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HOT CORROSION BEHAVIOR OF Ni-BASED SUPERALLOYS WITH HIGHER Cr CONTENTS – PART II. MECHANISM OF HOT CORROSION BEHAVIOR

CUI HUA[1)] ZHANG JISHAN[1)2)] MURATA Y[3)] MORINAGA M[3)] YUKAWA N[3)]
1) Department of Materials Science and Engineering, USTB, Beijing 100083, PRC
2) State Key Laboratory for Advanced Metals and Materials, USTB, Beijing 100083, PRC
3) Toyohashi University of Technology, Japan.

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ABSTRACT Based on the experimental results in the previous paper, the mechanism of the hot corrosion behavior of alloy system Ni-16Cr-9Al-2W-1Mo-4Co-(0 ~4)Ti-(0 ~4)Ta-(0 ~4)Nb (in at%) is investigated. In the Ti and Nb-rich corners, hot corrosion is controlled by the basic fluxing mechanism, and a dense and protective surface scale is formed which results in the better hot corrosion resistance for the alloys in these regions. While in the Ta-rich corner, the basic and acidic mechanisms function alternatively, which results in the catastrophic corrosion by forming the porous and non-protective scale, so the alloys in this region show poor hot corrosion resistance. In addition, the concept of "effective chromium content" seemed to give a correct prediction of the hot corrosion resistance of such alloy systems.

KEY WORDS hot corrosion, superalloy, alloying effects

THE hot corrosion behavior of the alloy system of Ni-16Cr-9Al-2W-1Mo-4Co-(0 ~ 4)Ti-(0 ~ 4)Ta-(0 ~ 4)Nb (in at%) has been studied and reported in the previous paper[1]. Some interesting phenomena have been noticed in such alloy system with high Cr contents. The mechanisms for such hot corrosion behavior will be given in this paper.

1 EVALUATION OF THE EXPERIMENTAL RESULTS

As mentioned in Ref. [1], the content of elements Cr, Ti, Al and Nb can introduce a certain beneficial effect to improve the hot corrosion resistance of an alloy under certain conditions. By comparing the compositions of the experimental alloys (see Table 1 in reference [1], it can be seen that the contents of Cr and Al are almost the same. So that, the effects of other elements should be taken into consideration. According to the test results, the effect of Ti and Nb may be of importance to the hot corrosion resistance of an alloy. Lewis and Smith[2] proposed an "effective chromium content" concept based on the hot corrosion tests with crucible method with the Nimonic alloys,

$$EC = w(Cr) + 1.1w(Ti+Nb) + 0.7w(Al)$$

where, EC is the "effective chromium content". All components are in mass fraction (w, %).

The distribution of the contour lines of the EC values in Ti-Ta-Nb compositional triangle is shown in Fig. 1. It is interesting that EC and hot corrosion resistance of the experi-mental alloys show similar behavior. In the Ti and Nb-rich corners, EC values are also higher (23.9% and 21.18% for alloys T1 and T15, respectively). While in the Ta-rich corner, EC values are the lowest (EC=16.03% for alloy 5). The alloy with the highest Nb content (alloy T1) has the highest EC value. However, the alloy showing the best hot corrosion resistance is alloy T6 with EC value 23.33% lower than alloy T1, for the severe segregation of Nb during solidification caused a great amount of Nb-rich eutectic (γ+γ') precipitating in the interdendritic regions[3]. Such non-equilibrium precipitates can not be eliminated through post heat treatment[3], which consumed certain amount of Nb and lowered the effective EC value as well as the hot corrosion resistance of the alloy. The typical hot corrosion resistant superalloy IN738 also has a high EC value (23.11%). So, the hot corrosion resistance of the alloy systems with high Cr contents could be predicted to a certain extent with above equation. However, only with the EC values, it will be difficult to understand the actual hot corrosion process and mechanism, so that the constituents and microstructures of the corrosion products have to be studied in detail.

