A thermodynamic approach to guide reactive element doping: Hf additions to NiCrAl

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Abstract. A method based on thermodynamic modeling was developed to determine optimal amounts of Hf additions to Al₂O₃-forming, γ - γ' NiCrAl alloys. The alloy ability to maintain Hf in solution was set by the Hf concentration required to form HfO₂ at the oxygen activity defined by the alloy/Al₂O₃ equilibrium. This Hf tolerance decreased with increasing temperature and increased with increasing γ' fraction. The latter was due to the higher solubility of Hf in γ' , compared to γ . The validity of the procedure was evaluated by oxidizing a series of NiCrAl-Hf alloys in dry air at 1000–1200 °C. The experimental results followed the predicted trends, although the Hf tolerance tended to be overestimated. The applicability of the criterion, and potential routes for improved predictability, were discussed by considering the influence of the compositional changes occurring at the metal surface during the transient and steady-state stages of the oxidation process.

Keywords: Reactive elements; Thermodynamic modeling; Coatings; High-temperature oxidation

1 Introduction

Reactive element (RE) addition to high-temperature materials is a widespread method of improving their oxidation resistance. Mechanistic and practical aspects of RE effects have been discussed extensively in the literature; reviews are found in Refs. [1–6] for example. Most common dopants include Y, Hf and Zr in Al₂O₃-forming systems, Ce and La in Cr₂O₃-forming systems. Their influence on oxidation behavior takes multiple forms, some of which are still open to interpretation. In particular, REs are known to yield significantly slower scale growth and improved scale adhesion. Although the two effects are related since a thinner scale will produce less growth stress, RE effects on scale adhesion appear to be more important than reduced scaling rates in determining the lifetime of a thermally cycled material [7]. A commonly accepted view is that REs neutralize S impurities and thus prevent a weakening of the metal/oxide interface [8–13]. Other aspects of improved scale adhesion are

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system-dependent, as they are related to the metal coefficient of thermal expansion, strength and microstructure, all of which influence the stress state and integrity of the metal-oxide assemblage. In particular, RE additions are known to mitigate interfacial void formation, which is often associated with scale spallation from β -NiAl and FeCrAl systems, but not necessarily NiCrAl or Ni-base superalloys [14]. MCrAlY systems (M = Ni, Co or both) typically benefit from the formation of Y oxide particles (pegs) at the base of the Al_2O_3 scale, which are thought to improve the scale adhesion via “mechanical keying” [1], although some disagreement exists as to their actual role [6].

As beneficial as REs may be when added in the right proportion, overdoping can have detrimental consequences on oxidation resistance. Not only does overdoping increase overall scaling rates, but more critically, it produces oversized pegs which may favor scale failure during thermal cycling [15,16], or act as initiation sites for accelerated corrosion under sulfate [17] or oxide-sulfate deposits [18]. Controlling RE additions, together with impurities such as S or C, is therefore a critical aspect of material design and manufacturing. To this end, computational thermodynamics provides a valuable tool in integrating experimental phase equilibrium data and predicting microstructures.

The present paper presents a study of Hf additions to Al_2O_3 -forming NiCrAl alloys. Based on thermodynamic equilibrium in the alloy system, a simple criterion is devised to predict the maximum amount of Hf which can be added without producing HfO_2 below the Al_2O_3 . The applicability of such a criterion, and potential routes for improved predictability, are discussed based on experimental results obtained with γ , γ - γ' and γ' alloys at 1000–1200 °C (γ and γ' designate the fcc Al solid solution based on Ni and the ordered cubic L_{12} compound based on Ni_3Al , respectively).

2 Experimental and computational procedures

2.1 Materials

The NiCrAl–Hf alloys used for the oxidation experiments were based on four NiCrAl compositions, which are plotted on an isothermal section of the Al–Cr–Ni phase diagram in Fig. 1. These were chosen so as to obtain γ , γ - γ' and γ' microstructures at 1000–1200 °C with varying Cr levels, while maintaining the ability to form an Al_2O_3 scale. Nominal compositions and equilibrium phase constitutions are summarized in Tables 1 and 2, respectively. Four alloys were cast with 0.1 at. % Hf; in two cases, 0.05 at. % Hf additions were also used. These Hf levels were low enough to avoid the formation of Hf-containing intermetallics. A version of the Ni–8Cr–17Al–0.1Hf alloy was made with 0.5 at. % Si.

