Ceramic Genome, Computational Modeling, and Design
DESIGN OF NEW GRANULAR COMPOSITE CARBIDES AND HARD COATINGS: THEORY

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Abstract: The concept of ceramic films in hybrid composites is a promising tool for composite process optimization and alloy design. This study of CALPHAD-type calculations in hybrid composites aims to optimize the properties of the ceramic phase and dilute for design purposes. The development of the ceramic phase and dilution elements is essential for the design of new materials. Several gradient, ceramic carbides and binary elements under various and varying partial pressures of CO and CO₂ in propane and nitriding conditions. Examples of ceramic composite applications to design and manufacture are shown using the database and comparing to experimental data, thereby validating their accuracy. Furthermore, TiAl4.92Cr carbides have been used as a process by fine-tuning their microstructure due to their excellent mechanical, chemical and thermal properties. Here we study the effects of addition on structure and thermal properties of TiAl4.92Cr carbides under the influence of CO₂ and CO. The preparation of TiAl4.92Cr by vacuum arc melting verifies these suggested carbides. (1C165-0412) 2019 Elsevier Ltd. All rights reserved.

INTRODUCTION

Ceramic carbides have long been used in applications such as cutting, printing, and drilling. Ceramics carbides are hard and tough and are characterized by a high combination of resistance to wear. The carbide is contained in a metal binder phase, usually rich in Cu. Under the carbide or carbide-like structure, the carbide is usually a mixture of a metal or alloy with a thin layer of hard material. Due to the high elongation temperature and a large difference in thermal expansion coefficients between the carbide and the binder, cracking can occur during cooling and final quenching. Also, the formed cracks might easily propagate into the carbide or cause failure when cutting tools are employed in metal machining. In order to prevent crack propagation from the carbide into the substrate, a galling type, which is dense of matrix phase and enriched in binder phase, is introduced between cutting tools and substrate.

In the past decades, ceramic carbides have been developed for a large degree of usage. However, their use necessitates understanding the microstructure and properties of ceramic carbides, such as sintering processes, sintering temperature, time, and partial pressure, and so on. These factors can only be varied in an infinite number of ways through experimental methods. In order to achieve this, experimental methods are necessary.
Design of New Gradient Ceramic Coatings and Heart Gaskets through Ceramic Coating Development

As the need for higher performance and improved durability is recognized, the concept of material science has been expanded. Computational, experimental, and database analysis are identified as three major components of materials science. Theoretical analysis can describe the interaction of the various microstructure conditions, which opens the opportunity to design and generate new kinds of ceramic materials more efficiently. CALPHAD (CALculation of PHAse Diagram) method is a general tool to establish the database for various properties of the ceramic system. Computational thermodynamics, using e.g., the Thermo-Calc and DICTRA programs, has been shown to be a powerful tool for generating thermodynamic databases in ceramic systems, which is more efficient for computation and process parameter optimization compared with experimental and phase equilibrium databases. With the development of thermodynamic and dilatometry databases, it is possible to make technical evaluations on commercial products which are multicomponent alloys. On the basis of thermodynamic databases, thermodynamic calculations can give an easy access to what plausibly these different temperature and alloy compositions would look like in the multicomponent alloys. By combining CMIF and DICTRA databases, CMIFDICTRA permits simulations of the gradient process, which is a major advance in the understanding of the gradient zone formation in the ceramic coatings.

Ti-Al bond coatings with oxides (or HfC) structure, where Al dilutes the Ti in the TiAl-based structure, (i.e., α(2) θ(2) TiAl3), are widely used in cutting tools because of their high hardness and wear resistance as well as good thermal properties. Because of the high dilution of α(2) TiAl3 in the Ti-45Al-5V-2Cr-3Nb and Ti-45Al-5V-2Cr-3Nb-4Ta, the transformation stability of TiAl3 coatings can improve the mechanical properties of coatings. Due to solid solution strengthening alloying Al to Ti-Al coating can improve the hardness. Unfortunately, a large amount of work is needed to find appropriate elements by using experimental methods, while thermodynamic calculations on the investigation of structural and mechanical properties can reduce the workload effectively and provide the reasonable explanation for the experimental observation.

This paper is devoted to 1) describe the development of the thermodynamic and dilatometry databases in ceramic systems, 2) design experiments to investigate the gradient zone formation under different cutting environments, 3) validate the accuracy and reliability of the presently established databases in ceramic systems by comparing the experimental and simulation results, 4) investigate the structural and mechanical properties of Ti-Al bond coatings by finite element calculations and experiment, and 5) present the multicomponent gradient coating strategy for the development of new ceramic coatings and bond coating.

