Some Effects of Interactions Among Minor Element Additions on the High-Temperature Oxidation Behavior of Ni-Base Alumina-Forming Alloys

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Introduction

- **Key routes to improving the oxidation lifetime of high-temperature alloys are:**
  - facilitate the rapid establishment of an α-Al_2O_3 scale
  - maximize its adhesion to the alloy substrate
  - minimize its rate of growth
- **Approaches of interest:**
  - addition of ‘reactive’ elements (e.g. Y, Zr, Hf, La…)
  - minimizing effects of indigenous S content
- **Procedures used:**
  - model alloys (superalloys and bond coatings)
  - isothermal and cyclic oxidation; characterization by optical microscopy, SEM and EPMA; TEM of scales and interfaces

Alloys of Interest

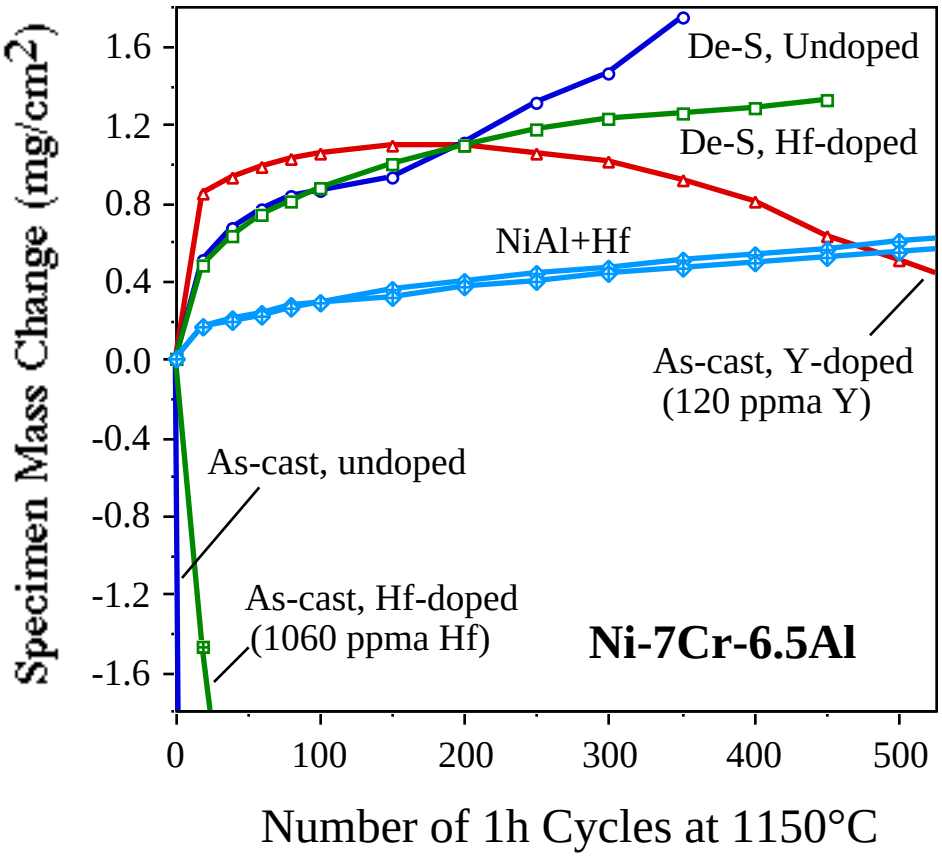
- **Alumina scale-forming alloys**
  - wrought alloys, e.g. Haynes 214 (Ni-16Cr-4.5Al-3Fe +Y,Zr) wt%
  - superalloys, e.g. René N5 (Ni-7.5Cr-6.5Al-Co,Ta,W,Re,Mo,Hf+Y)
  - TBC bond coating alloys, e.g. β-(Ni,Pt)Al; MCrAlYs

- **Model Alloys**
  - β-NiAl + Zr,Hf
  - MCrAls + Y,Hf based on
    - Ni-7Cr-6.5Al
    - Ni-20Cr-10Al

