Experimental Investigation and Computer Simulation of Gradient Zone Formation in WC-Ti(C,N)-TaC-NbC-Co Cemented Carbides

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The thermodynamic and diffusion databases for multi-component W-C-Co-Ti-Ta-Nb-N cemented carbides have been developed through a combination of experimental, theoretical and assessment work. Using the CALPHAD approach, the thermodynamic database has been established based on the literature information and experimental investigations. The diffusion database contains the atomic mobility parameters for different diffusing elements in liquid, which were calculated by a modified Sutherland equation. According to the present thermodynamic and diffusion databases, a gradiently sintered WC-Ti(C,N)-(Ta,Nb)C-Co cemented carbides has been designed and prepared. Scanning electron microscopy was employed to investigate the microstructure of the gradient zone, and electron probe microanalysis was used to determine the concentration profiles and distributions of the elements. The gradient zone formation of the cemented carbides was then simulated by DICTRA, and the simulation results show a good agreement with the experimental results.

Keywords cemented carbides, computer simulation, diffusion coefficient, gradient sintering, microstructure, thermodynamics

1. Introduction

Cemented carbides^[1] are hard and tough tool materials consisting of micrometer-sized carbides embedded in a metal binder phase, usually rich in Co. In order to increase the resistance of the cemented carbides to plastic deformation or behavior, gradient formers, in the form of carbides or carbonitrides with cubic structure, such as TiC, (Ti,W)C, and (Ti, Ta, Nb) (C,N), have been introduced into WC-Co matrix. Cemented carbides are widely used in industry as cutting tools, wear parts, and in machining and mining applications.^[2] In order to increase cutting performance of the cemented carbide inserts, the wear surface is usually coated with a thin layer of hard material such as TiC, TiN, TiCN, Al₂O₃ or their multilayers.^[3] Since the coating is often obtained by high-temperature chemical vapor deposition (CVD) technique,^[4] cracks would be introduced into the coating unavoidably due to the high deposition temperature and a large difference in thermal expansion coefficients between the coating and substrate. And the formed

cracks might easily propagate into the substrate to cause failure when coating tools are employed in metal machining.^[5] When gradient cemented carbides are used as the substrate of coated inserts, the surface gradient layer, which is free of cubic phases and enriched in binder phase, can prevent the crack formed in the coating from propagating into the bulk and causing failure, and hence extend the service lifetime of inserts.^[6]

Many investigators have studied the gradient zone formation in the cemented carbides.^[3,7-12] The formation of the gradient zone is controlled by the thermodynamic properties of the system and the diffusion in the liquid binder.^[3] With the development of thermodynamic and diffusion databases, Thermo-Calc^[13] and DICTRA^[14] softwares have become very important techniques in simulating and understanding the gradient zone formation in the cemented carbides. Up to now, thermodynamic^[15,16] and diffusion^[3,10,17] databases have been established and used to simulate the gradient sintering process.

With the development of cemented carbide industry in China, more and more companies in China have realized that the simulation can guide manufacturing process and reduce the cycle for the development of new cemented carbides significantly. Since the reported thermodynamic and diffusion databases for cemented carbide are for commercial purpose and thus not available in these publications,^[3,10,15-17] the development of these databases is of technical importance for us.

In this work, the establishment of thermodynamic and diffusion databases for multi-component W-C-Co-Ti-Ta-Nb-N cemented carbides through a combination of experimental, theoretical and assessment work is briefly described. A cemented carbide WC-Ti(C,N)-(Ta,Nb)C-Co was then designed and sintered under vacuum. The microstructure of the gradient zone was investigated with scanning electron

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Table 1 Chemical composition of the investigated alloy (wt.%)

Co	Ti	Ta	Nb	C	N	W
9	3	6	0.8	6.06	0.08	Balance

microscopy (SEM). The concentration profiles and mappings of the elements were determined with electron probe microanalysis (EPMA). Subsequently, the gradient zone formation was simulated by means of DICTRA with currently established thermodynamic and diffusion databases. The simulation results were compared with the experimental results to demonstrate the application of the established databases.

