



Contents lists available at ScienceDirect

Corrosion Science

journal homepage: [www.elsevier.com/locate/corsci](http://www.elsevier.com/locate/corsci)

# High-temperature oxidation paths, according to the oxide-alloy phases equilibria in the ternary Ni-Co-Fe system

Xin Lu\*, Takahiro Miki, Tetsuya Nagasaka\*

Department of Metallurgy, Graduate School of Engineering, Tohoku University, Sendai, Miyagi 980-8579, Japan

## ARTICLE INFO

## Keywords:

Cobalt  
Nickel  
Superalloys  
High temperature corrosion  
Oxidation  
Thermodynamic diagrams

## ABSTRACT

The physicochemical properties of the Ni-Co-Fe-O system are important to the high-temperature oxidation of the Ni-Co-Fe based alloy, such as superalloys and high-alloy steels. The equilibrium phase relations between the Ni-Co-Fe alloy and its oxide at elevated temperature were systematically investigated using experimental and assessment method. The iso- $p_{O_2}$  lines and iso-concentration lines of oxides in the entire range of the oxygen partial pressure and composition at 1673 K were evaluated, and the high-temperature oxidation path of the Ni-Co-Fe alloy was qualitatively examined. Using the thermodynamic findings allows to ascertain the high-temperature oxidation phenomena of the Ni-Co-Fe based alloy.

## 1. Introduction

High-temperature material is critical for aviation, aerospace and power generation industries. As the most typical high-temperature materials, superalloys are generally nickel-, cobalt-, or nickel-iron-based alloys, and they are predominantly used to fabricate turbine blades for aircraft engines and power turbines [1]. The severe operating environment, always high temperature and corrosive, asks the materials for various outstanding characteristics, such as excellent mechanical strength, resistance to creep and fatigue at elevated temperature, good surface stability in corrosive atmospheres, and oxidation resistance [2]. In recent years, large efforts have been made to improve the high-temperature oxidation resistance of various conventional superalloys and to develop novel superalloys [3–7].

Knowledge of the high-temperature physicochemical properties of the superalloys at oxidizing atmosphere is of significant scientific and industrial importance for understanding of the high-temperature oxidation behavior and promotion of the high-temperature oxidation resistance of superalloys [8–11]. A solid information of the phase equilibria of the Ni-Co-Fe-O system, in particularly the Ni-Co-Fe alloy phase and the oxide phase, is useful to predict and control the high-temperature oxidation behavior of the Ni-Co-Fe based alloy, such as superalloys and high-alloy steels [12,13]. Fig. 1 shows the values of the equilibrium oxygen partial pressure characteristic of pure nickel, cobalt, and iron and their oxides calculated based on the thermodynamic database [14], according to which the oxidation behavior of these pure metals at different temperature and oxygen partial pressure can be estimated. However, alloys instead of pure metals are industrially used,

and oxidation of alloy is much more complex [15]. Various factors will influence the alloy oxidation, such as the different affinities for oxygen of the components in alloy, the affinities among components, and the formation of ternary or high order oxide phases [16]. The thermodynamic equilibrium relations in Ni-Co-Fe-O system will provide fundamental idea to ascertain the high-temperature oxidation phenomena of the Ni-Co-Fe-based alloy under oxidizing atmosphere [17].

Information of the phase equilibria of the Ni-Co-Fe-O system is also essential for controlling the Ni-Co-Fe alloy composition by oxidizing during the high-temperature processing. The excellent performance of superalloys is on basis of an extremely careful and strict controlling of the alloy composition, and thus special technologies are always required for the high-temperature processing of superalloys, such as vacuum induction melting (VIM), vacuum arc re-melting (VAR), and electro-slag re-melting (ESR), and in these processing the operation condition must be carefully controlled [18]. Controlling of the desired alloy chemistry composition and elimination of the impurities are two important targets of the high-temperature processing of superalloys, which is achieved by a careful adjustment of the oxygen partial pressure. Processing superalloys with advanced characteristics requires addition of lots of alloy elements, such as aluminium, titanium, chromium, molybdenum, tungsten, and niobium, into the solvent alloy of Ni/Co/Ni-Fe [2,19–24]. Meanwhile, impurities must be removed and controlled at an acceptable level [2]. More attention should be paid on the impurity issue when the superalloys scrap is recently used as alternative source of nickel, cobalt or some critical alloy elements during the melting process, because the composition of these secondary resources is much more variable comparing with primary resource

\* Corresponding authors.