β-NiAl—model alumina-former

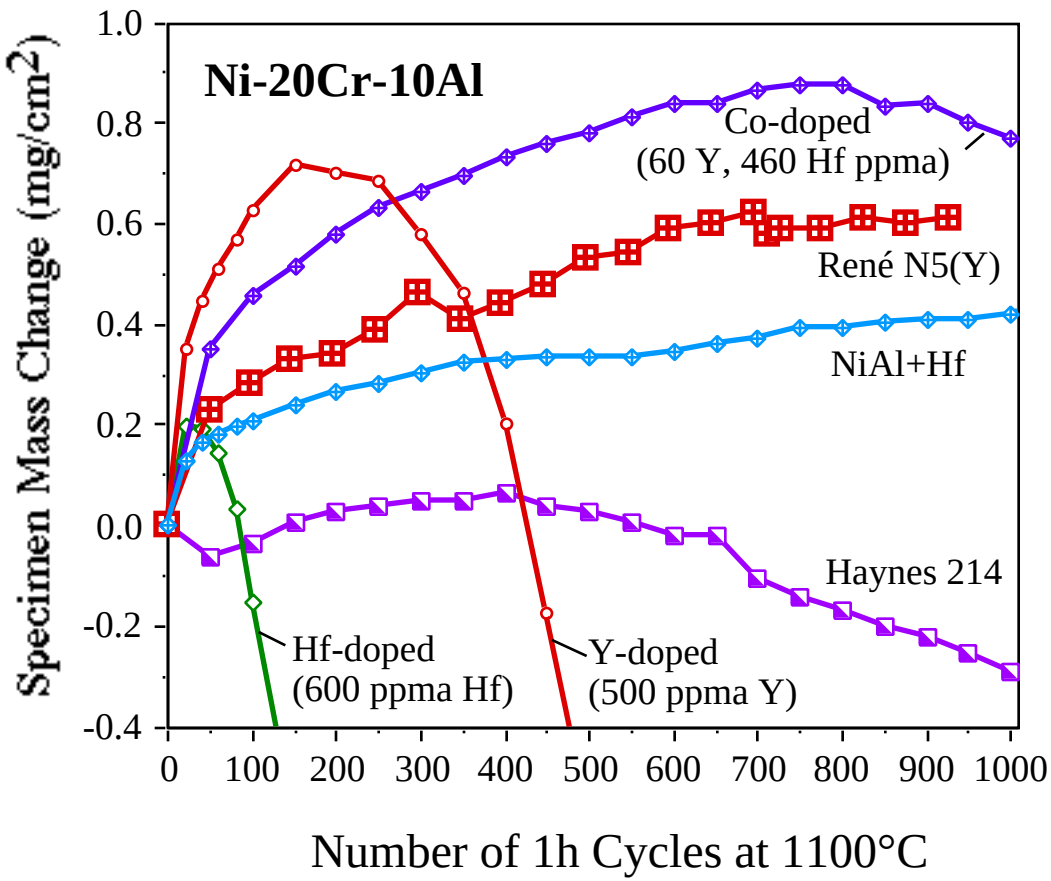
- **With RE addition → 'ideal' alumina-former**
  - no transient oxides, very adherent, slow-growing scale
  - used as a reference standard
- **Effectiveness: Hf > Zr >Y**
- **Optimizing the RE effect requires:**
  - uniform distribution (Ni-rich precipitates are detrimental)
  - 'correct' amount
    - over-doping increases oxidation rate
    - minimum level-possibly set by RE 'availability' (S effect)
  - solid solubility of the RE is an important consideration
- **For 'correctly-doped' model alloys, Hf-doping leads to a slower rate of scale growth**