The ingots were made by argon arc melting, followed by drop casting into 10-mm-diameter rods which were then homogenized in vacuum for 6 h at 1200 °C plus another 48 h at 1150 °C. All processing was conducted at the Materials Preparation Center of the Ames Laboratory [20]. Compositions measured by ICP–OES (Evans Analytical Group, Liverpool, NY, USA) for selected alloys were very close to the nominal compositions, as shown in Table 1. In particular, Hf concentrations, albeit small, were controlled with satisfactory accuracy.

Specimens approximately 1 mm thick were vacuum-encapsulated in quartz capsules and annealed in a tube furnace at 1000, 1100 and 1200 °C for 217, 100 and

Figure 1: Isothermal section of the Al–Cr–Ni system at 1100 °C, calculated from data in Ref. [19]. Portions of the $\gamma/\gamma-\gamma'$ and $\gamma-\gamma'/\gamma'$ phase boundaries at 1000 and 1200 °C are superimposed, and the base NiCrAl alloy compositions used for oxidation experiments are indicated (color figure online).

Table 1: Nominal composition of the alloys (at. %), balance: Ni. Included results of ICP–OES analysis of selected alloys are very close to nominal values.

Reference	Nominal				Measured (ICP–OES)			
	Cr	Al	Hf	Si	Cr	Al	Hf	Si
Ni–8Cr–13Al–0.1Hf	7.5	13	0.1					
Ni–8Cr–17Al–0.1Hf	7.5	16.8	0.1		7.6	16.6	0.098	
Ni–8Cr–17Al–0.1Hf–0.5Si	7.5	16.8	0.1	0.5	7.5	16.6	0.101	0.66
Ni–8Cr–17Al–0.05Hf	7.5	16.8	0.05		7.6	16.4	0.054	
Ni–13Cr–17Al–0.1Hf	13	16.8	0.1					
Ni–5Cr–23Al–0.1Hf	5	23	0.1					
Ni–5Cr–23Al–0.05Hf	5	23	0.05					

Table 2: Phases observed after annealing at the indicated temperatures and water quenching. Additions of Hf or Si did not modify the phase constitutions.

	<i>T</i> (°C)		
	1000	1100	1200
Ni–8Cr–13Al	$\gamma-\gamma'$	γ	γ
Ni–8Cr–17Al	$\gamma-\gamma'$	$\gamma-\gamma'$	$\gamma-\gamma'$
Ni–13Cr–17Al	$\gamma-\gamma'$	$\gamma-\gamma'$	γ
Ni–5Cr–23Al	γ'	γ'	γ'

Figure 2: Calculated phase compositions of γ - γ' alloy Ni-13Cr-17Al-0.1Hf as a function of temperature. Compositions measured by EPMA after equilibration heat treatments (symbols) are included.

50 h, respectively. Based on past experience, these durations were thought to be long enough to reach thermodynamic equilibrium. The heat treatments were terminated by water quenching to retain the equilibrated microstructures.

Polished sections of the equilibrated alloys were prepared by standard metallographic procedures. Phase compositions were determined by electron probe microanalysis (EPMA) using a JEOL JXA-8530F field emission gun instrument. The measured intensities were converted to concentrations via a built-in ZAF calibration procedure using pure metals as standards. The γ and γ' compositions were found to be in good agreement with equilibrium values calculated from Dupin et al.'s Al-Cr-Ni assessment [19]. Plots of measured versus calculated concentrations are given in Fig. 2 for Ni-13Cr-17Al-0.1Hf. In γ - γ' alloys, the Hf solubility in γ was too small to be accurately measured; however, the Hf concentration measured in γ' was in good agreement with the Hf solubility calculated using our developmental Al-Cr-Hf-Ni database (see modeling section below).

2.2 Oxidation experiments

Oxidation experiments were conducted at 1000, 1100 and 1200 °C using specimens equilibrated at the same temperatures. Approximately 100 μ m of material was ground off the specimen surfaces using SiC paper so as to remove any layer affected by oxidation or sublimation during the equilibration treatment. The specimens were then ground down to a P1200-grit finish, degreased with detergent and ultrasonically cleaned in ethanol. This procedure was used to have well-defined, equilibrium microstructures at the alloy surfaces from the beginning of the oxidation process.