2. Experimental Procedure

The alloys were prepared from a powder mixture of WC, (Ti,W)C, Ti(C,N), (Ta,Nb)C and metallic Co powder provided by Zhuzhou Cemented Carbide Cutting Tools Limited Company. The composition of the sintered material is given in Table 1. After milling and drying, the powders were pressed into cutting tool inserts. Samples were dewaxed and sintered in vacuum at 1723 K for 1 h. After sintering, the samples were cut, embedded in resin and polished. SEM (Nova NanoSEM 230, USA) was employed to investigate the microstructure of the gradient zone, and EPMA (JXA-8230, JEOL, Japan) was used to determine the concentration profiles of the elements. The phase volume fraction distributions were calculated by the software ImageJ based on the SEM images.

3. Modeling

3.1 Model for Diffusion

Schwarzkopf et al.^[8] found that the formation of the gradient zone is controlled by the thermodynamic properties of the system and diffusion in the liquid binder phase. Due to the strong thermodynamic interaction between N and Ti, Ta and Nb, as N diffuses out from the material, Ti, Ta and Nb diffuse in the opposite direction. The thermodynamic coupling between N and Ti, Ta and Nb may be expressed by the off-diagonal coefficients of the diffusion coefficient matrix D_{kj} of the Fick-Onsager diffusion equation^[10]

$$J_k = - \sum_{j=1}^n D_{kj} \nabla C_j \quad (\text{Eq 1})$$

where D_{kj} is the interdiffusion coefficient, C_j is the concentration in mole per volume, and ∇ denotes the divergence operator. The flux J_k of species k depends on the concentration gradients of all n species.

For a substitutional solution phase, the interdiffusion coefficients in terms of the volume-fixed reference frame is given by the following expression^[18,19]

Fig. 1 Calculated isothermal section at 1773 K of (a) C-Ta-Ti and (b) C-Ti-Nb systems, compared with the experimental data^[27]

$$\tilde{D}_{kj}^n = \sum_i (\delta_{ik} - x_k) \cdot x_i \cdot M_i \cdot \left(\frac{\partial \mu_i}{\partial x_j} - \frac{\partial \mu_i}{\partial x_n} \right) \quad (\text{Eq 2})$$

where δ_{ik} is the Kronecker delta ($\delta_{ik} = 1$ if $i = k$, otherwise $\delta_{ik} = 0$). x_i , μ_i , and M_i are the mole fraction, chemical potential, and mobility of element i , respectively. The element n is chosen as the dependent element.

Fig. 2 Calculated isothermal section at 1323 K of the Co-Cr-Ti system, compared with the experimental data^[28]

From the absolute reaction rate theory arguments, the mobility parameter M_i may be divided into a frequency factor M_i^0 and an activation enthalpy Q_i .^[18,19] Both M_i^0 and Q_i are in general dependent on the composition, temperature, and pressure. According to the suggestion by Jöns-son,^[18] the M_i for fcc alloys is expressed by an equation of the following form,

$$M_i = \exp\left(\frac{RT \ln M_i^0}{RT}\right) \exp\left(\frac{-Q_i}{RT}\right) \frac{1}{RT} \quad (\text{Eq 3})$$

where R is the gas constant and T the absolute temperature. Consequently, the composition dependence can be represented by a linear combination of the values at each endpoint of the composition space.

The simulation of gradient zone formation is based on the model for long-range diffusion occurring in a continuous matrix with dispersed phases. Due to the presence of dispersed phases (WC, carbides and carbonitrides), the diffusion is reduced in the matrix (the liquid binder phase).^[20] A so-called labyrinth factor $\lambda(f)$, where f is the volume fraction of the matrix, was introduced to reduce the diffusion coefficient matrix:

$$D_{k,j}^n = \lambda(f) D_{k,j}^n \quad (\text{Eq 4})$$

Frykholm et al.^[20] found that the labyrinth factor $\lambda(f) = f$ yields a good correspondence between experiment and simulation. It can be found that the gradient zone width and binder content show a linear relationship.^[20] In this work the labyrinth factor $\lambda(f) = f$ was thus chosen.

