



High-throughput characterization of early oxidation across $\text{Al}_x\text{Fe}_y\text{Ni}_{1-x-y}$ composition space



Matthew A. Payne, James B. Miller, Andrew J. Gellman *

Department of Chemical Engineering, Carnegie Mellon University, Pittsburgh, PA 15213, USA
DOE – National Energy Technology Laboratory, P.O. Box 10940, Pittsburgh, PA 15236, USA

ARTICLE INFO

Article history:

Received 1 August 2014

Accepted 24 October 2014

Available online 30 October 2014

Keywords:

A. Aluminium

A. Iron

A. Nickel

B. Raman spectroscopy

B. XPS

C. Oxidation

ABSTRACT

Improving our fundamental understanding of the oxidation of multicomponent alumina-forming alloys is crucial to their ongoing development. In this work, high-throughput methods were developed to study oxidation of $\text{Al}_x\text{Fe}_y\text{Ni}_{1-x-y}$ alloys in dry air at 427 °C using composition spread alloy films as combinatorial libraries ($x = 0 \rightarrow 1$, $y = 0 \rightarrow [1-x]$). The results divide the $\text{Al}_x\text{Fe}_y\text{Ni}_{1-x-y}$ composition space into four regions of phenomenologically distinct oxidation behaviour. The boundary defining the critical Al concentration, N_{Al}^* (x, y), for establishment of a passivating Al_2O_3 scale was determined across the entire continuous $\text{Al}_x\text{Fe}_y\text{Ni}_{1-x-y}$ composition space.

© 2014 Elsevier Ltd. All rights reserved.

1. Introduction

1.1. Internal vs. external oxidation and N_{Al}^* in alumina-forming alloys

Metal alloys are ubiquitous in modern technology, with applications in areas ranging from structural materials to electronics, catalysis, and more. Properly designed alloys can achieve otherwise-unattainable combinations of mechanical, chemical, and economic characteristics that are superior to those of any of their pure elemental components. An alloy's functional properties arise from interactions among its component species and with the local operating environment, and can vary drastically with atomic composition (i.e. atomic fraction of each component). When this is the case, composition optimization becomes an integral part of alloy design. Oxidation-resistant alloys are an important example of alloys for which key properties are highly dependent on composition [1,2]. Many next-generation structural applications of alloys require continuing development and improvement of their oxidation resistance for use in high-temperature environments. Selection of alloy composition is often critical to achieving the desired combination of mechanical properties and oxidation resistance in thermochemically harsh environments [1–3].

“Alumina formers” are a type of metal alloy widely developed for oxidation resistance in high-temperature applications. An alumina former is an alloy that, under operating conditions, preferentially forms a continuous alumina (Al_2O_3) layer or “scale” at or near its surface, creating a diffusion barrier that “passivates” the underlying material against further oxidation, greatly retarding bulk oxidation [3–7]. Passivation of an alloy surface by oxide scale formation is referred to as “external oxidation”, while progressive oxidation of the bulk is known as “internal oxidation” [2,7–12]. Provided that a sufficiently dense and adherent scale is maintained, Al_2O_3 can remain stable and protective in oxidizing environments at temperatures >1280 °C [1–4,6,13]. The α -phase of Al_2O_3 is the most desirable and protective, but is only formed significantly at temperatures >950 °C by the conversion of more rapidly growing, pseudo-stable Al_2O_3 structures [4,14,15]. A minimum “critical Al concentration”, N_{Al}^* , is required in an alloy for initial establishment of a continuous Al_2O_3 scale; for sub-critical Al concentrations, discontinuous Al_2O_3 is formed, leaving diffusion paths that allow continuing oxidation of the bulk [2,6,8,12,13,16]. The value of N_{Al}^* is dictated by a balance between the rate of oxygen permeation into the alloy and the diffusion of Al to the alloy surface [8]. Design of alumina-forming alloys is complicated by the fact that increasing Al content tends to mechanically compromise alloys by increasing their brittleness [2,9,13,17–19]. For this reason, it is desirable in structural applications to use the lowest Al content possible, while still providing adequate oxidation resistance. Therefore, rational design of any multicomponent alumina

* Corresponding author at: Carnegie Mellon University, Department of Chemical Engineering, 5000 Forbes Avenue, Pittsburgh, PA 15213, USA. Tel.: +1 (412) 268 3848.

