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Experimental investigation and computational study of atomic mobility in fcc ternary Co–Cr–W alloys ☆

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ABSTRACT

The interdiffusion coefficients in fcc Co–Cr–W alloys at 1373 K have been determined from the concentration profiles across the solid–solid diffusion couples using the Whittle and Green method. On the basis of the experimental interdiffusion coefficients in this work, together with the critically reviewed experimental diffusivities available in the literature, atomic mobilities of Co, Cr and W in fcc Co–Cr–W alloys were assessed as a function of temperature and composition by means of DICTRA (DIffusion Controlled TRAnsformation) software. Comprehensive comparisons between the calculated results and the experimental data indicate that the presently obtained atomic mobilities can reasonably reproduce most of the diffusivities, concentration profiles and diffusion paths in binary and ternary systems.

1. Introduction

Cemented carbides are widely used in industry as cutting tools, wear parts, and in machining and mining applications [1–4]. They consist of micrometer-sized hard refractory carbide phases embedded in a ductile metal matrix binder phase [5]. Usually, metallic cobalt is chosen as a matrix binder phase. Mechanical properties of cemented carbides are reported to be strongly dependent on the WC grain size, i.e. the smaller the grain size, the better wear resistance and strength [6,7]. Moreover, Cr_3C_2 has been used in small amounts in the cemented carbides as a grain growth inhibitor [8]. Although metallic cobalt and grain growth inhibitor are only a small part in cemented carbides, it has a great influence on the microstructure and the properties of cemented carbides [9]. During sintering, the densification of the carbide particles, dissolution–reprecipitation of carbide particles and chemical composition rearrangement occurs mainly in Co-rich regions [10]. Cr_3C_2 and WC dissolve into binder phase, and then precipitate at the grain boundary of WC/Co to retard the WC grain growth. Knowledge of both thermodynamic and diffusion kinetic characteristics of Co-based alloys is of critical importance in understanding how temperature, time and composition affect the microstructure and composition distribution during sintering. Such information is useful to investigate the sintering characteristics and optimize the sintering conditions. So far, the thermodynamic database of the cemented carbides, which can give an easy access to what phases form at different temperatures and alloy concentrations during the manufacture process, has been well established in our research group [11]. However, this is not the case for diffusion kinetic database, i.e., the so-called atomic mobility database, for Co-based alloys. One of the major obstacles is lack of the experimental information about diffusivities. Thus, there is a need to remedy this situation.

As a part of the research project aiming at development of an accurate atomic mobility database for fcc Co-based alloys, one of the key ternary systems in the multicomponent cobalt-based alloys, Co–Cr–W system, is chosen as the target in the present work. Up to now, there is no systematic investigation of atomic mobilities in Co–Cr–W system except for one piece of work on fcc Co–W alloys by Cui et al. [12]. Consequently, the major purposes of the present work are: (i) to critically review all the experimentally measured diffusivities in fcc Co–Cr alloys available in the literature; (ii) to experimentally measure the inter-diffusivities of fcc Co–Cr–W alloys at 1373 K; (iii) to evaluate the atomic mobilities of fcc Co–Cr and Co–Cr–W alloys by means of DICTRA based on the critically reviewed literature as well as the present experimental results, and (iv) to verify the reliability of the presently obtained mobility parameters by comprehensively comparing the different diffusivities, concentration profiles, and diffusion paths with the corresponding experimental data in various binary and ternary diffusion couples.

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Table 1
Summary of experimental diffusion coefficients in the fcc Co–Cr alloys from the literatures.

Type of diffusivities		Temperature range (K)	Method	Ref.
Impurity diffusivity	D^{Co}_{Cr}	1342	Extrapolated values	[13]
Inter-diffusivity	$\tilde{D}^{Co}_{CrCr}$	1273–1642	BDC, CAM	[13]
		1273–1573	BDC, MM, EPMA	[14]
		1273–1573	BDC, BMM, EPMA	[15]

Extrapolated values=extrapolated impurity diffusion coefficients from the inter-diffusion coefficients; BDC=bulk diffusion couple; CAM=chemical analysis method; EPMA=electron probe microanalysis; MM=Matano method; BMM=Boltzmann–Matano method.

Table 2
List of the nominal alloy compositions for the diffusion couples prepared in the present work.

Ternary diffusion couples	Composition (at%)
A1	Co–10.5Cr/Co–4.5W
A2	Co–20.3Cr/Co–9.5W
B1	Co/Co–20.5Cr–4.6W
B2	Co/Co–10.3Cr–7W

2. Evaluation of experimental data in the literature

No experimental data are available for the fcc Co–Cr–W system. There are only three pieces of literature data about the interdiffusion coefficients in fcc Co–Cr alloys. All the available experimental information for fcc Co–Cr alloys are summarized in Table 1, and presented as follows.

By employing various diffusion couples consisting of pure Co and Co–Cr alloys, Weeton [13] measured the interdiffusion coefficients in fcc Co–Cr alloys from 1273 to 1642 K by using eleven diffusion couples together with the chemical analysis method. Utilizing the Co/Co–15.2 at% Cr diffusion couples, Davin et al. [14] determined the interdiffusion coefficients in fcc Co–Cr alloys at 1273–1573 K by means of the Matano method together with electron probe microanalysis (EPMA) technique. Green et al. [15] obtained interdiffusion coefficients of fcc Co–Cr alloys in the temperature range between 1273 and 1573 K by means of the Boltzmann–Matano method coupled with EPMA technique.