3.2 Brief Description of the Thermodynamic Database

Thermodynamic calculations are very useful in alloy development and process design because they can easily predict phase relationships at different temperatures and calculate the concentrations during the sintering process. In

Fig. 3 Calculated projection at 1723 K with the carbon activity of one in the (a) C-W-Ta-N system; (b) C-W-Nb-N system

addition, application-related DICTRA simulations, such as the formation of the gradient zone, are performed based on the thermodynamic database in conjunction with the diffusion database. The accuracy of the simulations strongly depends on the quality of the two databases. Cemented carbides consist of WC, cubic carbides/carbonitrides and binder cubic (Co). The undesirable graphite and eta (M_6C or $M_{12}C$) phases often appear in cemented carbides, and the carbon content in cemented carbides should be carefully

Fig. 4 Calculated self-diffusion coefficients for pure liquid (a) Co and (b) Ti, compared with the corresponding data available in the literature^[32-38]

controlled to avoid the formation of these phases. As a result, the above five phases among the numerous phases in the systems are the main focus during the modeling.

Using the CALPHAD method,^[21] the establishment of the thermodynamic database is based on previous thermodynamic descriptions for all of the binary systems and most of the ternary systems reported in the literature. Some of the ternary systems are assessed according to experimental data including the C-Cr-Ta,^[22] C-Ta-Ti,^[23] C-Ti-Nb^[24] and Co-Cr-Ti^[25] systems. The description on the established thermodynamic database is given elsewhere.^[26] Figure 1 presents the calculated isothermal section at 1773 K of

Fig. 5 SEM micrograph of the cross section of the cemented carbide WC-Ti(C,N)-(Ta,Nb)C-Co after sintering in vacuum at 1723 K for 1 h

(a) C-Ta-Ti and (b) C-Ti-Nb systems, compared with the experimental data.^[27] As can be seen, a wide band of continuous solid solution is formed between fcc TiC and TaC/NbC carbides. For the Co-Cr-Ti system, all the experimental data in the whole composition and temperature ranges are assessed. Figure 2 shows the calculated isothermal section at 1323 K of the Co-Cr-Ti system, compared with the experimental data,^[28] which accurately describes the huge solubility of Ti and Cr in Co phase. Based on the presently established thermodynamic database, calculations on the solubility of WC in cubic carbide and the miscibility gap in the cubic carbide are performed in the quaternary C-W-Ta-N and C-W-Nb-N systems. These calculations are shown in Fig. 3.

3.3 Brief Description of the Diffusion Database

As for the diffusion database, due to the lack of detailed information on liquid diffusion, Ekroth et al.^[3] and Frykholm et al.^[10] assumed that all elements (Co, Ti, W, Ta, Nb, C and N) had the same mobility in the liquid. Garcia et al.^[17] assumed that the mobility of the metallic elements (W, Co, Ti, Ta and Nb) was two times slower than the mobility of light non-metallic elements (C and N) by comparing the measured graded layer thicknesses with the simulation ones. However, the above assumptions are far away from reality. Consequently, an effective method is needed to predict diffusivity in liquid. Recently, Chen et al.^[29] in our group derived a modified Sutherland equation, which is coupled with Kaptay's viscosity equation^[30] and Protopapas's temperature-dependent effective diameter^[31] to predict the temperature-dependence diffusivity in liquid metals.

$$D_{BB} = D_{BB}^0 \cdot \exp\left(-\frac{Q_{BB}}{RT}\right) \quad (\text{Eq 5})$$