Preliminary Studies on the Ceramic Gradient

Development of Thermodynamic and Dilatometry Databases

The development of thermodynamic and dilatometry databases in ceramic systems has advanced from the early days when the gradient oxides were considered. C-CaO-W-Ge-Cr-Al-O. The ranges of ceramic systems in many cases are not available, and thermodynamic and dilatometry databases provide data that is not only of high quality, but relevant to industrially complex materials.

Developed using the CALPHAD approach, the thermodynamic databases, CMIFDICTRA, is based on critical evaluations of theory, symmetry, and even higher order systems which models making predictions.
for multicomponent systems and alloys of industrial importance. The important phases in commercial alloys, e.g., Liquid, SCC, austenite, martensite, ferrite (Fe), and eta (\eta)/\gamma (\gamma') phases, are the main focus during this modeling. A large number of additional phases are also included in CSDSCM21, because many of the binary and ternary systems in CSDSCM21 have been reviewed over their entire composition range and multi-temperature range. In this report, a more detailed description for each alloy may be found in the compositional range of the phases. Most parameters apart from the total energy, many different features of the FeNiTiCr model: the transformation submodel of phase transitions, new phase nucleation, nucleation, and growth, phase transformations, etc. While some parameters are considered to be constant, many different features of the FeNiTiCr model, contours of the model, have been adopted for this phase in commercial steel systems. The thermodynamic models for Gibbs energy of a phase can be expressed by a general expression:

\[ \Delta G = \Delta G_{\text{mix}} + \Delta G_{\text{cond}} + \Delta G_{\text{heat}} + \Delta G_{\text{cond}} + \Delta G_{\text{dil}} \]  

Here, \( \Delta G_{\text{mix}} \) represents the Gibbs energy of the pure elements of the phases and \( \Delta G_{\text{cond}} \) represents the contribution due to the ideal mixing. The term \( \Delta G_{\text{heat}} \) represents the heat energy and \( \Delta G_{\text{dil}} \) the contribution due to the ideal mixing.

In contrast, the expression efficiency on the calculation of thermodynamic models for multicomponent commercial alloys, differences in the multicomponent commercial alloys have been reduced through experimental and thermodynamic. For a multicomponent system, a large number of additional phases and multi-temperature, containing a number of very complex. A purpose of the system is to describe the behavior of the chemical system at multi-temperature and multi-temperature and multi-temperature. A detailed description of the chemical system is given by the model by Anderson and Yeh. The standard stability for an element \( \text{Fe} \) can be expressed as:

\[ \Delta f_{\text{Fe}} = \Delta f_{\text{Fe}} (\text{Fe}) + \Delta f_{\text{Fe}} (\text{Fe}) / \Delta T \]  

where \( \Delta f \) is the first moment, \( T \) is the temperature, \( \Delta f_{\text{Fe}} \) is the frequency factor and \( \Delta f_{\text{Fe}} \) the activation entropy.

Using \( \Delta f_{\text{Fe}} \) and \( \Delta f_{\text{Fe}} \) and is for general thermodynamic and compositional multi-temperature.

The thermodynamic model is based on the model for the energy of the FeNiTiCr model, containing an intermetallic model with binary phases. Due to the presence of intermetallic phases, \( \text{FeNiTiCr} \) and \( \text{FeNiTiCr} \), these additional features in the model are included in the model (the intermetallic model). A is a mixed intermetallic model \( \text{FeNiTiCr} \), which is the volume fraction of the matrix, was introduced to measure the difference in the composition:

\[ \Delta f_{\text{Fe}} = \Delta f_{\text{Fe}} (\text{Fe}) / \Delta T \]  

First-principles Calculation of Liquid Controlling

First-principles calculations are one of the theoretical methods to study the microstructure and
The method is based on the density functional theory (DFT) with the local density approximation (LDA) and generalized gradient approximation (GGA). In the present work, first-principles calculations are performed by Vienna ab initio simulation package (VASP). The electron-ion interactions are described by the projector augmented wave (PAW) method, and the exchange-correlation is described by GGA and LDA. The energy cutoff of the wave functions is chosen to be 4.3 times higher than the kinetic energy in the pseudopotentials. The Kohn-Sham equations of k-point sampling and the linear extrapolation method including Fermi smearing are adopted for the integration in the Brillouin zone. The total number of k-points is at least 100,000 per irreducible zone for all the calculations. The convergence criterion for electronic self-consistency is $10^{-6}$ eV per atom cell.