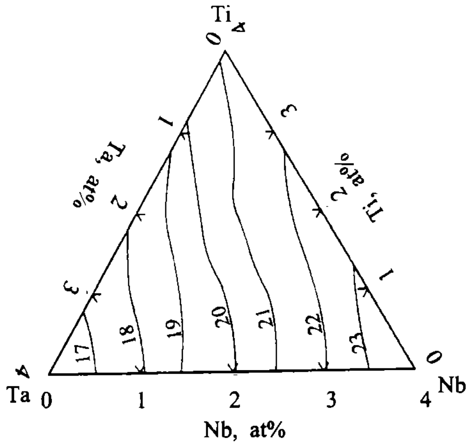
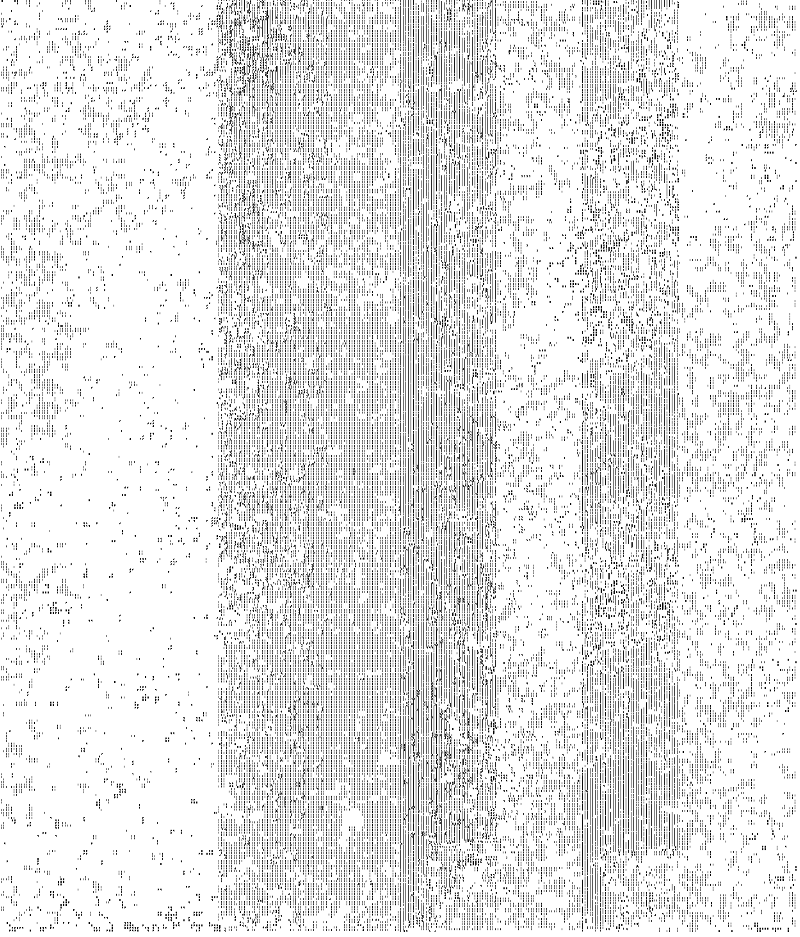


Fig. 1 The effective chromium content of the experimental alloys distributed in the Ti-Ta-Nb compositional triangle

The hot corrosion in an alloy is usually very complicated. The constituents and microstructures of the corrosion products formed on the surface of an alloy will clearly provide the important information about the mechanisms of the hot corrosion process. Figures 2 and 3 show the microstructures and element distributions in the surface scale of the corrosion scales on the surfaces of the typical alloys with high and low hot corrosion resistance (alloys T6 and T5), respectively. In the Ti and Nb corners, a thin layer (about 15 μm) of surface scale is formed during hot corrosion process that is actually composed of two layers, e. g., the continuous and dense protective outside layer and somewhat porous subsurface layer. While in the Ta corner, a thick layer (about 150 μm) of porous and nonprotective surface scale is formed. In Ti corner, a dense outside protective scale mainly composed of Al_2O_3 and small amounts of Cr_2O_3 and TiO_2 is formed on th surface of the alloy, which delayed the penetration of oxygen. While in the subsurface, Cr reacted with S forming Cr_3S_4, which delayed the penetration of S to the inner metal matrix. So that, the speed of corrosion reaction would be lowered after the formation of the above protective scale, because the contact of O and S with the matrix metals must depend on the diffusion of the elements through the scale. Similarly, in Nb corner, a dense outside protective scale mainly composed of Al_2O_3 and Cr_2O_3 is formed. However,



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occur through the liquid phase. In addition, oxidation of the chromium sulfide particles themselves is also observed to occur. Although the actual mechanism is somewhat obscure, some people suggested that chromium sulfide (CrS_x) might be oxidized directly to form Cr_2O_3, e.g.,

$$2CrS_x + (3/2)O_2 \rightarrow Cr_2O_3 + 2xS$$

However, if this is true, it would suggest that the reaction, $2xS + 2Cr \rightarrow 2CrS_x$, can also occur, e.g., the reaction is self-sustaining. If Cr_3S_4 formed at first, the operating mechanism was:

$$2Cr_3S_4 + 9O \rightarrow 3Cr_2O_3 + 8S$$
$$8S + 6Cr \rightarrow 2Cr_3S_4$$

If such a mechanism operated, it would suggest that only an initial contaminat with sulphur is required and that removal of the source of sulphur will not prevent subsequent propagation of the attack. General experience supports such a theory. Such reaction will form the sandwich-like structures of the corrosion products, which also indicates that the chromium content in an alloy is crucial to the hot corrosion resistance.

