Ti,Al,Nb), (Nb,Ti)C, Cr₂₃C₆ and (Nb,Ti)₆(Ni,Co)₁₆Si₇, respectively. The fractions of γ' (+ η) and M₂₃C₆ in the alloy exhibit no large changes as a result of thermal exposure but the fraction of G phase increases rapidly with an increase in temperature.
2. The main structure instability at high temperature of this new alloy except the γ' coarsening is mainly following 2 aspects: the formation of large amount of η phase and high fraction of G phase. The γ' particles exhibit cuboidal shape and follow a coarsening

behavior of the cube rate law: $\bar{r}^3 \propto t$. The η phase can develop to a Widmanstätten pattern structure at higher aging temperature. The alloy keeps a good microstructural stability during prolonged aging at 704 and 725 °C, but the structure stability of the alloy needs to be improved at 760 °C.

3. Low temperature hot corrosion of the alloy, results from the formation of low melting sulfates eutectics at 700 °C under the coal ash/flue gas environments, consists of two stages. The sulfidation of the alloy takes place at initial stage and the fluxing mechanism serves to the propagation stage. The internal sulfidation proceeds with increasing time.

4. The presence of water vapor leads to a significant acceleration in oxidation of the new alloy. The overall rate of oxidation remains low.

5. The investigated new Ni-Co-Cr-Mo-Nb-Ti-Al alloy, designated as INCONEL[®] alloy 740 by Special Metals Corporation, is still under development. It offers a good microstructural stability, high creep strength, and excellent resistance to corrosive attack at expected service temperatures and exhibits a bright future for high temperature application in the power industries.

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