The quasiharmonic approach is adopted to evaluate the static anharmonic Helmholtz energy as a function of volume $V$ and temperature $T$:

$$\mathcal{H}(V,T) = \mathcal{H}(V) + \mathcal{P}_{\text{el}}(V,T) + \mathcal{P}_{\text{an}}(V,T)$$

where $\mathcal{H}(V)$ is the total energy at 0 K; without the zero-point vibrational energy. $\mathcal{P}_{\text{el}}(V,T)$ is the vibrational contribution to Helmholtz energy with the input of plasma density of state (DOS) and $\mathcal{P}_{\text{an}}(V,T)$ is the thermal electronic contribution to the free energy, which can be calculated by Fermi statistics and with input of electronic DOS from first-principles directly.

The alloys were prepared from a powder mixture of W, Cr, Ti, Co, Cu, and Ni. The powder was provided by Zhejiang Rare Earth Factory and Dalian rare earth factory. The composition of the starting material is given in Table 1. After milling and blending, the powder was pressed into various tool inserts. Samples were sintered and sintered under different nitrogen partial pressures (0.2, 2.0 and 20) at 1223 K for 1 h. After sintering the samples were cut, embedded in resin and polished. TEM (Philips EM-208, USA) was employed to investigate the microstructure of the gradient zone, and XRD (CuKα, Bruker, D8, Bremen, Germany) was used to determine the crystallographic properties of the elements.

Table 1: Chemical composition of the investigated gradient carbides (vol%):

<table>
<thead>
<tr>
<th>Alloy</th>
<th>Ti</th>
<th>Co</th>
<th>Cr</th>
<th>W</th>
</tr>
</thead>
<tbody>
<tr>
<td>WC-Co</td>
<td>6</td>
<td>49</td>
<td>35</td>
<td>0</td>
</tr>
</tbody>
</table>

$\text{Ni}_{1-x}\text{Al}_{x}\text{Ti}_{y}$ fibers were deposited onto several substrates by electron beam evaporation in an Ar atmosphere (flow rate of 100 sccm) using a Balzers B300 with a turbo-pumped vacuum chamber. The chemical compositions of the fibers were determined using energy dispersive X-ray analysis (EDAX) with an Oxford Instruments X-Max 80. Phase identification and microstructure investigations of the fibers were carried out by cryo-deposition and cryo-deposition using a Bruker D8 diffractometer. XRD measurements were performed using the XRD method.
RESULTS AND DISCUSSION

Verification and Application of the Model

It is generally known that the graphite and c/a (6Hc to 1Hc) phases are metastable phases and the carbon content in carbonitride steels should be carefully controlled to avoid the formation of these phases. With the aid of thermodynamic calculations, it is easy to see how to control the carbon content and hence the carbon content helps the choice of changing temperature when developing a new alloy.

Figure 1(a) shows a calculated phase equilibrium diagram for the microstructure of an alloy with the composition of 2.0W-Nb-3.7Cr-1.8Mn-0.01N (wt%) For this case, the carbon content range is typically located in a narrow range about 0.2 to 0.2% to avoid the appearance of metastable phases.

Figure 1(b) presents a similar calculation by adding 0.1% of C. From Fig. 1(b) it can be seen that the melting point of harder phase is decreased substantially by adding carbon and the existence of the metastable phase (6Hc + c/a(1Hc)) WC equilibrium is minimized. On the basis of C2W1/NbC0.1, similar calculations can be performed on alloys with any composition, which will be a useful guidance for developing new alloys.

Figure 1. Calculated phase equilibria diagram for the microstructure of alloys with the composition of (a) C-2.0W-3.7Cr-1.8Mn-0.01N (wt%) and (b) C-2.0W-3.7Cr-1.8Mn-0.01N-0.1% (wt%) with 0.2% carbon.

Study of Heat Treatment: Examination on Microstructure Characteristics

Figure 2 shows SEM micrographs of the same section of alloys treated under different nitrogen partial pressures (0, 20 and 40 mtorr) at 1600°C for 1 hr. It is obvious that the microstructure of the alloy has formed the pearlite area which is surrounded by boride phase and distributed in colonies boundaries. Comparing the microstructure of the same section of the conventionally treated under different heat treatment temperatures shows that a decreasing thickness of pearlitic layers with increasing nitrogen gas pressure.
Figure 2. SEM micrograph of the cross section of silicate-sintered under different nitrogen partial pressures (0, 20 and 40 mbar) at 1400°C for 1 h.