The oxidation experiments were carried out in flowing dry air using a horizontal tube furnace. Gas flow rates were set to 100 ml/min (about 2 mm/s in the hot zone), with a pressure slightly over 1 atm. Prior to a given experiment, the furnace was stabilized at the desired temperature with the specimens positioned in a cold zone of the reaction tube, and the gas allowed to flow for 2 h. To start the experiment, the specimens were magnetically pushed in the hot zone. All alloys were oxidized

20 h at the three temperatures; shorter exposures were done in selected cases. After exposure, polished sections of the reacted alloys were examined by SEM (JEOL JSM 6510) and by EPMA in some cases.

2.3 Thermodynamic modeling

The Al–Cr–Hf–Ni system was modeled using the CALPHAD (CALculation of PHase Diagrams) method [21], where multicomponent sublattice models based on the compound energy formalism were used to describe the Gibbs free energy of the solid solution phases. Details of the modeling procedure will be described in separate publications. Briefly, the description of the Al–Cr–Ni system by Dupin et al. [19] was adopted and combined with that of the most relevant Hf-containing binary and ternary systems. The Hf–Ni system was remodeled based on the work by Wang et al. [22] with new experimental data (EPMA, DSC) and finite-temperature first-principles data (Debye, SQS) obtained by density functional theory. The Al–Hf–Ni and Cr–Hf–Ni systems were modeled by considering the ternary compounds as well as the Al and Cr solubility in the Hf_2Ni_7 phase.

The ability of NiCrAl–Hf alloys to maintain Hf in solution and hence limit the formation of pegs was determined by considering a simple variable, the Hf concentration required to form HfO_2 at the O activity defined by the alloy/ Al_2O_3 equilibrium (i.e., below a thermally growing Al_2O_3 scale at steady-state). HfO_2 is more stable than Al_2O_3 at unit activity of the respective metals; yet for a sufficiently low Hf activity in an alloy, HfO_2 will not be stable at the reduced p_{O_2} prevailing below the Al_2O_3 . This threshold activity is related to the energy of mixing of Hf, which also determines its solubility in a given alloy phase. Since Hf is more soluble in γ' than in γ (Fig. 2), at a given Hf activity, the Hf concentration is larger in γ' . Thus, the Hf concentration for HfO_2 formation, or Hf tolerance, is predicted to be larger in γ' than in γ (or in β , which dissolves very little Hf). Plots of the Hf tolerance as a function of Cr and Al concentrations at 1000–1200 °C are given in Fig. 3. All calculations were made using Thermo-Calc [23,24].

Figure 3 shows that the Hf tolerance is affected both by phase changes and by composition changes within a given phase field. Within γ or β , increasing the Al content causes a slight increase in Hf tolerance, while Cr variations have little effect. In γ' , however, the effects of Al and Cr variations are non-monotonic and can be large. Increasing Al generally causes the Hf tolerance to increase, especially at low Cr levels. The effect is limited and locally opposite at higher Cr levels, near the γ – γ' – β triangle. Conversely, increasing Cr leads to a decrease in Hf tolerance, except at low Cr levels where an opposite effect is observed. These variations reflect the complex interplay between phase equilibria in the metal system and in the alloy– HfO_2 – Al_2O_3 pseudo-ternary system: Al and Cr concentrations determine Al and Cr activities via activity coefficients in the Al–Cr–Ni ternary; the Al activity defines an equilibrium p_{O_2} at the alloy/ Al_2O_3 interface, which in turn yields an Hf activity for HfO_2 formation; finally, the threshold Hf concentration (Hf tolerance) depends on both this equilibrium Hf activity and the Al and Cr concentrations, via the topology of the quaternary Al–Cr–Hf–Ni system.

Figure 3: Calculated Hf concentration required to form HfO₂ at the O activity defined by the alloy/Al₂O₃ equilibrium, i.e., below a growing Al₂O₃ scale, as a function of Al concentration, at varying Cr levels. This “Hf tolerance” is the maximum Hf concentration which can be included in an alloy to avoid HfO₂ formation, based on the equilibrium alloy phase compositions. The yellow symbols represent the base NiCrAl compositions used for oxidation experiments (see Fig. 1) (color figure online).

