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Oxidation behavior of co-doped NiCrAl alloys in dry and wet air ☆

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ABSTRACT

Cast NiCrAl alloys with additions of Y, La, Hf and Ti were evaluated at 1100 °C in wet (10 and 50% H_2O) and dry air (0% H_2O) in order to optimize such dopants for superalloy bond coatings. The results suggest that the typical Y addition in most coatings could be replaced by La. Also, scale adhesion in cyclic testing was improved with the co-addition of Hf with La or Y. Ti was added to investigate its incorporation in coatings on superalloys containing significant Ti additions. Particularly with co-doped alloys, the addition of Ti had little effect on scale adhesion but did reduce the depth of internal oxidation. Water vapor increased spallation, especially for the least adherent alloys, such as Y,Ti-doped NiCrAl. For the co-doped compositions with Hf, water vapor had a limited effect on scale adhesion and on the alumina growth rate in isothermal exposures. In addition to specimen mass change, the extent of internal oxidation and the depletion of β phase in the substrate were evaluated. Analytical transmission electron microscopy showed that Y, La and Hf co-segregated to the alumina scale grain boundaries and formed dopant-rich oxide precipitates in the scale.

1. Introduction

The effect of reactive elements (RE) (e.g., Y, La, Hf, Zr and Ce) have been widely studied since they were patented more than 75 years ago [1,2]. Such dopants are an integral part of most high-temperature coating systems, especially for gas turbines. Two factors have led to the current reevaluation of dopant effects in NiCrAl alloys: (1) the desire to develop improved durability bond coatings for coal-derived synthesis gas (syngas)- or H_2-fired land based gas turbines [3] and (2) the current concern about rare earth element availability and the potential need to replace a critical dopant like Y [4]. Because of the importance of gas turbines for both power generation and transportation, there have been many recent studies of the oxidation behavior of NiCrAlY and NiCoCrAlY bond coatings [5–13]. It has become increasingly clear from the research and applications that co-doping leads to the best scale adhesion and coating lifetimes [14–19]. Another aspect is that as a coating, the role of substrate interdiffusion must also be considered and recently it was confirmed that superalloy substrate elements like Ti quickly become incorporated into the scale and may affect system performance [20]. Thus, cast model NiCrAl alloys were isothermally and cyclicly oxidized at 1100 °C in dry air and air with 10% and 50% H_2O to compare the performance of various dopants in these environments: less expensive La to replace Y in compositions co-doped with Hf and Ti additions to the same alloys. After exposure, characterization was conducted to study the morphology of the oxide scale, RE segregation within the scale, internal oxidation and β phase depletion in the substrate. An analytical transmission electron microscopy (TEM) was used to examine the dopant ionic segregation to the alumina scale grain boundaries [2,16,18,20–22]. Because all of these model NiCrAl alloys were doped and contained relatively little S (i.e. RE/S> > 1), the role of S on scale adhesion [23–25] is not discussed.

2. Experimental procedure

The composition of the cast NiCrAl alloys is shown in Table 1. Specimens with ~16 mm diameter and 1-1.5 mm thickness were polished to a 600 grit SiC (cyclic tests) or 0.3 μm Al_2O_3 (isothermal tests) final finish and ultrasonically cleaned in acetone and methanol prior to exposure at 1100 °C: (1) isothermally using a Cahn model

Table 1
Chemical composition in at. % determined by inductively coupled plasma and combustion analysis.

	Ni	Cr	Al	Y	La	Hf	Ti	C	S
NCAY	61.3	19.7	18.9	0.066	–	0.001	0.003	0.021	<0.0003
NCAYT	61.2	19.4	18.9	0.066	–	–	0.31	0.024	<0.0003
NCAYH	62.3	15.1	22.5	0.030	–	0.040	–	0.024	<0.0003
NCAYHT	61.9	15.2	22.6	0.020	0	0.043	0.31	0.017	<0.0003
NCALH	61.2	20.0	18.6	–	0.015	0.040	–	0.021	<0.0003
NCALHT	61.1	19.7	18.8	–	0.019	0.040	0.32	0.030	<0.0003

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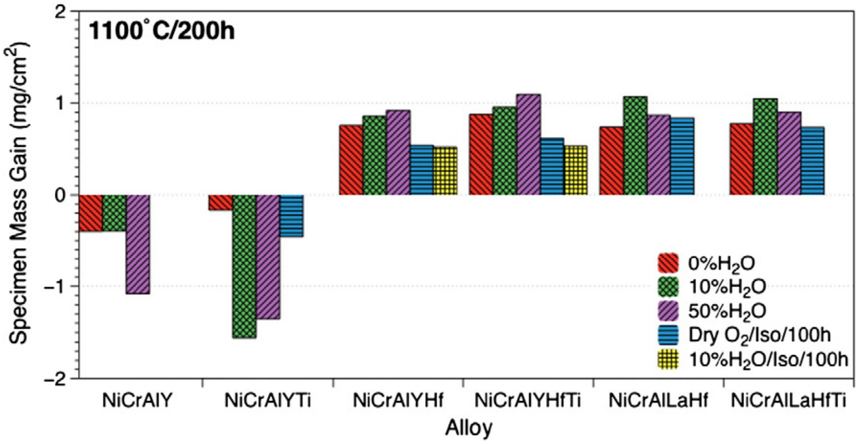

Fig. 1. Mass change data for NiCrAl alloys with addition of Y, Hf, Ti and/or La after exposure at 1100 °C for 200 1-h cycles and after isothermal exposure for 100 h in dry O_2 and 10% H_2O.