E-mail addresses: [xin.lu.a5@tohoku.ac.jp](mailto:xin.lu.a5@tohoku.ac.jp) (X. Lu), [t-nagasaka@m.tohoku.ac.jp](mailto:t-nagasaka@m.tohoku.ac.jp) (T. Nagasaka).<https://doi.org/10.1016/j.corsci.2018.04.045>Received 19 October 2017; Received in revised form 27 April 2018; Accepted 30 April 2018  
0010-938X/© 2018 Elsevier Ltd. All rights reserved.

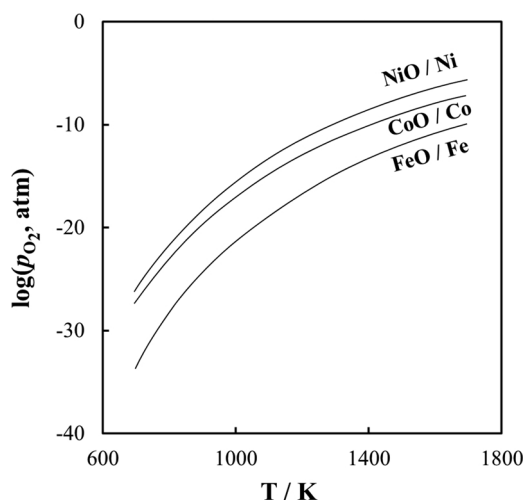


Fig. 1. Dependence of the equilibrium oxygen partial pressure of nickel, cobalt, and iron on the temperature.

[25–27]. The oxygen partial pressure of the high-temperature processing of superalloys must be controlled carefully to achieve a balance between maximum elimination of metallic inclusions and minimum oxidation losses of the solvent alloy, as well as accurate control of the refined Ni-Co-Fe alloy [28]. Owing to the high operation temperature in the furnace, the oxygen partial pressure is generally controlled by the equilibria of the solvent alloy and the oxide phases, and the thermodynamics of the Ni-Co-Fe-O system can provide fundamental guideline for oxygen partial pressure controlling.

Because of their scientific and industrial importance, the thermodynamics of the binary and ternary sub-systems of the Ni-Co-Fe-O system have been studied for several years. A summary focusing on the thermodynamic studies on the Ni-Co-Fe-O system in recent years was carried out and is shown below, and it is shown that only limited information is available about this quaternary system. In this study, some key experiments were carried out to directly measure the phase equilibria relations between the solid Ni-Co-Fe alloy phase and the oxide phase in the Ni-Co-Fe-O system at 1673 K using the gas/oxide/metal equilibrium technique at controlled oxygen partial pressures. Based on the obtained phase equilibria and thermodynamic properties, the  $p_{O_2}$  lines and iso-concentration lines of oxides in the entire range of the oxygen partial pressure and composition in the Ni-Co-Fe-O system at 1673 K were evaluated. Further, the high-temperature oxidation path of the Ni-Co-Fe alloy in an oxidizing atmosphere was quantitatively examined as an application of the obtained thermodynamic findings. Using of the thermodynamic findings allows to easily ascertain the high-temperature oxidation phenomena of the Ni-Co-Fe based alloy.

### 1.1. Ni-Co-Fe system

The ternary system of Ni-Co-Fe has been extensively investigated by many researchers because of its importance as a base material for commercial alloyed steels, superalloys, and magnetic materials. The binary sub-systems of Fe-Co [29–31], Fe-Ni [32–34], and Co-Ni [35,36] have been extensively investigated and systemically assessed. The solid-liquid two-phase fields for the three binary systems have been found to be very narrow, and the solidification has been found to place within a temperature range of only a few degrees. Reviewing of the ternary system have been carried out by Guillermet [37], Raghavan [38], and Tedenac [39]. No ternary compounds have been reported in the Ni-Co-Fe solid phases [39]. The solid system is characterized by a continuous miscible solid solution (fcc) and a narrow single-phase region of ( $\delta$ -Fe) near the iron corner at higher temperatures [40]. The liquidus and solidus in the ternary system are also very close to each other, which

reflects the very similar thermodynamic properties of the solid and liquid phases near the melting temperature in the ternary system [40].