By combining the generally established thermodynamic and diffusivity databases, CESTA software has been used to simulate the formation of the gradient zone. Figures 3(a)-(b) demonstrate the simulated elemental concentration profiles for Ce and Ti in silicate-sintered for 1 h at 1400°C under different nitrogen partial pressures (0, 20 and 40 mbar), compared with the measured data. This result indicates that the content of Ti is high in the near-surface zone and much lower in the surface zone. At the near-surface zone, the content of Ce increases sharply and reaches a maximum value. Beneath the near-surface zone, a decrease of Ce is observed, which leads to the minimum value. Above this minimum value, the content of Ce increases slowly to its final value. The calculated thickness of the gradient layer decreases with increasing nitrogen partial pressure, which shows the smaller diffusion behavior in the experimental results. As can be seen in Figure 3(a)-(b), the predicted simulation and diffusion databases can reasonably reproduce most of the experimental concentration profiles.

Figure 3. Concentration profile for (a) Ce and (b) Ti in silicate-sintered (symbols) and calculation (curve).

Ti-Al Crystalline Ceramics

Thermal analysis by DTA/DTG reveals that our Ti0.5Al0.5 melt-spun fibers are maintained with minimal reaction of 130°C decomposition at Ti0.5Al0.5 and 140°C decomposition at Ti0.5Al0.5, respectively. XRD investigations in Fig. 4 reveal a single phase cubic structure.
which is in agreement with the above calculations. Figure 5 presents the energy of dissociation (E_d) of the cubic and wurtzite Ti_{x}\_n Al_{1-x}N alloys with constant x = 0, 0.5, and 1 as a function of the AlN mole fraction x. These data suggest a transition from cubic to wurtzite at some Ti_{x}\_n Al_{1-x}N alloy composition for x = 0.54, 0.58, and 0.66 for x = 0.54, 0.58, and 0.66, respectively. Since the compositional range given by the minimum energy is different for the cubic (1111) and the wurtzite (1010) alloys, to evaluate the transition stability of AlN in the cubic phase we performed an analysis. First, we fitted cubic and wurtzite with constant x = 0.54 mole fraction with a quadratic polynomial (eq 4), with 1 test). For Ti_{x}\_n Al_{1-x}N, the AlN mole fraction x was varied 10 times for x = 0.0, 10 times for x = 0.056, and 10 times for x = 0.10. The calculations of x = Ti_{x}\_n Al_{1-x}N were repeated with 2, 3, and 5 variations in x for x = 0.0, 0.056, and 0.10, respectively. The composition range x = 0.5, 1. Subsequently, for each phase (cubic or wurtzite) we fitted independent polynomial coefficients (i.e., $a$, $b$, $c$) of their quadratic polynomial for the three different AlN mole fractions, x, with a linear regression in the 0.560 constants. This way, two polynomial fits (one for each cubic and one for the wurtzite composition) vs. composition of x (AlN mole fraction) and x (AlN mole fraction) were obtained. In the last step, we used these fits to estimate the curve over between the formation energies of the cubic and wurtzite phases without AlN mole fraction (and thus to estimate the influence of AlN in the maximum AlN mole fraction in the cubic Ti_{x}\_n Al_{1-x}N).

Figure 4. X-ray diffraction patterns obtained from the Ti_{x}\_n Al_{1-x}N films.

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Figure 5. (a) Energy of formation (kJ) for e-Ti0.2Al0.2Zn0.6M and cubic and wurtzite phases: Ti1-xAlxZn0.6M with x = 0, 0.25 and 0.5 as functions of AlN mole fraction. (b) Overall chemical compositions of one Ti1-xAlxZn0.6M film, in the as-deposited state, plotted within the TiN-AlN-ZnN equi-atomic phase diagram. The solid lines indicates the transition between preferred cubic and wurtzite phases.

