



## Microstructural modelling solution for complex Co based alloys and coatings

S. Salam<sup>a</sup>, P.Y. Hou<sup>b</sup>, Y.-D. Zhang<sup>a</sup>, X.-H. Zhang<sup>a</sup>, H.-F. Wang<sup>a</sup>, C. Zhang<sup>a</sup>, Z.-G. Yang<sup>a,\*</sup>

<sup>a</sup> Key Laboratory of Advanced Materials, Ministry of Education, School of Materials Science and Engineering, Tsinghua University, Beijing 100084, PR China

<sup>b</sup> Materials Sciences Division, Lawrence Berkeley National Laboratory, Berkeley, CA 94720, USA

### ARTICLE INFO

#### Article history:

Received 23 August 2013

Accepted in revised form 26 October 2013

Available online 1 November 2013

#### Keywords:

Thermo-Calc

MCrAlY

Bond coat

Microstructure

Hardness

### ABSTRACT

Microstructural changes following oxidation at high temperatures of a complex coating or alloy can significantly influence its properties. This paper investigates possible solutions that can accurately model alloy microstructures that result from such a process in a cobalt-rich CoNiCrAlReY bond coat alloy system. Four different alloys with varying aluminum content were studied after heat treatments at 1000 °C or 1150 °C. SEM, EPMA and XRD were used to characterize the alloy microstructure, and hardness testing was performed to determine the role of microstructure on mechanical properties. Experimental microstructures were modeled using two databases of Thermo-Calc, namely TTNI8 and SSOL5. Effects of Al content on phase changes and materials properties were quantitatively investigated. Data showed that a 1 wt. % increase of Al in the alloy caused an 8% increase in the beta phase, and a Cr and Re rich sigma phase precipitated preferentially at high Al concentrations. In addition, alloy hardness was found to increase by 4 and 81%, respectively, with a 10% increase in the beta and sigma phases. Modeled results using the TTNI8 database showed excellent agreement with experimental observations, but the SSOL5 database produced erroneous information.

© 2013 Elsevier B.V. All rights reserved.

### 1. Introduction

The CoNiCrAlReY alloy system is a complex cobalt based bond coat material that is applied between a nickel based super alloy substrate and a thermal barrier top coat (TBC) to provide the substrate with oxidation and corrosion resistance at elevated temperatures, and to provide better bonding between the substrate and the top coat [1–3]. Depending on their composition, such coating usually contains gamma ( $\gamma$ -Ni) and beta ( $\beta$ -NiAl) phases with small amounts of gamma prime ( $\gamma'$ -Ni<sub>3</sub>Al) and/or alpha ( $\alpha$ -Cr), sigma ( $\sigma$ -CoCr) and Ni-Y intermetallic [4]. Slight changes in composition often results in noticeable changes in microstructure, which can in turn affect physical properties that are key to bond coat performance. For example, addition of a few percent of Re can cause excessive  $\alpha$ -Cr precipitation, thus lowering the alloy's coefficient of thermal expansion [5]; precipitation of  $\sigma$  phase can increase hardness [6], and an increase in the Co concentration increases the amount of the  $\beta$  phase [7], which is the main reservoir of Al for the formation of the protective thermally grown Al<sub>2</sub>O<sub>3</sub> oxide (TGO).

Mechanical properties that are important to bond coat performance, such as hardness, yield strength, ductility, creep, and ductile to brittle transition temperature (DBTT), are also sensitive to coating microstructure [8]. Among these properties, hardness is often the most frequently

quoted one for coating alloys [9], through which the ultimate tensile strength (UTS) could be estimated [10] and used in life prediction of coatings under thermal fatigue. Furthermore, the DBTT of a bond coat can be described by a direct relationship between the yield strength,  $\sigma_y$ , and the coating's hardness ( $\sigma_y = H/3$ ) [6,11].