Hf/Y-doping of NiCrAl model alloys



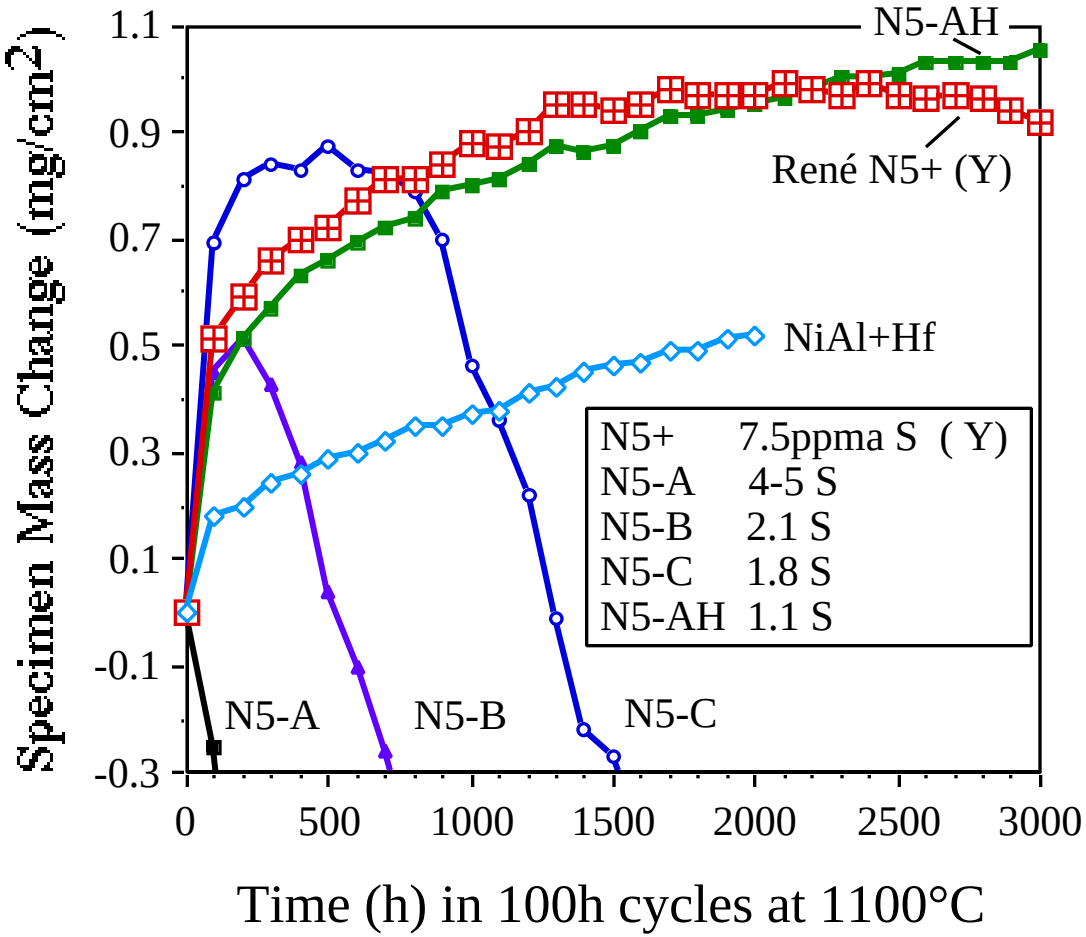
- as cast, Hf only marginally effective
- 500 ppma Y forms Ni_xY phases
- significant improvement, vs Y or Hf alone, by:
  - desulfurizing (H_2)
  - co-doping with Hf + Y (solubility argument?)

Co-doping of model NiCrAl alloys



- René N5+:
  - 34 ppma Y
  - 537 ppma Hf
  - Y added for oxidation resistance
  - Hf added to improve mechanical properties
  - C > Hf
- Haynes 214:
  - 25 ppma Y
  - 120 ppma Zr
  - C >> Zr