(2) Thermodynamic mechanism: from the thermodynamics of sulphuration and oxidation processes, the sandwich-like structures could also be explained. Taken Ni as an example, the reaction Gibbs free energies of the process can be written as,

$$2Ni + O_2 \rightarrow 2NiO \qquad \Delta G_1^o = a_1 + b_1T$$
$$3Ni + S_2 \rightarrow Ni_3S_2 \qquad \Delta G_2^o = a_2 + b_2T$$
$$\text{So,}\quad 2NiO + S_2 + Ni \rightarrow Ni_3S_2 + O_2 \qquad \Delta G_2^o - \Delta G_1^o = \Delta G^o$$

Where a_1, a_2, b_1, b_2 are constants. The equilibrium constant of above reaction can be expressed as,

$$\ln K_p = -\Delta G^o / RT$$

where, $K_p = P_{O_2} / P_{S_2}$. So,

$$P_{O_2} / P_{S_2} = \text{antilog}(\Delta G^o / 2.303\, RT)$$

where, P_{O_2} and P_{S_2} are the fractional pressures of O_2 and S_2, respectively.

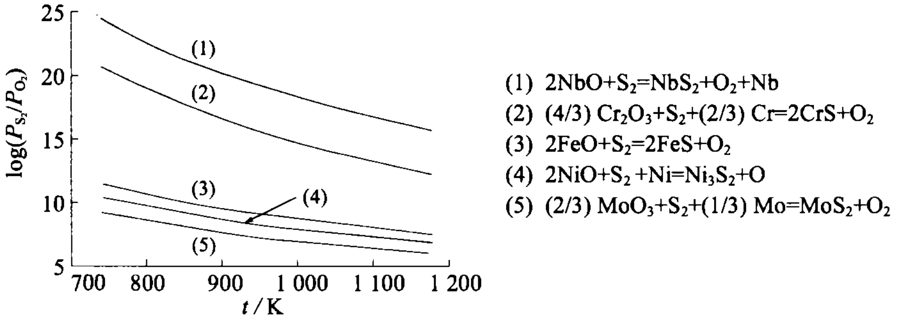

Fig.4 Calculated dependence of P_{S_2}/P_{O_2} upon temperature

Figure 4 shows the calculated results for elements Mo, Cr, Nb, Fe and Ni. It can be seen that when sulphuration and oxidation take place at. the same time, very high S_2 potential is needed, for which a layer of oxide has to form outside the sulfide to maintain so high a S_2 potential. We can expect the distribution of potentials of S_2 and O_2 in the sandwich-like structures (Fig.5).

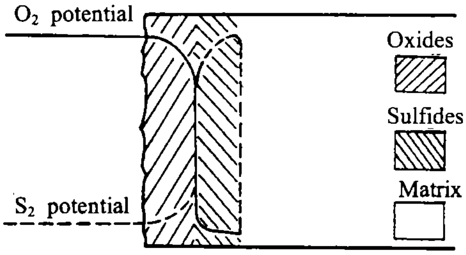

Fig.5 Distribution of S_2 and O_2 potentials in a corrosion layer

The most commonly used theory to explain the hot corrosion process is the acidic-basic vluxing mechanism proposed by Goebel, et al[9, 10]. The basis of this model is the loss of the protective function of surface oxide layer because of the fluxing of the layer in the molten salt. In this process, the behavior of the O^{2-} plays an important role. This model has been widely applied to explain the hot corrosion behavior of superalloys. In general, hot corrosion of the alloys with high Al and Cr contents occurs following the basic fluxing mechanism, while for the alloys with high W, Mo or V contents, hot corrosion takes place following the acidic fluxing mechanism. Although the basic fluxing is still an accelerated oxidation process, it is not as severe as the catastrophic oxidation caused by the acidic fluxing mechanism. The alloys used in this study are based on the hot corrosion resistant IN738LC alloy that contains high Al and Cr contents. The hot corrosion of IN738LC occurred following the basic fluxing mechanism[11]. According to this study, the hot corrosion of the alloys around the Ti and Nb corners may occur following the basic fluxing model. However, for the alloys around the Ta corner, catastrophic hot corrosion took place, which seems hard to be explained by the acidic-basic fluxing model, because basic fluxing should occur in such alloys with so high Al and Cr contents. This phenomenon may be explained by an alternative basic-acidic fluxing model[12, 13], according to the results of analyses of constituents and microstructures of the oxidation scales.

