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Computer simulating the diffusion behavior of V and W in Co binder layer of WC–Co cemented carbide

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Abstract

Computer simulation was conducted in a VC-doped WC-Co system to understand the diffusion behaviour of W and V atoms in Co binder phase. Different diffusion couples, WC/Co-C, V_8C_7/Co and WC/Co-V-C were constructed and annealed at temperatures in the range $1100-1300\,^{\circ}C$. The concentration profiles of V and W atoms in these couples were measured by EPMA, while the diffusion behaviour was also simulated by coupling thermodynamic and kinetic properties of W-C-Co-V system. The simulation results were in good agreement with the measured concentration profiles showing the validity of revised dynamic parameters of W-C-Co-V system.

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1. Introduction

WC–Co based cemented carbides are widely used as cutting tools and wear resistant pieces due to their excellent mechanical properties and thermal stability. These materials normally consist of WC grains and Co-rich binder phase. Mechanical properties of WC–Co cemented carbide are reported to be strongly dependent on the WC grain size, i.e. the smaller the grain size, the better wear resistance and strength [1,2]. Moreover, VC has been recognized as the most effective grain growth inhibitor to retard the WC grain growth [3–5].

During the sintering process, small WC grains are dissolved into Co binder as W and C atoms and precipitated to large WC grains. It is well known that the WC grain growth is largely affected by VC addition, say, the diffusion of WC into Co binder phase is controlled by VC content. With some similarities, VC also has to be dissolved into binder phase, then precipitated at the grain boundary of WC/Co [3,6]. Therefore the whole process can be considered as a diffusion process in a W–C–Co–V system. The theoretical treatment of diffusion in a multicomponent single-phase system has been well established and the

merit of computer simulations of diffusion is the possibility of treating complex systems, i.e. multi-component systems and complex heat treatments or long term service conditions. A variety of examples have been published illustrating the capability of DICTRA program in simulation of diffusion controlled transformations in multicomponent alloys [7–9]. Haglund and Ågren [7] simulated the dissolution behavior of WC in Co binder during sintering of cemented carbides and the calculated results were in agreement with experimental information. It is worth to note that they re-evaluated the diffusion coefficients for the ternary W–C–Co system in the database of DICTRA before obtaining the correct simulated results. It is necessary to test the validity of the revised parameters [7] in order to understand how the composition of the binder varies during heating.

The present paper aims to simulate the concentration profiles of W and V in the established diffusion couples by means of combining the thermodynamic data and kinetic data of the W-C-Co-V system. Based on the knowledge of experimental results, the validity of revised diffusion parameters of the quarternary system W-C-Co-V is evaluated.

2. Simulation model

In calculation, the moving phase boundary model is applied to simulate the diffusion behavior of the W–C–Co–V system in

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the assumption that the composition of phases at the interface is in equilibrium during the moving of interface.

The diffusion rate is controlled by the mass transportation process at the interface. For the WC/Co diffusion couple, the flux of components passing the interface can be calculated by the following flux balance condition according to the law of mass conservation [10]:

$$\upsilon^{\text{fcc}} C_k^{\text{fcc}} - \upsilon^{\text{mc-shp}} C_k^{\text{mc-shp}} = J_k^{\text{fcc}} - J_k^{\text{mc-shp}},$$

$$k = 1, 2, \dots, n$$
 (1)

where $C_k^{\rm fcc}$ and $C_k^{\rm mc-shp}$ are the concentrations of component k in the fcc Co binder phase and the WC phase at the interface, $v^{\rm fcc}$ and $v^{\rm mc-shp}$ the interface migration rates with same value, and $J_k^{\rm fcc}$ and $J_k^{\rm mc-shp}$ are the diffusion fluxes of component k in fcc and mc-shp phases, respectively. $J_k^{\rm fcc}$ or $J_k^{\rm mc-shp}$ depends on the concentration gradients of all elements in the system, it can be expressed by Fick–Onsager law [11]:

$$J_k = -\sum_{j=1}^{n-1} D_{kj}^n \nabla c_j \tag{2}$$

where n is the number of species, D_{kj}^n the diffusion coefficient matrix, and ∇c_j is the concentration gradient for species j.

Three kinds of calculation are therefore necessary to obtain the solution of such problem, i.e. equilibrium calculation, solving flux equations and solving diffusion equations.