Desulfurization effects obvious in cyclic oxidation behavior of René 5 variants

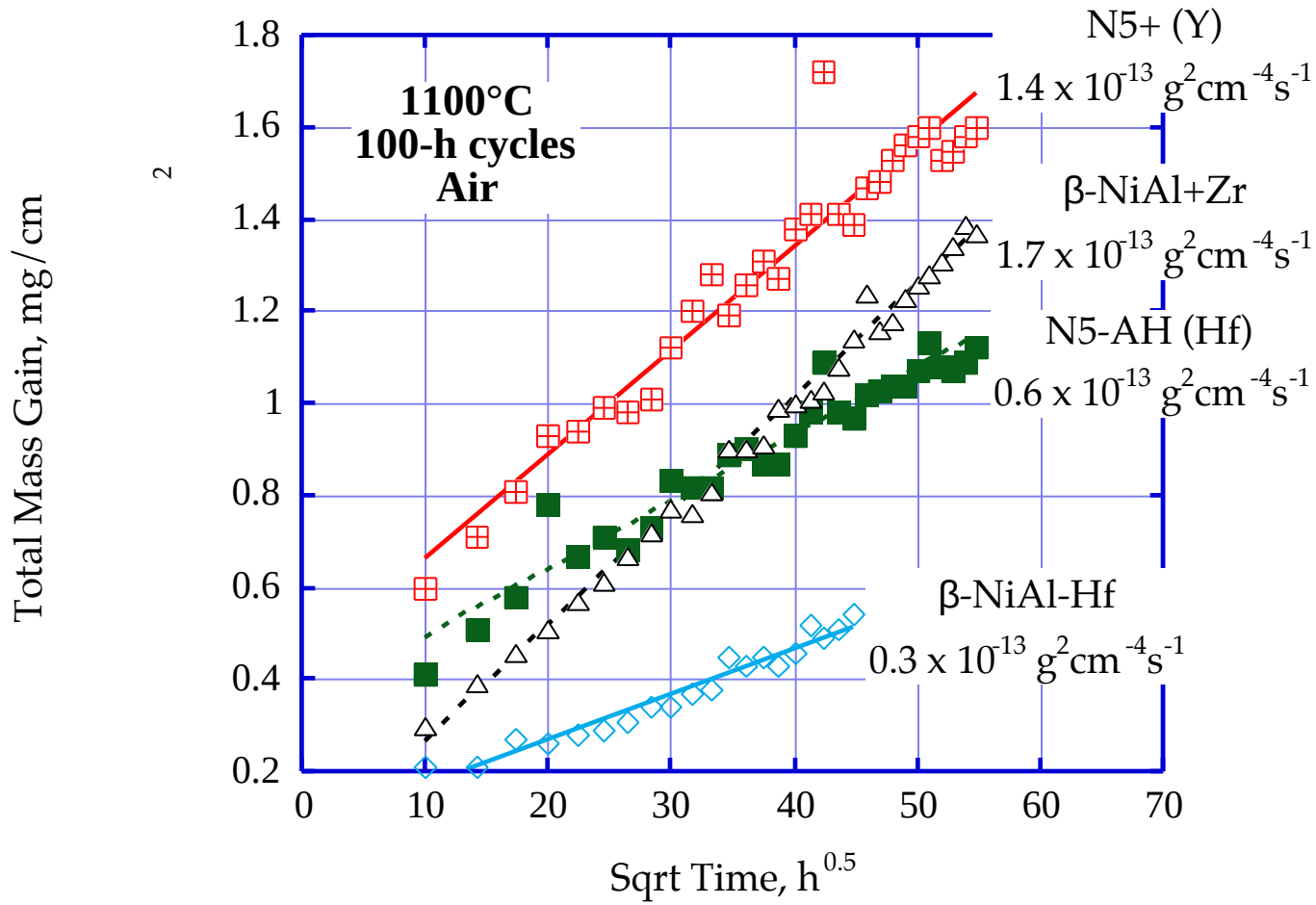


Relative levels of ‘excess’ Hf in René N5 variants

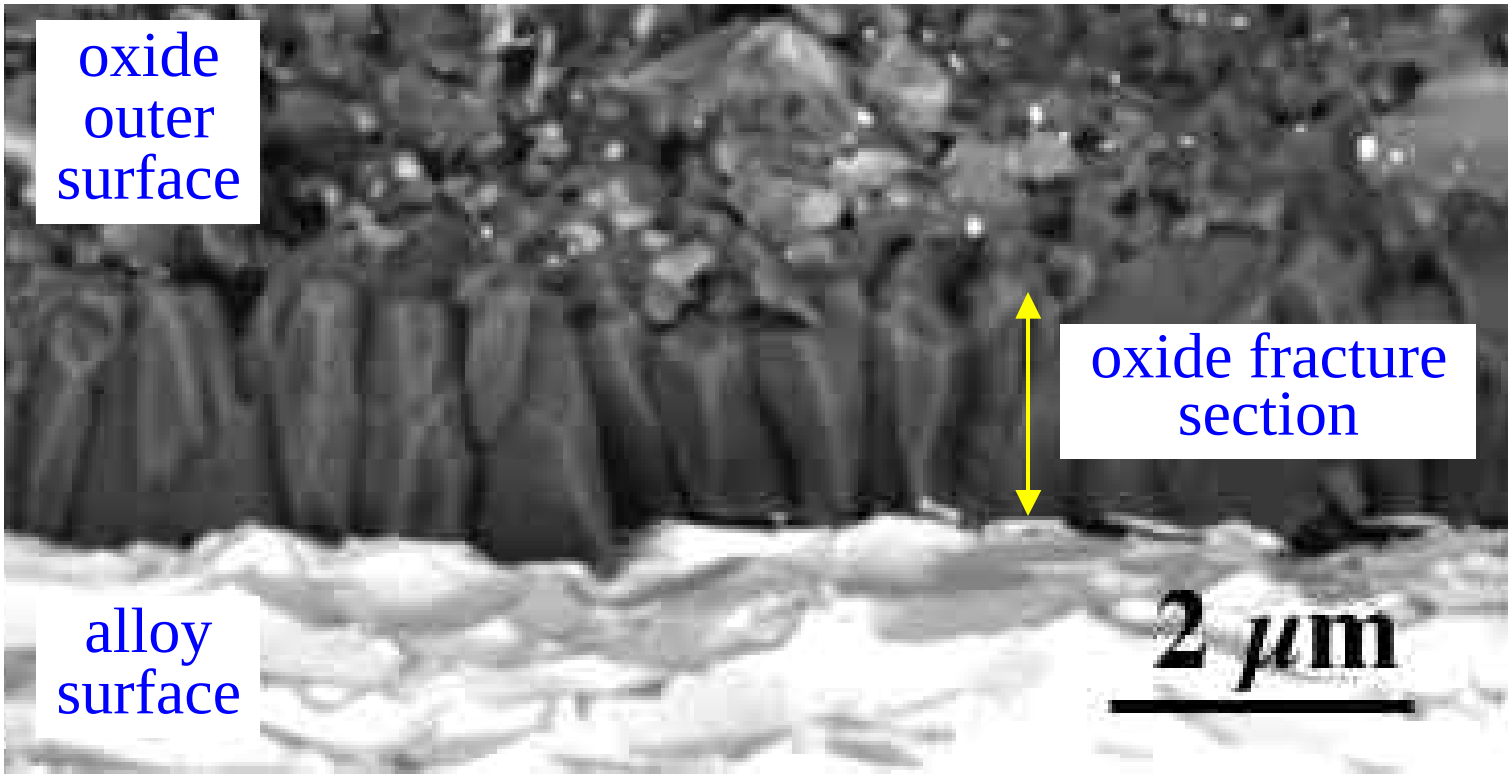
Alloy	**S,** ppma	**C,** ppma	**Hf,** ppma	***XS Hf***[a]
René N5+ [b]	7.5	2,494	537	0.21[c]
N5A [b]	5.5	2,467	398	0.16
N5B[d]	2.1	4,449	159	0.04
N5C[d]	1.8	5,282	137	0.03
N5AH[d]	1.1	24	169	3.36

[a] *XS Hf* = Hf/(C+1/2O+N)
[b] analysis by plasma-coupled arc, not GDMS
[c] contains 34 ppma Y (30 ppma free Y)
[d] GDMS analysis