3 Results and discussion

3.1 General observations

Cross-sections of the NiCrAl–0.1Hf alloys after 20-h oxidation at 1000, 1100 and 1200 °C are shown in Fig. 4. The Ni–8Cr–13Al–0.1Hf alloy was a marginal Al₂O₃-former at 1000 and 1100 °C, in that it locally formed nodules of NiO and mixed Ni–Cr–Al oxide in addition to Al₂O₃ at these temperatures. Similarly, the Ni–5Cr–23Al–0.1/0.05Hf alloys locally formed mixed oxide scales with internal Al₂O₃ at 1000 and 1100 °C. The other alloys produced thin Al₂O₃ scales at all three temperatures. Particles of a Hf-rich oxide, referred to as HfO₂ hereafter, formed in varying quantities within or below the Al₂O₃. In order to assess the results of the thermodynamic calculation, the alloys were divided into three categories, based on whether HfO₂ particles were (1) not observed (see for example Ni–5Cr–23Al–0.1Hf at 1200 °C in Fig. 4), (2) observed locally (see Ni–8Cr–17Al–0.1Hf at 1100 °C) or (3) observed consistently (see Ni–13Cr–17Al–0.1Hf at 1200 °C).

Due to the discrete nature of the HfO₂ particles, their varying size and volume fraction, the outcome of any classification necessarily depends on the methods used. Here, Hf oxidation was deemed localized when micron-scale HfO₂ particles were spaced by more than $\sim 5 \mu\text{m}$ apart along the Al₂O₃ scale, as observed by SEM. Smaller ($\sim 50 \text{ nm}$), isolated HfO₂ particles were observed at high magnification, including in the case of alloys classified as “no HfO₂,” and it is recognized that particles too small to be detected by SEM likely also existed. These submicron HfO₂ particles are believed to form, in part, in the transient initial stage of the oxidation process. Increasing the oxidation temperature generally accelerates the establishment of a continuous α -Al₂O₃ scale and limits the formation of transient oxides, i.e., θ -Al₂O₃ and oxides of Ni and Cr. Indeed, from 1000 to 1200 °C, the amount of submicron HfO₂ particles decreased (see Ni–5Cr–23Al–0.1Hf in Fig. 4), despite a predicted rise in the driving force for Hf oxidation.

Figure 4: Cross-sections of the Ni-8Cr-13Al-0.1Hf, Ni-8Cr-17Al-0.1Hf, Ni-13Cr-17Al-0.1Hf and Ni-5Cr-23Al-0.1Hf alloys oxidized 20 h at 1000, 1100 and 1200 °C. The bright particles visible within or below the Al₂O₃ scales consist of Hf-rich oxide, referred to as HfO₂.

	Prediction			Observation			
	T (°C)			T (°C)			
	1000	1100	1200	1000	1100	1200	
Ni-8Cr-13Al-0.1Hf	yes	yes	yes	yes	yes	yes	Agreement
Ni-8Cr-17Al-0.1Hf	no	no	yes	loc	loc	yes	
Ni-8Cr-17Al-0.05Hf	no	no	no	loc	loc	loc	
Ni-13Cr-17Al-0.1Hf	no	no	yes	loc	yes	yes	Disagreement
Ni-5Cr-23Al-0.1Hf	no	no	no	loc	loc	no	
Ni-5Cr-23Al-0.05Hf	no	no	no	no	no	no	

Figure 5: Summary of predicted formation of HfO_2 below an Al_2O_3 scale based on calculation shown in Fig. 3, compared with experimental observations after 20-h oxidation of equilibrated alloys. Experimental results were divided into three categories, based on whether HfO_2 particles were not observed (=“no”), observed locally (=“loc”) or observed consistently (=“yes”). See details in text (color figure online).

3.2 Factors affecting Hf tolerance

The observed presence or absence of HfO_2 is compared in Fig. 5, for each alloy and temperature, with the prediction based on the Hf tolerance plots (Fig. 3). In general, the prediction was rather good, in that whenever Hf was predicted to oxidize, HfO_2 was indeed observed, and when Hf was predicted not to oxidize, HfO_2 was either not observed or observed locally. Factors affecting the Hf tolerance are now addressed individually.