1000 microbalance and (2) using 1 h cycles with 10 min cooling between cycles using an automated system and weighing the specimens every 20 cycles on a Mettler-Toledo model XP205 balance with an accuracy of 0.01 mg/cm^2. Three environments were used: dry air (0% H_2O) and air with 10% or 50% H_2O. Specimens were characterized by scanning electron microscopy (SEM) (Hitachi model S3400 and S4800), scanning-transmission electron microscope (STEM) (Philips model CM200) equipped with a Schottky field emission gun (FEG) and x-ray energy dispersive spectrometer (EDS) and operated at 200 kV. For polished cross sections, specimens were Cu-plated prior to sectioning. TEM specimens were prepared via the focus ion beam (FIB) in-situ lift-out technique using a Hitachi NB5000 FIB-SEM. Internal oxidation and the ß depletion zone beneath the oxide scale were measured using approximately 40 measurements from the polished cross sections using ImageJ software.

3. Results and discussion

Figs. 1 and 2 summarize the cyclic oxidation resistance of the six NiCrAl alloys in the three different environments at 1100 °C. Fig. 1 shows the final mass change after 200 1-h cycles. From this summary, it is clear that the single-doped NiCrAlY and YTi alloys showed a mass loss in the cyclic tests due to scale spallation. In contrast, all of the co-doped alloys showed mass gains throughout. Most importantly, there was little difference between the YHf and the LaHf alloys and the addition of Ti appeared to have little effect. Fig. 2a–c show the mass gain curves as a function of exposure time in cyclic testing for each of the environments to reinforce the information in Fig. 1. The NiCrAlYTi data also clearly shows that Ti does not produce the same benefit as Hf. For the Y and Hf co-doped alloys, the addition of water vapor appeared to increase the mass gain after 200 cycles but the changes

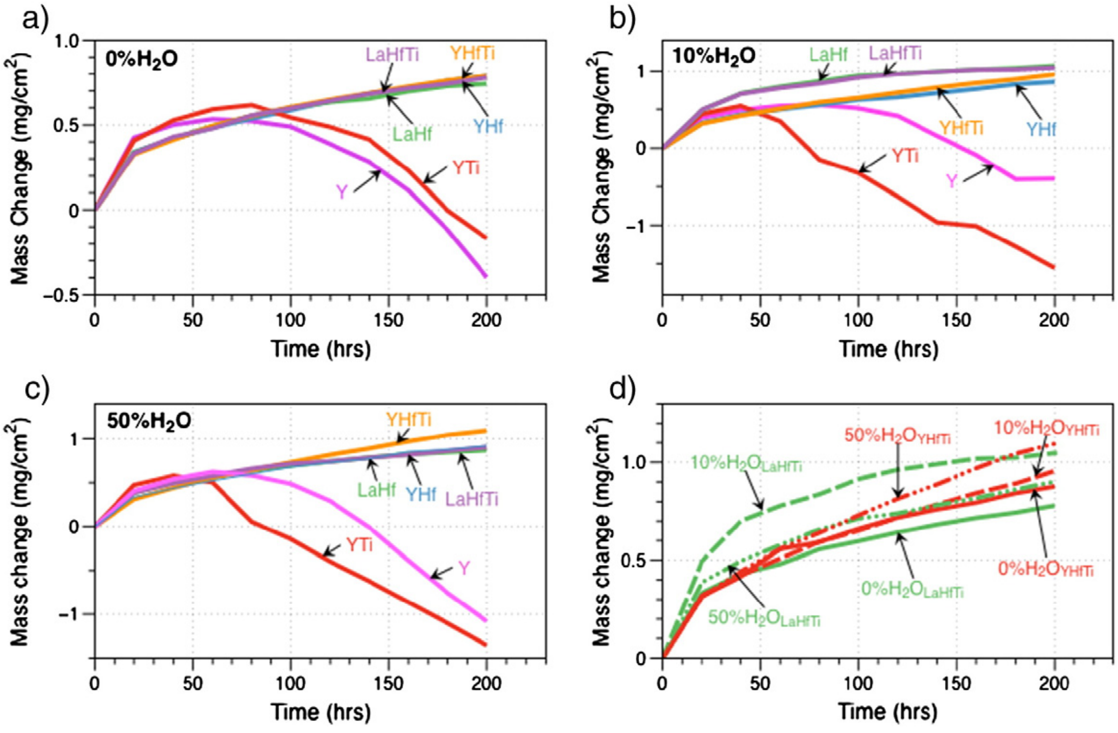

Fig. 2. Specimen mass change for specimens tested in 200 1-h cycles at 1100 °C in laboratory air with various addition of water vapor (a) 0% H_2O, (b) 10% H_2O and (c) 50% H_2O. (d) YHfTi-doped NiCrAl vs. LaHfTi-doped NiCrAl at different water content exposure.