Although microstructural influence on bond coat performance can be profound, the experimental evaluation of microstructural changes with temperature and bond coat compositions requires extensive efforts. Modern day computer aided technologies for the modeling of phase diagrams have made phase equilibrium calculations possible for multicomponent systems with reasonable accuracy. Computational methods such as CALPHAD (CALCulation of PHASE Diagram) have been extensively used, for example, to predict phase contents in Ni based super alloys [12–15]. These computer aided modeling methods, which take advantage of efficient and reliable equilibrium calculations, can easily provide any microstructural changes that should take place at different service temperatures. The calculations thus allow an optimum coating microstructure to be tailored from a carefully designed coating composition. Commercial Thermo-Calc software [16] coupled with thermodynamic databases is widely used for these calculations. Thermo-Calc databases TCNI5 (TCS Ni-based super alloys database version 5) and TTNI8 (TT Ni-based super alloys database version 8) are commonly used to describe the thermodynamic equilibrium in Ni-based super alloys. The database SSOL5 (SGTE Solutions database version 5), on the other hand, is usually used for more general alloys. Co-rich alloys have often been modeled using either the SSOL5 [19–21] or the TCNI5 or TTNI8 databases [17,18], even though they pose some

\* Corresponding author.

E-mail address: [zgyang@tsinghua.edu.cn](mailto:zgyang@tsinghua.edu.cn) (Z.-G. Yang).

limitations on alloys with large quantities of Co. Presently no database exists specifically for alloys with a high Co content; for example, TTNi8 is reliable for alloys in which the content of Co is no more than 25 wt. % [18].

The aim of the present work is to investigate possible modelling solutions to microstructural changes under oxidation or heat treatment processes in a complex CoNiCrAlReY coating system. Alloys with Co between 32 and 38 wt. % and varying Al content were chosen for this study. Experimental microstructures were modeled using two databases of Thermo-Calc, namely TTNi8 and SSOL5. Results were compared with experimental microstructures to find possible modelling solution for this coating system. The Al content in a coating is often one of the most important variables, since it is the key element for the formation of the protective TGO and its concentration in a coating diminishes with time due to consumption by oxidation and interdiffusion. Furthermore, changes in the Al concentration of the alloy change its microstructure. Due to different solubility of alloying elements in different phases, this can give rise to the precipitation of secondary phases. Therefore, a second aim of this work is to determine the effect of Al content on the amount of  $\beta$ -phase in the alloy, and subsequently on the precipitation of other phases. The presence of secondary phases can have a significant strengthening effect on the alloy. In order to relate the amount of these phases to the alloy's mechanical properties, hardness testing is performed on each alloy. For an accurate comparison of the experimental microstructure with theoretical predictions free standing CoNiCrAlReY alloys are used thus avoiding interdiffusion between the substrate and the bond coat.

## 2. Modeling background

In a multicomponent system, the calculation of phase equilibrium using a software such as Thermo-Calc requires the minimization of the total Gibbs free energy of all the phases that are present at equilibrium [19]. The description and procedure of such modeling are detailed in many references [19,20]. In this work, substitution and sub lattice models are applied to describe equilibrium phase formations.

Thermo-Calc databases SSOL5 and TTNi8 [21] both include elements Co, Ni, Cr, Al and Re. The reactive element Y is not included in TTNi8 but is in SSOL5. However, modeling using the SSOL5 database resulted in a liquid Y phase at the studied temperature range, between 1000 and 1150 °C. Henceforth any phase containing Y such as Ni–Y intermetallic was not taken into account in the equilibrium calculations. Since the amount of Y in the alloy is less than 0.1%, this omission is not expected to substantially affect the formation of the other phases. Due to the absence of volume data of each phase in both databases, the volume fraction calculated from the microstructures was converted to weight fraction as:

$$f_{w(\varphi_j)} = \left( f_{v(\varphi_j)} \times \rho_{\varphi_j} \right) / \sum_i \left( f_{v(\varphi_i)} \times \rho_{\varphi_i} \right) \quad (1)$$

Where  $f_{v(\varphi_j)}$  = volume fraction of phase  $\varphi_j$ ,  $f_{w(\varphi_j)}$  = weight fraction of  $\varphi_j$ , and  $\rho_{\varphi_j}$  = density of  $\varphi_j$ .