Fig. 6 The distribution of the elements (a) Co, (b) Ti, (c) Ta and (d) Nb in the gradient zone of the cemented carbide WC-Ti(C,N)-(Ta,Nb)C-Co

Fig. 7 Experimental and calculated phase fractions in the cemented carbide WC-Ti(C,N)-(Ta,Nb)C-Co after sintering for 1 h at 1723 K in a N-free atmosphere

with

$$D_{BB}^0 = \frac{3.3737 \times 10^{-16} V_B^{1/3} \sqrt{T_B^m}}{C_1 M_B^{1/2}} \quad (\text{Eq 6})$$

$$Q_{BB} = \left(C_2 + \frac{1}{1.776} \right) \cdot R T_B^m \quad (\text{Eq 7})$$

where T is the absolute temperature, and M_i , V_i and T_i^m are the atomic mass, the absolute molar volume and the melting point under one atmospheric pressure of the given metal i , respectively. The constants C_1 and C_2 were found to be $(1.80 \pm 0.39) \times 10^{-8} (\text{J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1/3})^{1/2}$ and (2.34 ± 0.20) , respectively.

The self-diffusivity parameters of Co and Ti in metallic liquid phase were calculated by the modified Sutherland equation and optimized by DICTRA software, respectively. The comparison of the self-diffusivity parameters for Co and Ti in liquid via the two methods is used to verify the accuracy of the modified equation. There exist some theoretical and experimental self-diffusion coefficients for Co and Ti in liquid state. Using the pair and triplet correlation entropies, Yokoyama et al.^[32,33] calculated the self-diffusion coefficient based on Dzugutov's scaling law.

◀ **Fig. 8** Experimental and calculated elemental concentration profiles for (a) Ti, (b) Ta, (c) Nb, (d) Co and (e) W in the cemented carbide WC-Ti(C,N)-(Ta,Nb)C-Co after sintering for 1 h at 1723 K in a N-free atmosphere

By means of molecular dynamics (MD) simulation with Pasianot's and Stoop's embedded-atom-method (EAM) potentials, Han et al.^[34] calculated the self-diffusion coefficient of liquid cobalt at temperature above and below the melting temperature. Employing the MD method with the semi-empirical potentials derived from the second-moment approximation to the tight binding method (TBM-SMA), Yang et al.^[35] calculated the self-diffusivity of Co in liquid Co in the temperature range from 1768 to 3100 K. Iida et al.^[36] predicted the self-diffusivity in liquid Co and Ti by combining the modified Stokes-Einstein formula with the Iida's model. Meyer et al.^[37] and Horbach et al.^[38] measured the self-diffusion coefficients in liquid Ti by means of incoherent QNS in the temperature range of 1953-2110 K. Only theoretically predicted self-diffusion coefficients exist for liquid Co. The theoretically predicted Co self-diffusion coefficients from different sources^[32-36] exhibit a relatively large scatter. Considering the fact that all the reported self-diffusion coefficients in liquid Co except Han et al.'s^[34] agree with each other to a certain degree, they are used to assess the atomic mobility for pure Co in the present work. The self-diffusion coefficients in liquid Ti have been measured by Meyer et al.^[37] and Horbach et al.^[38] and utilized to evaluate the atomic mobility for pure Ti. While those theoretically predicted ones^[36] are only used for a comparison with the finally obtained atomic mobilities. Figure 4(a) and (b) presents the calculated self-diffusion coefficients for pure liquid Co and Ti, compared with the corresponding data available in the literature.^[32-38] The solid lines refer to the diffusion coefficients from the modified Sutherland equation. The dashed lines refer to the diffusion coefficients according to DICTRA assessment. The calculated self-diffusivity of Co by the modified Sutherland equation agrees reasonably with the theoretically predicted data by Yang et al.^[35] and Iida et al.^[36] It is clearly shown that the measured self-diffusivities of Ti^[37,38] can be well described by the modified Sutherland equation. The results show that the modified Sutherland equation can be used to calculate the diffusivity in liquid metals when there is no experimental or theoretical information on the diffusivity in liquid. The presently established diffusion database is given elsewhere.^[39]