γ/γ' phase fractions. The experimental results followed the trend expected from the equilibrium calculation, i.e., alloys with a larger γ' fraction tended to form less HfO_2 , due to the larger solubility of Hf in γ' (compare Ni-8Cr-13Al-0.1Hf with Ni-8Cr-17Al-0.1Hf and Ni-5Cr-23Al-0.1Hf, and Ni-8Cr-17Al-0.05Hf with Ni-5Cr-23Al-0.05Hf).

Cr concentration. The Hf tolerance is predicted to slightly decrease with increasing Cr in Ni-Cr-17Al alloys. This was verified to some extent, as larger amounts of HfO_2 formed in Ni-13Cr-17Al-0.1Hf than in Ni-8Cr-17Al-0.1Hf; however, no significant difference between the two alloys was observed at 1000 or 1200 °C. Other factors affecting Hf oxidation in these alloys are discussed subsequently. It is noted that a much sharper decrease in Hf tolerance with increasing Cr concentration is predicted to occur at high Al and low Cr concentrations, within the single-phase γ' field and into the $\gamma'-\beta$ field. This region of the phase diagram was not explored experimentally.

Si concentration. Although Si is not included in the thermodynamic modeling at present, previous experimental results [25] indicated that 0.5–1.0 at. % Si additions to Hf-Y co-doped $\gamma-\gamma'$ alloys reduced Hf oxidation, suggesting that Si lowered the Hf activity. At variance with those results, it was found in the present study that adding 0.5 at. % Si to Ni-8Cr-17Al-0.1Hf had no significant effect. Further investigation of the role of Si is in progress.

Temperature. For a given alloy, the Hf tolerance is expected to decrease with increasing temperature, and indeed, the extent of Hf oxidation in γ – γ' alloys Ni–8Cr–17Al–0.1Hf and Ni–13Cr–17Al–0.1Hf increased from 1000 to 1200 °C. This is consistent with the simultaneous decrease in γ' fraction in this temperature range. Although this trend is also expected within the single-phase γ' field, the Ni–5Cr–23Al–0.1Hf alloy formed less HfO₂ as the temperature increased. As discussed earlier, this is inferred to be due to the faster establishment of Al₂O₃ and reduced transient oxidation at higher temperatures, a factor which is independent from the thermodynamic considerations involved in the Hf tolerance calculation.

3.3 Role of subsurface compositional changes due to oxidation

The equilibrium calculation failed to predict the local HfO₂ formation observed in the γ – γ' alloys. In examining this discrepancy, we note that while the Hf tolerance is calculated based on equilibrium phase compositions, i.e., on the composition of the alloy surfaces prior to oxidation, the composition of an alloy at the metal/oxide interface changes as oxidation proceeds, due to selective Al removal to form Al₂O₃ (if scale growth is parabolic, a constant interfacial composition is reached at steady state [26–29]). An obvious manifestation of this change is the dissolution of γ' below the scale.

Composition profiles measured by EPMA in the Ni–8Cr–13Al–0.1Hf, Ni–8Cr–17Al–0.1Hf and Ni–13Cr–17Al–0.1Hf alloys after oxidation at 1100 °C are shown in Fig. 6. In the case of Ni–8Cr–17Al–0.1Hf, the interfacial concentrations of Cr and Al are measured to be ~ 9 and 11 at. %, respectively. If these values are used instead of the bulk concentrations, Fig. 3 predicts an Hf tolerance of about 0.01 at. %, well below 0.1 at. %. Qualitatively, this is consistent with the observed Hf oxidation in this alloy. Yet the Hf tolerance obtained this way is probably underestimated, since Hf oxidation was only local. Furthermore, a detailed analysis of depletion kinetics during the initial stage of selective oxidation shows that the interfacial alloy composition goes through a minimum before attaining the steady-state value [27,29]. Taking this minimum into account would lead to an even larger underestimation of the Hf tolerance.