DICTRA [12], a program equipped with databanks of thermodynamics and kinetics and connected with three relevant calculation modules, is available to solve the diffusion equations numerically. In this paper, diffusion in the WC or VC carbide is neglected in all calculations. The thermodynamic data for the W–C–Co–V system was assessed by Huang et al. [13,14]. The calculations are based on the following dilute solution data for diffusion in fcc Co phase. The diffusion data of the C, Co, W and V in fcc Co phase are after Refs. [15–17]:

$$D_{\rm C}^{\alpha} = 8.72 \times 10^{-6} \exp\left(\frac{-149,300}{RT}\right) \,\mathrm{m}^2 \,\mathrm{s}^{-1}$$
 (3)

$$D_{\text{Co}}^{\alpha} = 1.7 \times 10^{-5} \exp\left(\frac{-260, 500}{RT}\right) \text{ m}^2 \text{ s}^{-1}$$
 (4)

$$D_{\rm W}^{\alpha} = 7.0 \times 10^{-5} \exp\left(\frac{-282, 100}{RT}\right) \,\mathrm{m}^2 \,\mathrm{s}^{-1}$$
 (5)

$$D_{\rm V}^{\alpha} = 2.8 \times 10^{-4} \exp\left(\frac{-175,600}{RT}\right) \,\mathrm{m}^2 \,\mathrm{s}^{-1}$$
 (6)

The individual mobility M_k can be obtained according to the well-known Einstein relation:

$$M_{\rm k} = \frac{D_{\rm k}}{RT} \tag{7}$$

where k stands for the C, Co, W or V component.

Then the four mobilities can be regarded as the diagonal elements in a diagonal 4×4 matrix and a full multicomponent diffusivity matrix can be calculated by multiplying the mobility matrix with a thermodynamic factor matrix [18]. The diffusion

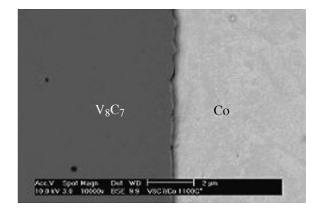


Fig. 1. Micrograph of the cross-sectioned V_8C_7/Co couple annealed for 36 h at $1100\,^{\circ}\text{C}.$

coefficients used in the calculations thus have a concentration dependence, which stems from the thermodynamic factor.

3. Experimental

Each diffusion couple consists of two parallel bars (2 mm \times 4 mm \times 15 mm) with mirror polished surfaces, which are cut from 99.5% dense hot pressed discs (φ = 30 mm, h = 5 mm) by diamond sawing.

For diffusion couple of V_8C_7 and Co, the starting powders are V_8C_7 (Treibacher Powdermet, $1.15\,\mu m$). V_8C_7 is hot pressed (FCT system, W100/150-2200-50 LAX) in a graphite die under a mechanical load of 30 MPa for 90 min at 1950 °C (the detailed method of preparing densified V_8C_7 carbide is described in Ref. [14]). A layer of graphite foil is embedded between the powder and the die to facilitate sample removal. Pure cobalt (99.98 wt.%) is put as the other couple material. The components of the interaction couple are ground and polished, sandwiched and annealed under a small load of 2.5 MPa. The polished cross-section of V_8C_7/Co couple after 36 h annealing at 1100 °C is shown in Fig. 1. The V concentration in Co phase is measured by EDS on Jeol 733 Microprobe (20 kV) with pure V_8C_7 and Co samples as standard.

For the diffusion couple of WC and Co/0.3 wt.% V_8C_7 , the starting powders are WC (Eurotungstene grade CW5000, 0.9 μ m), V_8C_7 (Treibacher Powdermet, Austria, 1.15 μ m) and Co (Eurotungstone grade CO6104, 1.25 μ m).

Hot pressing (FCT system, W100/150-2200-50 LAX) is performed in a graphite die under a mechanical load of 30 MPa, 60 min soaking at 1460 °C for Co/0.3 wt.% V_8C_7 and 90 min at 2050 °C for WC. The components of the diffusion couple are ground and polished, sandwiched and annealed under a small load 2.5 MPa.

4. Results and discussion

4.1. WC/Co couple

Chemical diffusion with the couples of WC and Co components were performed in Ref. [19]. In the WC/Co-1 at.% C couple, the W profile inside Co alloy was reported after annealing at 1200 °C for 4 h. The distance in Fig. 2 is defined as the distance from the moving phase interface. It can be seen that the experimental W profile (symbols) is well reproduced by the present simulation (solid line), where the moving boundary model is assumed and the same database for C, Co and W in fcc Co phase as in Ref. [7] is applied.

4.2. V₈C₇/Co couples

The diffusion couples consist of two parallel bars, pure V_8C_7 and Co with mirror polished surfaces. The polished components

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