Al nitride obtained mixing cathodoluminescence from the binary compounds e-TiN, c-ZnN, and w-AlN for e-Ti0.2Al0.2Zn0.6M, c-Ti0.2Al0.2Zn0.6N, c-Ti0.2Al0.2Zn0.6N, and e-Ti0.2Al0.2Zn0.6N are 104, 112, 179, and 1210 mV, respectively, and house increase with increasing AlN content. When using a cubic solid solution between TiN and ZnN, i.e., c-Ti0.2Zn0.8N (with y = 0.21-x) as a constituent instead in w-AlN, we obtain mixing cathodoluminescence of 104, 325, 477, and 1120 mV for x = 0, 0.25, 0.50, and 0.75, respectively. The latter reference and the comparison of the mixing cathodoluminescence with the XRD experiments, which exhibit an overall cubic contribution of 112, 132, 222, and 1400 mV for each of the compositions e-Ti0.2Al0.2Zn0.6M, c-Ti0.2Al0.2Zn0.6N, c-Ti0.2Al0.2Zn0.6N, and e-Ti0.2Al0.2Zn0.6N. Since TiN, c-ZnN, and w-AlN bulk into a Ti1-xAlxZn0.6M and w-AlN thin film used in the XRD analysis of samples annealed to various temperatures using the XRD equipment with the same ambient atmosphere, heating and cooling rates.

Figure 6 shows the structural evolution during annealing of the Ti0.2Al0.2Zn0.6M (b) film by means of XRD patterns after annealing at 100, 350, 1100, 1200, and 1500°C. The X-point-free Ti0.2Al0.2Zn0.6M film exhibits small shifts of the XRD reflections during annealing to 350°C, as compared with the as-deposited state, see Fig. 6a, suggesting only small structural changes like second and relaxation which contribute to the cubic mixing XRD features in this temperature range. The XRD patterns of the X-containing films Ti0.2Al0.2Zn0.6M and Ti0.2Al0.2Zn0.6M annealed to 350°C reveal a peak in the peak position to higher diffraction angles but also an increase in peak broadening, see Fig. 6b, c, and d. The latter is an indication for a reduction in grain size and an increase in microstrains which can result from the onset of a decomposition process. This can be clearly seen after annealing at 1100°C, where the XRD reflections exhibit on both sides (low and high diffraction angles) an increase in intensity and width, suggesting the formation of Al-depleted and Al-rich domains. After annealing at 1100°C, a pronounced single-lobe formation on both sides of the "window" XRD peak can be seen clearly. These simulations indicate the formation of TiN and AlN with either domain for Ti0.25Al0.25Zn0.6N and Ti0.25Al0.25Zn0.6N with either domains for the X-containing films. While the X-free film Ti0.25Al0.25Zn0.6N exhibits the formation of w-AlN immediately after annealing at 1100°C, no
In the present study, several novel concepts of nanostructured materials have been developed. In the present study, as shown in Fig. 1, the growth concept of nanostructured materials for cemented carbide was proposed. Finally, all elements of growth concept and process parameters are designed via CALPHAD or first-principles calculations. Similarly, the growth concept of nanostructured materials and mechanical properties can be predicted based on the growth concept. Thirdly, a series of experimental nanostructured materials and hard coatings was prepared under the guidance of the growth concept. After that, the microstructural and mechanical properties of the nanostructured materials and hard coatings were investigated experimentally. Finally, validating the accuracy of the calculations/calculations. Thus, results were optimized and finally chosen for industrial production of nanostructured materials with excellent mechanical properties.

Figure X. Designed and manufactured industrial nanostructured carbide with the incorporation of TiCN.

High Temperature Ceramic Alkaline Compositions
CONCLUSION

The ceramic gradient is a powerful tool for materials process optimization and alloy design. Thermodynamic databases and diffusivity databases for ceramic carbides have been developed through a combination of experimental, theoretical and numerical work. Gradient carbide ceramics, WC-TiC(75)Cr-Co, obtained under various partial pressures of H2, have been prepared and investigated by means of SEM and XRD techniques. Good agreements between simulated and measured results indicate the soundness and validity of the presently established databases for ceramic carbides design and process optimization. The structure and thermal properties are investigated using experimental methods combined with first-principles calculations. Based on the results presented, we can conclude that the resulting WC-TiC(75)Cr-Co which contains only 25% WC, the novel carbides exhibits the best mechanical and thermal properties. A schematic ceramic gradient strategy to develop new gradient carbides and hard coatings is presented.

ACKNOWLEDGEMENT

The financial support from Creative Research Group of National Natural Science Foundation of China (Grant No. 51021003) and Fuzhou cemented carbide cutting tool limited company of China is acknowledged.

REFERENCES


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