It may be argued that by the time the metal/oxide interface reaches its steady-state composition, much of the Hf initially present in the subsurface could be consumed to form HfO₂, and Al depletion is of little importance. Indeed, is Hf oxidation governed by transient processes, or does the scale equilibrate with the underlying alloy at steady-state? A related question concerns the influence of Hf segregation on the local Hf concentration at the alloy surface in the early stage of oxidation. Elucidation of these questions would require a quantitative mass balance on Hf in the scale and the alloy after varying reaction times, which would be challenging in practice given the small size of HfO₂ precipitates in the scale and the low Hf solubility in the alloy γ phase. In considering the relative importance of transient oxidation, we note that cases of localized Hf oxidation were observed for the γ – γ' alloys Ni–8Cr–17Al–0.1Hf and Ni–13Cr–17Al–0.1Hf. The question of whether local Hf oxidation in the early stage is related to the initial two-phase alloy microstructure is examined next.

Figure 6: Composition profiles measured by EPMA below Al_2O_3 scales after 20-h oxidation at 1100 °C. For each alloy, two profiles were recorded at random locations, and found to be consistent; only one is showed for clarity. In the case of Ni-8Cr-13Al-0.1Hf, the γ' present in the bulk precipitated during air cooling at the end of the oxidation test. No γ' was observed when the alloy was water-quenched. Interdiffusion work in Ref. [30] showed that both $\bar{D}_{\text{Al,Al}}^{\text{Ni}}$ and $\bar{D}_{\text{Al,Cr}}^{\text{Ni}}$ varied significantly with Al concentration but not with Cr. These thermodynamic interactions and the relative values of the main and cross terms explain why the Al depletion profiles measured here were flat for both Ni-8Cr-17Al-0.1Hf and Ni-13Cr-17Al-0.1Hf, but not for Ni-8Cr-13Al-0.1Hf.

3.4 Early stage oxidation processes

Short-term, 3-min oxidation tests were conducted on the γ - γ' alloys Ni-8Cr-17Al-0.1Hf and Ni-13Cr-17Al-0.1Hf at 1100 °C. Based on past experience, it takes about two minutes for the specimens to heat to 1100 °C after being pushed in the hot zone in these experimental conditions. Thus, the 3-min exposure was mostly anisothermal, with only about a minute at 1100 °C.

After short-term exposure, a thin Al_2O_3 scale had formed, γ' had started to dissolve, and HfO_2 particles were observed within the Al_2O_3 and at the metal/oxide interface (Fig. 7). The scale and subscale regions were analyzed by EPMA; an example of X-ray maps obtained from Ni-13Cr-17Al-0.1Hf is given in Fig. 8. In the Al map, a band of γ' -free material (i.e., a γ -band) is seen below the scale, which is also visible in the back-scattered image. Remarkably, the Cr concentration is not evenly distributed in this γ -band: it is lower in regions located directly above γ' and higher above γ . Point analysis confirmed that concentrations in the γ -band were all between the bulk γ and γ' values, but with differences of up to 3 at. % depending on whether the phase located directly below was γ or γ' . A similar trend was observed for the Hf level, which was slightly higher above γ' than above γ .

Chemical and microstructural analysis of the subscale region suggests that following Al removal and γ' dissolution, Cr and Hf diffusion was not fast enough to remove the original γ - γ' partitioning, which resulted in a local Cr undersaturation and Hf supersaturation in the newly formed γ . Thus, in the first minutes of exposure, the γ -band was in a state of non-equilibrium with respect to Cr and Hf, resulting in local variations of the Hf activity (a_{Hf}) across the prior- γ/γ' assemblage. In particular, because of the difference of Hf solubility between γ and γ' , the phase change involved a rise of a_{Hf} in prior- γ' regions. This is represented in Fig. 9, where a_{Hf} in the non-equilibrium γ -band was obtained by suspending γ' in the equilibrium calculation. For each region of the γ -band, γ' dissolution is seen to cause both an increase in a_{Hf} and a decrease in the a_{Hf} required to form HfO_2 at the

Figure 7: Cross-sections of the (a) Ni-8Cr-17Al-0.1Hf and (b) Ni-13Cr-17Al-0.1Hf alloys oxidized 3 min at 1100 °C. An automatic edge detection routine was used to outline the γ/γ' phase boundaries. In (b) a zoomed view of the Al_2O_3 scale is shown, with arrows pointing to the location of HfO_2 precipitates.

Figure 8: Back-scattered image and corresponding Al, Cr and Hf X-ray maps recorded by EPMA after 3-min oxidation of alloy Ni-13Cr-17Al-0.1Hf at 1100 °C. The Cr concentration is non-uniform in the γ' -depleted band (color figure online).

