



## Factors affecting isothermal oxidation of pure chromium in air

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### ABSTRACT

Isothermal oxidation kinetics of pure chromium at 950–1200 °C in purely oxidizing (Ar-20%O<sub>2</sub>), purely nitriding (N<sub>2</sub>-5%H<sub>2</sub>), and oxidizing-nitriding (synthetic air, N<sub>2</sub>-20%O<sub>2</sub>) atmospheres were studied. Effects of factors such as oxide volatilization, multiple mass-gains, and nitridation on oxidation kinetics of chromium were investigated using thermal analysis, acoustic emission analysis, and electron microscopy. Results obtained in single oxidant atmospheres compared to those obtained in air clearly showed the transparency of chromia against nitrogen in air. The abrupt mass gain steps observed during isothermal oxidation were appeared due to the local oxide scale failure resulting from growth stresses in the thermally grown chromia scale.

### 1. Introduction

Chromium is one of the most important alloying elements in engineering alloys usually offering a marked improvement in high temperature oxidation resistance and an increase in mechanical strength. The oxidation resistance of chromium containing alloys is due to the formation of a dense protective chromium oxide layer (Cr<sub>2</sub>O<sub>3</sub>) or Cr-rich oxides which form a barrier between the oxidizing atmosphere and the metal substrate. Often, long term oxidation performance of these alloys solely depends on the chemical, physical, and mechanical stability of the chromium oxide scale formed.

From the application point of view, chromia volatilization in dry oxidizing atmospheres (e.g. air) and nitridation in nitrogen containing atmospheres become significant above 900 °C which challenges the applicability of chromium-based alloys [1]. Recent developments in the fabrication of chromium-based alloys as potential candidates for high temperature structural applications (typically above 900 °C) raised again interest to focus on the mechanisms and kinetics of oxidation of pure chromium in this temperature range [1,2]. Nevertheless, although the oxidation behavior of pure chromium has been extensively investigated in the past decades mainly by Kofstad, Lillerud, Caplan, and Tsai et al. [3–10], some aspects of the oxidation mechanism and the role of some parameters affecting oxidation are still under debate. Today, novel characterization methods and sophisticated microscopic techniques such as atom probe tomography are able to shed new light on this issue in addition to novel theoretical approaches such as atomistic simulation methods [11–15].

The kinetics of chromium oxidation has often been described using the parabolic rate constant ( $k_p$ ) for isothermal oxidation. Kofstad and

Lillerud [6] summarized the  $k_p$  values obtained in different studies, a summary which has recently been updated by the authors [1]. One can notice a significant difference between the values reported in different publications which can be as high as four orders of magnitude. Caplan et al. related this difference to the surface preparation of the chromium substrate [16]. However, other factors during isothermal oxidation of chromium in air – especially nitridation, which significantly changes the oxidation behavior of Cr-based alloys [17–19] – must also be taken into account to explain this discrepancy.

In the present study, additional factors affecting the oxidation kinetics of chromium in air are addressed. Firstly, the impact of chromia volatilization is discussed. Secondly, influences and the origin of multiple mass gain steps during the isothermal gravimetry are discussed. In addition, the impact of subscale nitridation resulting from the reaction of Cr metal and the secondary oxidant in air, namely nitrogen, is discussed. A systematic approach combining several investigation methods including isothermal tests in different atmospheres composed of purely oxidizing, purely nitriding, and oxidizing-nitriding atmospheres was employed to reveal the impact of each parameter, experimentally.

### 2. Experimental

Chromium specimens were fabricated using analytical, high purity chromium pieces (99.995%, Alfa Aesar, Germany) which were drop casted and cut to rectangular specimens (5 mm length × 5 mm width × 2 mm thickness). The detailed specimen preparation procedure is explained elsewhere [18].

Simultaneous thermal analysis (thermogravimetry (TG) and differential thermal analysis (DTA)) were conducted using a Netzsch STA

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449-F3 (Netzsch GmbH, Germany) at 950 °C, 1050 °C and 1200 °C. Oxidation kinetics and nitridation kinetics of the alloys were investigated by exposures in synthetic air (N<sub>2</sub>-21%O<sub>2</sub>, Air Liquide), Ar-20%O<sub>2</sub> (O<sub>2</sub>, 99.995%, Air Liquid and Ar 99.995% Linde), and forming gas (N<sub>2</sub>-5%H<sub>2</sub>, Air Liquide, O<sub>2</sub> < 20 ppm), respectively. For exposures in Ar-20%O<sub>2</sub> and N<sub>2</sub>-5%H<sub>2</sub>, the chamber was evacuated twice prior to the measurements to ensure the removal of residual gases. A heating rate of 10 K min<sup>-1</sup> and a linear flow rate of 217 cm h<sup>-1</sup> were applied for all measurements. Isothermal exposures were conducted for up to 50 h. Random TG-measurements were repeated to verify the reproducibility of the test. In addition, Acoustic Emission (AE) was used to characterize the formation of scale cracks and/or delamination during isothermal oxidation of chromium. This experiment was only performed at 1050 °C.

AE is a technique based on high frequency elastic waves which are generated as a result of stress induced structural changes in materials. The frequencies of these waves are much higher than those of the noise from the surrounding test environment and therefore, clearly detectable. In this work acoustic waves with the threshold signal amplitude of 30 dB were recorded during the isothermal experiment using a PCI-2 setup (Physical Acoustics). Two wave guide Pt-wires were spot welded onto the two sides of a pure Cr specimen (20 mm length × 5 mm width × 2 mm thickness). The other end of each wire was soldered to stainless steel cone sensors (type WD, Physical Acoustics) which were connected to an amplifier and a computer which recorded the AE signal (Fig. 1). The specimen was inserted into a vertical tube furnace operated at 1050 °C. The exposure was isothermally continued for 100 h in air while the AE signals were monitored.