3. Experimental procedure

3.1. Diffusion couples preparation

Cobalt (99.99 wt%), chromium (99.99 wt%) and tungsten (99.99 wt %) were used as starting materials. Four diffusion couples, as shown in Table 2, were prepared with the following steps. First, the Co–Cr, Co–W and Co–Cr–W alloys, the nominal compositions of which were listed in Table 2, were prepared by arc melting the pure elements in an arc furnace under high purity argon atmosphere using a non-consumable tungsten electrode (WKDHL-1, Opto-electronics Co., Ltd., Beijing, China). The buttons were remelted 5 times to improve their homogeneity. No chemical analysis for the alloys was conducted since the weight losses of alloys were all less than 1 wt% during arc-melting. Then, the buttons were linearly cut into suitably sized blocks, $4\times4\times10\ mm^3$ after mechanically removing the surface material, and then sealed into an evacuated quartz tube, homogenized at 1373 ± 5 K for 15 days. After that, all the samples were grounded on SiC papers to remove surface contamination. After ground, polished, and cleaned, the blocks were bound together with molybdenum wires to make four diffusion couples with end members shown in Table 2. Subsequently, the diffusion couples, which were sealed in quartz tubes under vacuum atmosphere, were annealed at 1373 K for 432,000 s (i.e., 5 days) in an L4514-type diffusion furnace (Qingdao Instrument & Equipment Co. Ltd., China). After annealing, the diffusion couples were quenched into cold water.

The quenched diffusion couples were cut parallel to the diffusion direction. After standard metallographic preparation, the concentration profiles were obtained by means of EPMA (JXA-8230, JEPL, Japan) on a polished section, parallel to the diffusion direction. The concentrations were calculated by comparison with standards of the pure elements Co, Cr and W, after absorption and fluorescence corrections. Considering that all the diffusion couples are in single fcc phase region, one typical microstructure and the distributions of the elements Co, Cr and W in diffusion couple B2 annealed at 1373 K for 432,000 s are given in Fig. 1.

3.2. Evaluation of ternary diffusion coefficients

Assumed component 3 as the solvent, the interdiffusion in a ternary alloy 1–2–3 can be expressed by an extended Fick's second law on the basis of Matano coordinates:

$$\frac{\partial C_i}{\partial t}=\sum_{j=1}^{2}\frac{\partial}{\partial x}\left(\tilde{D}^3_{ij}\frac{\partial C_j}{\partial x}\right)\quad \text{for } i=1,2 \tag{1}$$

where x is the distance, t represents time, C_i is concentration of element i, and $\tilde{D}^3_{ij}$ are the interdiffusivities. The main interdiffusion coefficients, $\tilde{D}^3_{11}$ and $\tilde{D}^3_{22}$, represent the influences of the concentration gradients of elements 1 and 2 on their own fluxes, respectively. $\tilde{D}^3_{12}$ and $\tilde{D}^3_{21}$ are the cross interdiffusion coefficients which represent the influences of the concentration gradients of element 2 and element 1 on the fluxes of element 1 and element 2, respectively. For semi-infinite diffusion couples, the initial and boundary conditions are

$$\begin{aligned} &C_i(-x,0)=C_i(-\infty,t)=C_i^-\\ &C_i(x,0)=C_i(+\infty,t)=C_i^+ \end{aligned}\quad \text{for } i=1,2 \tag{2}$$

Interdiffusion coefficients $\tilde{D}^3_{ij}$ in a ternary alloy can be evaluated by the following equations:

$$\int_{C_1^-}^{C_1^+} x\,dC_1=-2t\left(\tilde{D}^3_{11}\frac{\partial C_1}{\partial x}+\tilde{D}^3_{12}\frac{\partial C_2}{\partial x}\right) \tag{3}$$

and

$$\int_{C_2^-}^{C_2^+} x\,dC_2=-2t\left(\tilde{D}^3_{21}\frac{\partial C_1}{\partial x}+\tilde{D}^3_{22}\frac{\partial C_2}{\partial x}\right) \tag{4}$$

Whittle and Green [16] have shown that by introducing the normalized concentration parameter $Y_i=(C_i-C_i^-)/(C_i^+-C_i^-)$, Eqs. (3) and (4) yield:

$$\begin{aligned} Y_1&=\frac{1}{2t}\frac{dx}{dY_1}\left[(1-Y_1)\int_{-\infty}^{x}Y_1dx+Y_1\int_{x}^{+\infty}(1-Y_1)dx\right]\\ &=\tilde{D}^3_{11}+\tilde{D}^3_{12}\frac{C_2^+-C_2^-}{C_1^+-C_1^-}\frac{dY_2}{dY_1} \end{aligned} \tag{5}$$

$$\begin{aligned} Y_2&=\frac{1}{2tdY_2}\left[(1-Y_2)\int_{-\infty}^{x}Y_2dx+Y_2\int_{x}^{+\infty}(1-Y_2)dx\right]\\ &=\tilde{D}^3_{22}+\tilde{D}^3_{21}\frac{C_1^+-C_1^-}{C_2^+-C_2^-}\frac{dY_1}{dY_2} \end{aligned} \tag{6}$$

The ternary interdiffusion coefficients in Eqs. (5) and (6) are estimated at the common composition of the intersection of the diffusion paths from two diffusion couples.

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