At first, hot corrosion took place following the basic fluxing model. The reactions between Na_2SO_4 and surface metals Al, Ni and Cr occurred as follows,

$$2Al+Na_2SO_4 \rightarrow Al_2O_3+S+2Na^{+}+O^{2-}$$
$$2Cr+Na_2SO_4 \rightarrow Cr_2O_3+S+2Na^{+}+O^{2-}$$
$$3Ni+2S \rightarrow Ni_3S_2$$

In the meantime, Cr reacted with Ni_3S_2, as mentioned above, to form Cr_2S_4.

Layered reaction structures were formed, e.g., the Al, Ni and Cr oxides formed in the outside surface, while in the subsurface, the Cr sulphide and degenerated Ni existed. As the result of above reactions, the local O^{2-} activity at the interface of metal/molten salt increased, which caused the following basic fluxing process:

$$Al_2O_3 + O^{2-} \rightarrow 2AlO_2^{-} \rightarrow \text{fluxing}$$
$$NiO + O^{2-} \rightarrow NiO_2^{2-} \rightarrow \text{fluxing}$$

$$Cr_2O_3 + O^{2-} \rightarrow CrO_4^{2-} \rightarrow \text{fluxing}$$

The oxide scale composed of Al_2O_3, NiO and Cr_2O_3 was fluxed by decomposing into anions of AlO_2^-, NiO_2^{2-} and CrO_4^{2-}. The sulphidation reaction took place at the interface of inner metal/oxide.

During the above process, W and Mo in the alloys were also oxidized to release O^{2-}. When the O^{2-} content in the molten salt reached a critical level, the following reactions took place,

$$MoO_3 + O^{2-} \rightarrow MoO_4^{2-}$$
$$WO_3 + O^{2-} \rightarrow WO_4^{2-}$$

Much O^{2-} were consumed in such reactions, which greatly reduced the O^{2-} activity in the molten salt.

To maintain an equilibrium concentration of O^{2-}, the following acidic fluxing reactions took place:

$$Al_2O_3 \rightarrow 2Al^{3+} + 3O^{2-} \rightarrow \text{fluxing}$$
$$Cr_2O_3 \rightarrow 2Cr^{3+} + 3O^{2-} \rightarrow \text{fluxing}$$

which would accelerate the decomposition of the protective oxide layer.

During the hot corrosion of the Ta-rich alloys, the basic-acidic fluxing processes took place alternatively as mentioned above and promoted each other, which caused the catastrophic corrosion. The results of X-ray diffraction phase identification showed the existence of $NaAlO_2$, $NaNiO_2$, Na_2SO_4, $AlWO_4$ and $CrWO_2$ as the corrosion products in alloy T5 (see Tab. 2 in Ref. [1]), which were also the reaction products in the basic and acidic fluxing models.

2 CONCLUSIONS

(1) In Ti and Nb-rich regions, hot corrosion process is controlled by basic-fluxing mechanism, and a thin layer of protective oxide forms on the surface; while in the Ta-rich region, it is controlled by an alternative basic-acidic fluxing mechanism, a layer of porous nonprotective corrosion product forms and results in the catastrophic hot corrosion attack.

(2) To a certain extent, the concept of "effective chromium content" can be used to predict the hot corrosion resistance of the alloy systems with high Cr contents.

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高 Cr 含量 Ni 基高温合金热腐蚀行为研究

—— II. 热腐蚀机制分析

崔 华[1)]张济山[1)2)] 村田纯教[3)] 森永正彦[3)] 汤川夏夫[3)]

(1) 北京科技大学材料科学与工程系，北京 100083
(2) 新金属材料国家重点实验室，北京 100083
(3) 日本丰桥技术科学大学

摘要 研究了合金系统 Ni-16Cr-9Al-2W-1Mo-4Co-(0～4)Ti-(0～4)Ta-(0～4)Nb(at%)热腐蚀过程受碱性熔融机制控制，形成了致密的保护性表面膜.因此在这些成分范围内的合金表现出较好的热腐蚀抗力.而在富 Ta 区内，交替发生碱性和酸性熔融，结果导致多孔性非保护性表面膜的形成，生成严重热腐蚀. 此外，“等效铬含量”概念可以在一定程度上预测此类合金的热腐蚀抗力.

关键词 热腐蚀，高温合金，合金化影响