Journal of Alloys and Compounds 710 (2017) 8–19

Contents lists available at ScienceDirect

Journal of Alloys and Compounds

journal homepage: http://www.elsevier.com/locate/jalcom

Effect of refractory elements and Al on the high temperature oxidation of Ni-base superalloys and modelling of their oxidation resistance

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A R T I C L E I N F O

Article history:
Received 23 November 2016
Received in revised form
20 February 2017
Accepted 17 March 2017
Available online 19 March 2017

Keywords:
High-temperature alloys
Superalloys
Nickel
Oxidation
Modelling
SEM

A B S T R A C T

The oxidation resistance of Ni-Co-Cr-Al-W-Mo-Ta-Re-Ru alloys is evaluated by cyclic oxidation at 1100 °C and modelled using an artificial neural network. The database required for the modelling was constructed using design of experiment (the Box-Behnken method) followed by oxidation experiments. The obtained model with a *7-10-1* architecture exhibits consistent prediction of the experimental data (R = 0.999). Cr and Al enhance the oxidation resistance by promoting the formation of a protective $NiAl_2O_4$ layer. Mo and Ru are detrimental to the oxidation resistance. W, Ta and Re exhibit complex behaviours depending on the contents of other alloying elements.

1. Introduction

Gas turbines are key systems in both the aerospace and thermal power plant industries. Since gas turbine components are exposed to high mechanical loading and severe environmental attack at high temperatures, Ni-base superalloys are widely used in gas turbine engines. Increasing the turbine inlet temperature results in a favourable reduction in the fuel cost and emission by enhancing the efficiency of gas turbine engines [1]. However, mechanical properties, such as the high temperature tensile strength and creep strength, and the environmental resistance, such as the oxidation resistance of materials for turbine components, should be further improved to increase the operating temperature. To enhance the high temperature tensile strength and creep strength of Ni-base superalloys, the content of refractory metals such as Mo, W, Ta, Re and Ru has been increased, and the content of Cr, which provides oxidation resistance, has been decreased. Although these compositional changes improve the mechanical properties [2–5], they can be detrimental to the oxidation resistance [6–8]. In particular, Ru, Mo and Re can form volatile oxide species; therefore, the oxidation resistance of alloys containing a large amount of these elements can be deteriorated [9–12]. Since both the mechanical and oxidation properties are important in superalloys, it is important to balance both properties in the development of superalloys.

For a large number of alloying elements used in superalloys, computational modelling can be an effective tool in the development of superalloys with balanced mechanical and oxidation properties [13–16]. In a previous study on Ni-Cr-W-Mo alloys, artificial neural networks (ANN) were successfully employed to model the oxidation properties [16]. However, the growing number of variables exponentially increases the number of experiment required to generate the database for the modelling. For a full factorial design with 7 variables and 3 levels, 2187 samples have to be tested, which is practically impossible. Therefore, design of experiments (DOE) can solve this problem by reducing the number of experiments required to obtain relations between the variables and properties. By combining computational modelling with DOE, a promising tool can be created for the development of superalloys.

In this study, 6 refractory elements (Cr, Mo, W, Ta, Re and Ru) and Al were selected as variables with a compositional range of Ni-6Co-(2–8)Cr-(0–3)Mo-(2–10)W-(4.5–6.5)Al-(2–10)Ta-(0–6)Re-(0–6)Ru in wt%. If a full factorial design were employed with 3 levels in each component, 2187 samples would be tested, as mentioned earlier. By using the Box-Behnken method, the number of samples required to generate the database for ANN modelling is reduced to 62 samples with 57 different compositions. In the Box-

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http://dx.doi.org/10.1016/j.jallcom.2017.03.179

Behnken design for 7 factors, 6 samples with identical chemical compositions with the centre point of the compositional range (Ni-6Co-5Cr-1.5Mo-6W-5.5Al-6Ta-3Re-3Ru) should be tested due to the statistical importance.

The oxidation resistance of the samples was evaluated by a cyclic oxidation test for 50 cycles with a one-hour dwell at 1100 °C. The database of the weight changes after 50 cycles was constructed and modelled by using ANNs, which is similar to a previous study [16]. The model was successfully constructed in the Cr-Mo-W-Al-Ta-Re-Ru space and was consistent with the experimental data (with multiple correlation coefficient R = 0.999). The weight change behaviour was analysed using a simple statistical spalling model proposed by Poquillon and Monceau [17]. The oxide microstructure was analysed with scanning electron microscopy (SEM) to study the effect of each element on the high temperature oxidation.

2. Materials and methods

In the alloy design framework, the goal was to find out the effect of alloying elements including Cr, Mo, W, Al, Ta, Re, and Ru on the oxidation resistance of Ni-base superalloy. The Box-Behnken design was employed to DOE to minimize the number of samples in this study. This design scheme requires smaller experiment runs than the other schemes such as central composite design (CCD); the CCD gives 152 runs for 7 independent variables while the Box-Behnken design [18] gives 62 runs for the same number of variables.