After exposure cross-sections were prepared by mounting specimens in hot epoxy resin, grinding through 1200 grit SiC paper, and polishing with diamond (3 and 1 μm) and colloidal silica (0.02 μm) pastes.

The oxidized specimens were sputtered with gold and coated with electroplated nickel before being mounted in epoxy resin. The electroplated nickel layer protects the oxidation products during metallographic preparation and avoids the loss of contrast at the specimen-epoxy interface during microscopic investigations [18].

A Philips XL40 electron microscope was used for detailed microscopic analysis of the oxide scales formed. Elemental distribution maps of the oxidized specimens were characterized by wavelength dispersive spectrometry (WDS) using a JEOL JXA-8100 electron probe micro analyzer (EPMA). Post-oxidation cross-sections were investigated with both, element distribution maps and quantitative line scans, using 15 kV and one micrometer step size. The oxidized metals were quantitatively characterized using Fe<sub>4</sub>N and Al<sub>2</sub>O<sub>3</sub> standards for nitrogen and oxygen, respectively.

### 3. Results and discussions

#### 3.1. Kinetics of oxidation

The influence of single oxidants (i.e. nitrogen, and oxygen) on the overall oxidation kinetics of chromium in air was studied by a series of experiments conducted in Ar-20%O<sub>2</sub>, N<sub>2</sub>-5%H<sub>2</sub>, and synthetic air (N<sub>2</sub>-21%O<sub>2</sub>). Fig. 2 shows the isothermal oxidation behavior of pure chromium at 950, 1050, and 1200 °C in different environments. It is obvious that specimens exposed at higher temperatures show higher final mass gains. For instance, the final mass gain of pure Cr after 50 h oxidation in synthetic air was 4.49, 9.37, and 21.70 mg cm<sup>-2</sup> at 950 °C, 1050 °C, and 1200 °C, respectively. It is known that oxidation kinetics of chromium at temperatures higher than 900 °C follows a parabolic behavior according to Eq. (1):

$$\Delta m/A = (k_p t)^{1/2} - k_v t \quad (1)$$

where  $\Delta m$  is mass change,  $A$  is surface area,  $t$  is the exposure time,  $k_p$  is the parabolic rate constant (mass increase by solid oxide) and  $k_v$  is the volatilization rate. Detailed discussion about the origin of this equation and its deviations from Tedmon's equation [20] is given elsewhere [1].

According to Eq. (1), the oxidation kinetics of chromium can be divided to two kinetic terms including a positive term representing the parabolic oxide growth and a negative term representing linear evaporation. The parabolic weight gain is based on diffusion-controlled reactions between metal and oxidants which is the governing growth kinetics for slow-growing or protective oxides e.g. Cr<sub>2</sub>O<sub>3</sub>. When using pure chromium or chromium-based alloys in oxygen or air, chromia scales may form volatile species. In the absence of water vapor and at temperatures above 900 °C, volatile CrO<sub>3</sub> which results from reaction (2) is significant [1].



Volatilization of chromia has a linear kinetics and thus, the negative linear term in Eq. (1) represents it.

The mass gain kinetics was obtained by fitting the mass gain data with a parabolic relation Eq. (1), which is shown as continuous lines in Fig. 2.

The occurrence of sudden mass gain steps during the isothermal test avoided an accurate fit over the total time domain. Thus, the calculated fit was applied up to the first significant discontinuity which occurred during the isothermal test leading to abrupt mass gains. Small discontinuities that occurred before 10 h were ignored during fitting (Fig. 2). The term  $k_v$  is assigned to the linear chromia volatilization rate when Cr was exposed to Ar-O<sub>2</sub> or synthetic air atmosphere. The experimental kinetic parameters are listed in Table 1. For the sake of

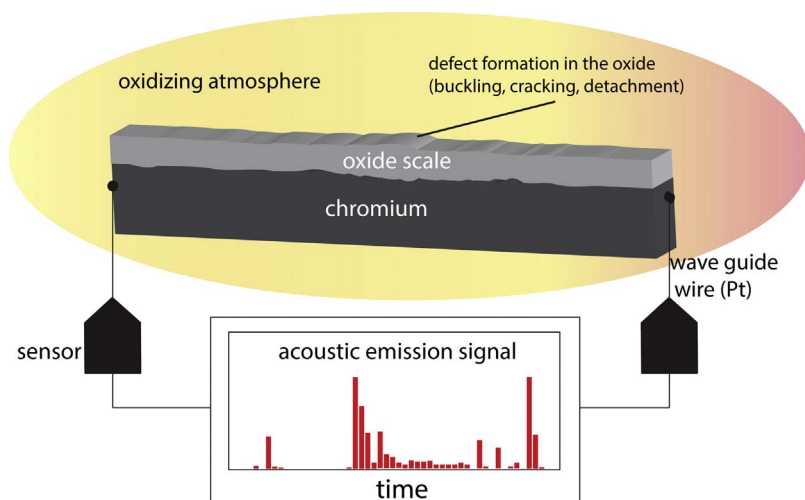


Fig. 1. The schematic illustration of the acoustic emission arrangement used during isothermal oxidation of chromium.

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