## 3. Experimental details

Four CoNiCrAlReY alloys with varying Al content were designed and melted in an electric arc furnace [SK-II non-consumable vacuum arc furnace] from pure elements (>99.99%). The designed compositions represent common Co based bond coats used in industrial turbines. Each cast ingot weighed 60 g, and they were subjected to vacuum annealing at 1150 °C for 24 h. Composition of the four alloys determined using an X-ray fluorescence (XRF) spectrometer [XRF-1800] is given in Table 1. Disc shaped samples with dimensions  $\Phi$  10 mm  $\times$  1 mm were cut from the cast ingots using an electrical discharge machine. Because duplicate samples were used in oxidation studies in a separate study, all

**Table 1**  
Composition of experimental alloys determined by XRF.

Alloy ID	Composition in wt. %					
	Co	Ni	Cr	Al	Re	Y
6Al	Bal.	31.5	22.0	6.2	3.0	<0.1
8Al	Bal.	30.8	21.9	7.9	3.2	<0.1
10Al	Bal.	31.1	21.7	10.1	3.2	<0.1
12Al	Bal.	31.1	21.3	12.1	3.3	<0.1

the samples were ground to 2000 grid and subsequently polished using diamond paste down to 0.05  $\mu$ m. Finished samples were rinsed in excess water and ultrasonically cleaned in absolute ethanol prior to heat treatments.

Specimens were placed in alumina crucibles and heat treated in static air at 1000 °C or 1150 °C for 100 h in a box furnace [Nabertherm] and then quenched in water to preserve their high temperature microstructure. All the surface oxide and oxidation affected sub-scale regions were carefully ground and polished away in order to study the microstructure of the bulk alloy. Following polishing, the specimens were analyzed using a scanning electron microscope (SEM) [Jeol JSM-7001 F] operated at voltage and spot size of 15 kV and 4 nm, respectively. X-ray diffraction (XRD) [Rigaku/SmartLab] using Cu  $\alpha$  radiation at 40 kV was used for phase analysis and an electron probe micro-analyzer (EPMA) [Jeol JXA-8230] coupled with wave length dispersive X-ray analysis (WDX) was used to accurately determine phase composition. The volume fraction of major phases that were present in each alloy was determined through the digital image processing of SEM micrographs. The hardness of each sample with its unique microstructure was investigated using a micro hardness tester [MCO10-HVS-1000Z]. Table 1 lists composition and the heat treatment conditions along with specimen IDs that will be used from here onward.

## 4. Results

### 4.1. Experimental microstructural evolution

Phases that were present in the four CoNiCrAlReY alloys with varying Al content were investigated experimentally using SEM and XRD. Fig. 1 shows the alloy microstructures after heat treatment at 1000 °C. EPMA point analysis was used to determine phase composition; results from different phases, marked as points 1–4, are given in Table 2. Fig. 1 shows that alloys with 6 and 8 wt. % Al had a two-phase microstructure consisting of a lighter  $\gamma$  and a darker  $\beta$ -phase. Occasionally, small particles of Ni–Y intermetallics could be observed; an example is marked as point 3 on Fig. 1(b). Major proportion of Co and Cr partitioned in the gamma phase while Ni and Al in the beta phase. Increasing the amount of Al led to an increase in the amount of the  $\beta$ -phase. As the Al content was increased to 10 wt. % or higher (12 wt. %) a third phase appeared within the  $\beta$  phase and at the  $\beta/\gamma$  phase boundary. It had high amounts of Re, Cr, and Co; XRD analysis (Fig. 2) confirmed it as a topological closed packed (TCP)  $\sigma$ -phase. Comparing Fig. 1c and d, the amount of  $\sigma$  is seen to increase noticeably with increasing Al. At 1150 °C, the alloys are again seen to consist mainly of  $\gamma$  and  $\beta$  phases (Fig. 3). The amount of  $\beta$  increased with increasing Al, as it did at 1000 °C. The  $\sigma$ -phase also appeared at higher Al content, but unlike that at 1000 °C, its presence was not observed in alloys with less than 12 wt. % Al.

To experimentally estimate the relative amount of different phases in each alloy, digital image processing of SEM micrographs was performed, in which phase contrast was selected by thresholding and then the number of pixels in the contrasted areas was calculated. The ratio of the threshold pixels to the total pixels gave an estimate of the surface fraction of each identified phase [22]. Generally for a uniform microstructure at equilibrium the surface fraction in two dimensions should be equal to the volume fraction in three dimensions. Fig. 4 shows an example of a binary threshold segment of the 10 wt. % Al

Download English Version:

<https://daneshyari.com/en/article/8029082>

Download Persian Version:

<https://daneshyari.com/article/8029082>

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