Figure 9: Hf activity changes induced by selective oxidation of Ni–13Cr–17Al–0.1Hf at 1100 °C. After 3-min exposure, the γ' -depleted band is in a non-equilibrium state, with partial retention of the original Cr and Hf partitioning, because of the slow diffusion of these elements, relative to Al. The non-equilibrium regions were modeled by suspending γ' and setting the Cr and Hf concentrations to those of the original γ and γ' , while using experimentally measured Al concentrations. For each phase, the calculated Hf activity is compared with that required to form HfO₂ at a p_{O_2} defined by the alloy/Al₂O₃ equilibrium (which determines the Hf tolerance). The difference represents the driving force for HfO₂ formation and is largest in the prior- γ' (color figure online).

p_{O_2} defined by the metal/Al₂O₃ equilibrium. The difference between these two activities represents the driving force for HfO₂ formation, and is seen to be the largest in the prior- γ' . This local supersaturation is expected to favor preferential HfO₂ nucleation. Close examination did not show any significant difference in the quantity of HfO₂ precipitates between the regions identified as prior- γ and prior- γ' (see Fig. 7b). An even shorter exposure might provide more conclusive results, although an added complication would be that this would necessarily be anisothermal.

Whether Hf oxidation occurred preferentially in prior- γ' regions or not, HfO₂ particles were formed during a transient stage, before a steady-state was reached. By definition, this limits the applicability of an Hf tolerance criterion based solely on thermodynamic equilibrium. However, two limiting cases can be studied, defined by the initial and steady-state alloy composition at the metal/oxide interface. Qualitatively, in an alloy with an Hf content slightly below the tolerance calculated on the basis of the initial composition, removing Al by oxidation would rapidly lower the tolerance and cause HfO₂ nucleation. The fact that Hf oxidized locally even in Ni–8Cr–17Al–0.05Hf (Figs. 4, 5) suggests that in the γ – γ' field, reducing the Hf concentration to a level where HfO₂ is totally avoided is on the limit of being impractical, at least for the NiCrAl–Hf system considered in this study. A Calphad-guided strategy to increase the Hf tolerance would be to judiciously add elements that either increase the fraction of γ' or have a negative interaction parameter such that they cause the Hf activity to decrease. Platinum is an example [31], but for

most applications it is too expensive to be a viable alloying addition. Future work by our group is being directed at determining cost-effective alloying additions that act to decrease the Hf (and Y) activity in NiCrAl-based systems. It is noted, however, that a relatively high Hf tolerance is more easily sustained for single-phase γ' compositions.

4 Conclusions

A criterion based on thermodynamic equilibrium was devised to predict the Hf tolerance of Hf-doped, Al_2O_3 -forming NiCrAl alloys, i.e., the maximum amount of Hf that can be added without forming HfO_2 beneath the Al_2O_3 scale. This criterion was applied considering the equilibrium composition of alloys in the γ , γ - γ' and γ' fields. Since the Hf solubility in γ' is larger than that in γ , the tolerance is predicted to increase with increasing γ' fraction.

The experimental results followed this trend, although some discrepancy existed: in particular, the model failed to account for localized HfO_2 formation in γ - γ' alloys, i.e., it slightly overestimated the Hf tolerance. This is in part due to the fact that selective oxidation of Al causes γ' dissolution, which reduces the Hf tolerance. In addition, short-term oxidation tests showed that following γ' dissolution, a non-equilibrium situation prevailed in the subscale γ -band, where prior- γ' regions were supersaturated in Hf. The local rise in Hf activity increased the driving force for Hf oxidation. The specifics of HfO_2 nucleation in this non-equilibrium state remain to be elucidated.

Routes for improving the tolerance criterion can be found in the thermodynamic model and in the boundary conditions chosen to represent the oxidation process. A more complete analysis would, for example, include the evolution of HfO_2 solubility in Al_2O_3 with temperature, and account for the compositional changes due to Hf segregation to the metal surface as it is heated. Nevertheless, the approach adopted here proved useful in predicting the formation of micron-sized HfO_2 particles, which may have adverse effects in practice, in terms of Al_2O_3 adhesion during thermal cycling or reactivity with molten sulfates. Future work to optimize reactive-element doping of NiCrAl-based systems includes the expansion of the thermodynamic model to other alloying elements.

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