E-mail address: gellman@cmu.edu (A.J. Gellman).

former requires a thorough understanding of how N_{Al}^* varies across the viable composition space.

1.2. Development of AlFeNi-based alumina formers

Al, Fe, and Ni are three of the main components in many alumina-forming structural superalloys [7,17,20–23]. Cr is often included as a fourth major component because it lowers the N_{Al}^* needed for establishment of an Al_2O_3 scale by what is termed a “third-element effect” [1–3,6,7,20,21]. In many oxidation-resistant alloys that do not contain Al (such as traditional stainless steels), Cr is incorporated to allow protective Cr_2O_3 scale formation, but these materials exhibit oxidation resistance at >900 °C that is inferior to that of the alumina formers. This is particularly true in environments containing both H_2O and O_2 due to the formation of volatile Cr-oxyhydroxides and the resulting evaporation of the scale [1–3,5,7,17,20,24,25].

AlCrFeNi-based alloys constitute a class of superalloys that behave as alumina-forming austenitic stainless steels (AFASSs) in various environments at temperatures <900 °C [7,17,20,21]. Increasing the Fe content of an AlCrFeNi-based AFASS decreases raw-material cost and increases the melting point. However, Ni must be maintained at a high enough concentration to induce formation of a mechanically robust, austenitic (face-centred cubic) matrix structure [7,17,20,21]. Increasing the Fe, Al, and/or Cr content of the AFASS stabilizes a ferritic (body-centred cubic) matrix structure (observed at <912 °C in pure Fe), which causes brittleness at low temperatures and poor creep resistance at high temperatures [7,17,20,21]. As a consequence, increases in the Al and/or Cr content to improve oxidation resistance requires the replacement of some fraction of Fe with Ni in order to maintain mechanical integrity, which both makes the alloy more expensive and lowers its maximum operating temperature. Thus, as is the case with most alumina formers, accurate knowledge of the dependence of N_{Al}^* on composition is central to the design of AFASS alloys.

A significant limitation to determining optimum compositions of high-temperature AlCrFeNi-based alloys is that experimental studies of their properties have focused on single-composition samples [7,17,20,21,23]. Understanding of the influence of composition on oxidation behaviour has been achieved by cumbersome methods using large numbers of samples. Efforts to rigorously maximize the potential of these alloys must focus on development of materials models for accurate prediction of oxidation behaviour as a function of composition. Such models would be significantly improved by comprehensive experimental measurement of oxidation behaviour across continuous, multi-dimensional composition spaces, but this is prohibitively time consuming when using single-composition alloy samples.

1.3. High-throughput assessment of $Al_xFe_yNi_{1-x-y}$ oxidation

Experimental study of alloy properties across composition space traditionally requires preparation and characterization of a large set of discrete, single-composition samples. The time investment required for thorough exploration of a composition space quickly becomes impractical as either the number of components or the desired composition resolution increase. Measurement of properties in alloys can be greatly expedited through the use of composition spread alloy film (CSAF) sample libraries [26]. CSAFs are substrate-supported alloy films with continuous, lateral composition gradients. Since a ternary composition is specified by two, bounded degrees of freedom, an entire ternary composition space can, in principle, be contained on a finite, two-dimensional surface. CSAFs with properly positioned gradients can, therefore, serve as libraries containing all possible compositions of a ternary alloy, as shown in Fig. 1. When coupled with rapid, spatially