The activity of the components in the molten Ni-Co-Fe system at 1850 K was measured by Knudsen cell mass spectrometry [41]. The results obtained at 1873 K (1600 °C), determined based on the thermodynamic properties of the binary alloy system, were found to be in satisfactory agreement with the experimental results [42]. The activity of the components in the fcc Ni-Co-Fe solid solution at 1600 K was also measured by Knudsen cell mass spectrometry [43]. In both the molten and fcc solid solution systems, only very small deviations from ideality were observed for all three components, and the thermodynamic properties of the systems at 1873 K and 1600 K were found to be very similar.

### 1.2. Fe-Co-O system

The Fe-Co-O system was recently reviewed and evaluated by the CALPHAD method by Zhang et al. [44] and Jung et al. [45]. It was found that both CoO and FeO are rock salt-structured phases and that they can form a continuous solid solution [44–46]. The equilibrium relations of the CoO-FeO solid solution and Co-Fe alloy at 1473 K (1200 °C) were experimentally investigated [47]. Subramanian and Dieckmann [48] measured the FeO and CoO activity in the oxide phase coexisting with the alloy phase at 1473 K (1200 °C) by thermogravimetric experiments and observed a slightly positive deviation from the activity predicted by Raoult's law for this system.

Based on the experimental results available, Jung et al. [45] assessed the thermodynamic properties of a Fe-Co-O system in which the FeO-CoO solution was treated as an ideal solution. Zhang et al. [44] carried out the most recent review of the Fe-Co-O system and conducted a reassessment of this system that yielded new experimental results. In their work, the compound energy formalism was used to model all the phases in the Fe-Co-O system, and the activity of CoO was found to exhibit a slightly positive deviation from ideality.

### 1.3. Fe-Ni-O system

An early review of this ternary system was carried out by Raghavan [49], who presented partial isothermal sections at 1813 K (1540 °C) and 1273 K (1000 °C), a schematic liquidus projection, and a reaction scheme. Schneider [50] subsequently determined the phase boundaries of the wustite and spinel fields and the nonstoichiometry of the (Ni, Fe) O using high-temperature in situ coulometric titration with solid oxygen ion electrolyte. Recently, Rhamdhani [51] studied the phase equilibria of the Fe-Ni-O system in the temperature range of 1073 K (800 °C) to 1873 K (1600 °C) at various oxygen partial pressures. Using the CALPHAD method, Pelton et al. [52] assessed and Luoma [53] reassessed this system, improving on the high-temperature phase relations by using an ionic liquid model and compound energy formalism to describe the liquid, spinel, wustite, and hematite phases. Later, on the basis of the results from Luoma [53], Kjellqvist et al. [54] reassessed the spinel phase in this system and the magnetic contribution to Gibbs energy was modelled. In the thermodynamic analysis on SiO<sub>2</sub>-NiO-FeO system carried out by Cruz et al. [55], the NiO-FeO system was simply assumed to be an ideal solution, and the assessment results agreed well with the experimental results.

### 1.4. Co-Ni-O system

Only a few studies carried out on the Co-Ni-O system if compared with the other sub-systems. Moore and White [56] determined the equilibrium relations in the NiO-CoO-O<sub>2</sub> system using a thermogravimetry and constructed an isobaric ternary diagram of the system. Kuboon and Hu [57] investigated the formation of NiO-CoO and Co<sub>3</sub>O<sub>4</sub>-Ni<sub>3</sub>O<sub>4</sub> solid solutions by calcination of Ni(NO<sub>3</sub>)<sub>2</sub> and Co(NO<sub>3</sub>)<sub>2</sub> at different temperatures and found that the NiO-CoO solid solution was

Download English Version:

<https://daneshyari.com/en/article/7893222>

Download Persian Version:

<https://daneshyari.com/article/7893222>

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