4. Results and Discussion

4.1 Microstructure and Elemental Distributions

Figure 5 shows SEM micrograph of the cross section of the cemented carbide after sintering under vacuum at 1723 K for 1 h. In the micrograph, bright contrast is WC phase, grey is cubic phase, and dark is Co-rich binder phase. It is obvious that the near-surface of the alloy has formed the gradient zone which is enriched in binder phase and depleted in cubic carbides. The distributions of the elements Co, Ti, Ta and Nb on the gradient zone of the cemented

carbide are shown in Fig. 6. As seen from Fig. 6, the near-surface of the gradient zone is rich in Co, and inside the surface zone there is a depletion of Co. It is also shown that the elements Ti, Ta and Nb exist mainly in the cubic phase. The distributions of the elements Ti, Ta and Nb result from the similar diffusion behavior. According to the color contrast, some of the cubic phase has formed core-rim structure consisting of a (Ti, W, Ta, Nb)(C,N) phase. From the core to the rim, the content of the elements Ti, Ta and Nb decreases.

4.2 Diffusion Simulation

The thermodynamic^[26] and diffusion^[39] databases for cemented carbides described above have been established by experimental, theoretical and assessment methods. Although the databases^[26,39] can be used to perform thermodynamic and diffusivity calculations, the simulation of gradient zone formation by DICTRA is an indication to show the application of the established databases.

Figure 7 shows the measured and calculated phase fractions in the cemented carbide after sintering for 1 h at 1723 K in a N-free atmosphere. As can be seen in Fig. 7, the near-surface zone is free of cubic phase since the outward diffusion of N causes the inward diffusion of Ti. Inside the surface zone, the cubic phase appeared rapidly and reached a maximum. Because the inward diffusion of Ti leaves a lot of holes which could be fulfilled through the outward diffusion of Co, the binder phase is enriched in the near-surface zone. The WC phase has the highest content in the near-surface zone which is free from cubic phase. Subsequently, there is a decrease in WC phase because of the formation of the cubic phase. The presently calculated results are in good accordance with the presently experimental data. The measured thickness of the gradient zone is about 16 μm .

Figures 8(a)-(e) illustrates the experimental and calculated elemental concentration profiles for Ti, Ta, Nb, Co and W in the cemented carbide after sintering for 1 h at 1723 K in a N-free atmosphere. This result indicates that the elemental concentration profiles for Ti, Ta and Nb show the similar behavior. The content of Ti, Ta and Nb is free in the near-surface zone and enrichment inside the surface zone. At the near-surface zone, the content of Co increases sharply and reached a maximum value. Beneath the near-surface zone, a decrease of Co is observed, which leads to the minimum value. Above this minimum value, the content of Co increases slowly to its bulk value. The W curve has a maximum just at the surface of the cemented carbides. Comparing the concentration profile of W with the volume profile for WC phase, it can be seen that both curves show the same behavior. As can be seen in Fig. 8(a)-(e), the presently obtained thermodynamic and diffusion databases can reasonably reproduce most of the experimental concentration profiles.

5. Conclusion

A gradiently sintered WC-Ti(C,N)-(Ta,Nb)C-Co cemented carbides has been prepared by sintering at 1723 K for 1 h in a N-free atmosphere. The microstructure of the

gradient zone has been investigated with SEM, and the concentration profiles and distributions of the elements has been determined with EPMA. In order to accurately simulate the gradient zone formation of the cemented carbides by DICTRA, thermodynamic and diffusion databases for multi-component W-C-Co-Ti-Ta-Nb-N cemented carbides have been developed through a combination of experimental, theoretical and assessment work. Comparisons between the calculated and measured results show that most of the experimental data can be well reproduced by the presently obtained databases.

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