In Box-Behnken design, the levels of the concentrations of alloying elements were determined according to three coded levels designated as −1, 0, and +1. These codes represent the lower limit, the central value, and the upper limit of an independent variable, respectively. The zero level is presented as the central design point, corresponding to the central value of the range of independent variables under interest. The central points were repeated for 6 times to stabilize the extrapolation around the central region. The −1 and +1 levels are edge points which correspond to the maximum and the minimum values to be tested. The compositional ranges of tested alloys are shown along with the coded levels in Table 1. The lower limit and the upper limit of each factor represent reasonable range of alloying elements in single crystal Ni-base superalloys. 62 alloy compositions were designed according to the Box-Behnken method for 7 alloying elements (Table 2). The alloys from A57 to A62 have an identical composition as a centre point of the compositional range. To save space, the weight changes after 50 cycles, which are used in ANN modelling, are also listed in Table 2.

The samples were prepared by vacuum arc melting. Impurities that are detrimental to the oxidation resistance, such as S, are strictly controlled during the raw material selection and the melting process under 1 ppm. From each ingot, the oxidation samples are prepared by electrical discharge cutting and micro-cutting to make discs with 10 mm diameters and 3 mm thicknesses. The samples were ground using SiC papers up to 1000-grit and cleaned in acetone and ethanol before the cyclic oxidation experiments.

Cyclic oxidation is performed in an open-end furnace equipped with a programmable specimen in/out system. One cycle of experiments in this study is composed of heating at 1100 °C for 60 min and cooling in open air for 30 min to room temperature. Fig. 1 shows the actual temperature profile during the cyclic oxidation experiment. The weights of samples are measured after 0, 2, 4, 16, 20, 32, 36 and 50 cycles using a digital balance with an accuracy of 10^{-4} g. Spalled oxide scales were not incorporated in the weight measurement. After the oxidation experiment, the oxide scale of the specimens was examined by SEM in the back-scattered electron imaging (BEI) mode and energy dispersive spectroscopy.

Table 1
Level values used in the Box-Behnken method.

	Level		
	−1	0	+1
Cr	2	5	8
Al	4.5	5.5	6.5
W	2	6	10
Mo	0	1.5	3
Ta	2	6	10
Re	0	3	6
Ru	0	3	6
Co	–	6	–
Ni	–	Bal.	–

3. Results and discussion

3.1. Weight changes during cyclic oxidation

The weight change of selected experimental alloys during the cyclic oxidation is shown in Fig. 2. One thermal cycle consisted of exposure at 1100 °C for 1 h and cooling for 30 min to room temperature. The alloys shown in Fig. 2 contain 5 wt% Cr except A47 and A48. The alloys with 8 wt% Cr or 5 wt% Cr + 6.5 wt% Al, including the alloys that are not presented in Fig. 2, showed no significant weight gain or loss during the experiment, which indicates excellent oxidation resistance. The oxidation resistance of these alloys were better than that of CMSX-4, which is known to have excellent oxidation resistance among single crystal Ni-base superalloys, in the literature [19]. The other alloys showed significant amounts of weight loss. In general, the addition of Cr and Al was beneficial to the oxidation resistance. The addition of Ta was slightly beneficial in some cases. Mo, W and Ru were detrimental to the oxidation resistance as known in the literature [6–8]. Re had no significant effect on the oxidation resistance.

For an in-depth study of the effect of alloying elements, the weight change after 50 cycles of the oxidation experiment with respect to the content of each alloying element is plotted in Fig. 3. An increase in the Cr content from 2 wt% to 8 wt % significantly improved the oxidation resistance (Fig. 3(a)). An increase in the Al content from 4.5 wt% to 6.5 wt% also improved the oxidation resistance, except for the alloys with 8 wt% Cr (Fig. 3(b)). Mo addition up to 3 wt% was detrimental to the oxidation resistance. However, its detrimental effect was reduced when the content of W was 2 wt% (Fig. 3(c)). The effect of W on the oxidation resistance was generally negative. However, its negative effect was diminished when the contents of Cr and Al were sufficiently high, as in the case of the alloys with 8 wt% Cr and 5 wt% Cr + 6.5 wt% Al (Fig. 3(d)). The addition of Ta was somewhat beneficial up to 10 wt %, except for the alloys with 2 wt% Cr or 8 wt% Cr (Fig. 3(e)). For the alloys with 2 wt% Cr, the addition of Ta showed a negative effect. Moreover, no significant effect was observed for alloys with 8 wt% Cr. Both positive and negative effects of Ta on the oxidation resistance of Ni-base alloys were reported in the literature [20,21]. The effect of Re on the oxidation resistance was not monotonous, and it differed depending on the content of Cr and Al (Fig. 3(f)). Moniruzzaman et al. reported that the harmful effect of Re was altered by the content of Al [22], which is similar results with this study. The addition of up to 6 wt % Ru resulted in an adverse effect on the oxidation resistance. Similar to the effect of W, the adverse effect of Ru was reduced when the contents of Cr and Al were sufficiently high (Fig. 3(g)).