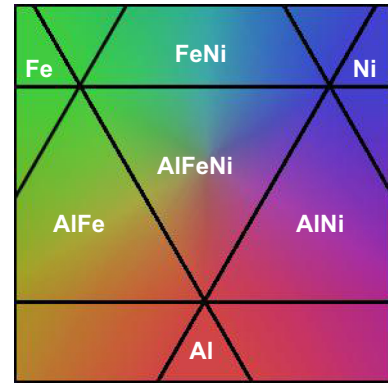


Fig. 1. Targeted spatial distribution of $Al_xFe_yNi_{1-x-y}$ CSAF compositions on the substrate surface. The central triangular region contains all ternary compositions and is surrounded by full-range binary and pure-component regions.

resolved characterization techniques, CSAFs allow measurement of composition-property relationships across the entire ternary composition space in a single experiment. Such combinatorial methods have been used increasingly for study of a diverse range of problems in materials science [15,19,26–29].

We have used $Al_xFe_yNi_{1-x-y}$ (subscripts designate atomic fractions) CSAF libraries to develop an experimental methodology for high-throughput assessment of oxidative passivation across alloy composition spaces. Basic oxidation behaviour relevant to AFASS alloys and other alumina formers of interest can be observed in the ternary $Al_xFe_yNi_{1-x-y}$ system. Of particular interest are the $Al_xFe_yNi_{1-x-y}$ composition regions that establish a protective Al_2O_3 scale under a given set of oxidation conditions, i.e. the exposure history of an initially clean alloy to various temperatures and partial pressures of ambient O_2 and/or other oxidizing species. Spatially resolved characterization of an oxidant-exposed $Al_xFe_yNi_{1-x-y}$ CSAF can reveal whether or not oxidation of a given composition has resulted in the establishment of a continuous Al_2O_3 passivation layer. Depending on alloy composition and the environment to which an alumina former is exposed, a passivating Al_2O_3 scale may develop either at the surface or in the subsurface beneath one or more layers of other oxides [2–4,6,8–10,12,17,18,22,30–33]. Once a continuous Al_2O_3 layer is established, further oxidation by scale thickening occurs with a slow parabolic growth rate [2,6,15]. Using AlNi alloys, Pettit showed that a second critical Al concentration, N_{Al}^{**} , is required for an alloy to supply sufficient Al to maintain this slow parabolic growth and ensure long-term scale stability, but his findings suggest that N_{Al}^{**} is only greater than N_{Al}^* at temperatures >630 °C [34].

In this work, $Al_xFe_yNi_{1-x-y}$ CSAFs spanning all of ternary composition space ($x=0 \rightarrow 1$, $y=0 \rightarrow [1-x]$) were deposited across 14×14 mm² polycrystalline Mo substrates and used for high-throughput, oxidation-characterization experiments. The targeted composition spread geometry is shown in Fig. 1. Our CSAF deposition capabilities limit their thickness to <200 nm. Therefore, we have focused on the early oxidation mechanisms occurring in CSAFs exposed to dry air for ≤ 4 h at 427 °C (relatively mild conditions for alumina formers). The goal was to locate the boundaries between composition regions that exhibit different internal and external oxidation behaviour, particularly the boundary defining the critical Al content for establishment of a passivating Al_2O_3 scale, N_{Al}^* (x, y). To accomplish this, we developed a novel methodology for high-throughput oxidation studies on CSAFs. Characterization of $Al_xFe_yNi_{1-x-y}$ CSAF composition gradients was performed in a scanning electron microscope (SEM) by automated composition mapping using energy-dispersive X-ray spectroscopy (EDX). For CSAFs exposed to dry air at 427 °C, visual analyses of oxidation-induced colour changes on their surfaces were sufficient to identify

Download English Version:

<https://daneshyari.com/en/article/1468519>

Download Persian Version:

<https://daneshyari.com/article/1468519>

[Daneshyari.com](https://daneshyari.com)