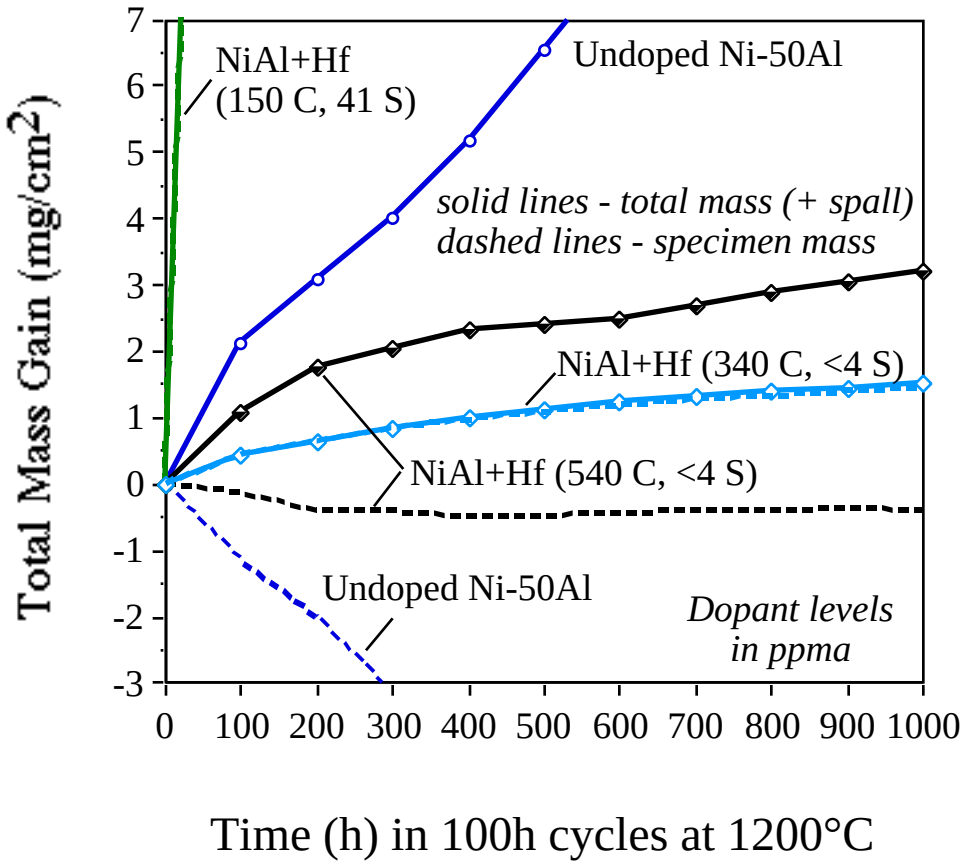
Decarburized René N5 exhibits slower oxidation rate than Y-containing alloy



Scale morphology on decarburized alloy resembles that associated with RE doping



Increased S and C levels also have large effects on Hf-doped β-NiAl



Time (h) in 100h cycles at 1200°C

- Nominal levels:
  - <4 ppma S
  - <400 ppma C
  - *XS Hf* ≈ 1.53
- Addition of C so that *XS Hf* ≈ 0.91
  - significant increase in scale spallation
- 41 ppma S (<400 ppma C)
  - rapid oxidation rate

Conclusions

- RE effectiveness depends on having a uniform distribution and a sufficient amount (i.e. in solution, not as intermetallic particles)

- Co-doping (e.g. Hf + Y) may simply provide a means of obtaining sufficient RE in solid solution ($N5^+$: Hf <<Y; Haynes 214: Zr <<Y)

- Possible synergistic effects of co-doping? —none seen

- Y has obvious beneficial effects on scale adherence (S?), on the scale morphology, and on the mode of growth/growth rate

Conclusions-2

- Hf can exhibit same (or more powerful) effects as Y, but these are greatly reduced in the presence of sufficient C to form HfC, or at high S levels

- Commercial alloys appear to exploit these issues, and use low levels of RE additions to achieve excellent oxidation resistance; however:
  - in René N5^{+}, C > Hf, and the Hf ‘RE effect’ is ±not active; Y is needed to counteract S
  - in Haynes 214, C >> Zr, but Zr and Y appear to be ‘active’

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