On gradient formation in alternative binder cemented carbides☆

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ABSTRACT

In this work ICME (Integrated Computational Materials Engineering) has been applied to help understanding gradient formation in today's state-of-the-art cutting tool inserts. The approach was used to carefully design the experimental setup to learn about the controlling mechanisms on gradient formation in Co/Ni/Fe binder systems. The model considers activities, phase fractions and solubilities of diffusing elements in the liquid in these multicomponent systems. It was observed that the gradient thickness is the same for Ti-W-C-N-Co and Ti-W-C-N-Ni at 1410 °C - despite the higher solubility of Ti in liquid Ni compared to Co. This was also true for more complex Ti-Ta-Nb-W-C-N-Co and Ti-Ta-Nb-W-C-N- Fe-Ni at 1410 °C in this study. At 1450 °C the gradient thickness increases for all binders, showing a large increase in the gradient thickness. The thickest gradient was observed for X = Ni in the Ti-W-C-N-X system and thinest for X = Fe binder despite similar N and C activity differences. The Ti-Ta-Nb-W-C-N- Ni-Fe (85Ni-15Fe) had a thicker gradient compared to the Ti-Ta-Nb-W-C-N-C- Co system.

1. Introduction

Gradient sintered cemented carbides are used in steel turning and then coated with a multilayer Chemical Vapor Deposition (CVD) coating. Gradient sintered cemented carbides consists of a surface zone enriched in binder phase and depleted of γ-phase compared to the bulk. The major impact of the γ-phase free surface zone is that it is tougher than the bulk and thus effectively stops the cracks in the CVD coating (formed during the cooling step of the deposition process) from propagating into the cemented carbide and thereby retarding bulk breakage. Another important feature is that the gradient forms a cone of γ-phase that stretches out to the insert edge and hence reinforces the edge so it can withstand higher temperatures before thermal softening sets in. Gradient sintered cemented carbides consist of WC + binder + γ-phase (where γ-phase is a (Ti,Ta,Nb,W)(C,N)) where the surface zone depleted of γ-phase usually is around 20–30 μm.

Gradient sintered cemented carbides were first developed by Suzuki, Nemeth and Yohe [1–3] in the 1980s [1–3] and the governing mechanisms were explained by Schwarzkopf [4] and later further clarified by Gustafsson [5]. The gradient is created during the sintering step by having a lower nitrogen and or carbon activity in the furnace atmosphere than in the material [2,4,5]. Thus, nitrogen will degas from the surface of the insert then Ti will diffuse inwards to areas richer in N due to its very high affinity to N and due to the overall potential equilibrium [4–7]. The Ti containing γ-phase close to the surface will

dissolve in the liquid binder and it will gradually deplete in the surface zone. The controlling mechanisms for gradient thickness and growth are as given by [4,5] the nitrogen activity difference between the cemented carbide body and the atmosphere, the amount of liquid binder and the volume fraction of γ-phase. Gradients have been successfully modeled qualitatively by Ekroth [6,7] using the Dictra software [8]. In these cases, based on the assumption of equal mobilities of all elements in the liquid, later it has been shown that depending on the liquid mobilities the gradient thickness is altered [9–12]. It is also important for metal cutting insert to have the so-called cone, however, as shown by Schwarzkopf and Gustafson [4,5] this will not form if the gradient growth is only limited by N loss at the surface, because the gradient will be thicker at corners as N is here lost from more several surfaces. However, if the growth is limited by the solubility of an element in the liquid, such as Ti, this will create a cone, due to the geometrical effect that at the corner the element is enriched to the liquid from several directions and thus the solubility limit reached earlier. When there is abundance of N the limiting factor controlling the growth of the gradient switches from Ti in-diffusion to rate of N loss; in this case, no cone will form at the corners.

In this work, we investigated gradient formation in cemented carbides with Co, Ni and Fe alternative binders as well as Ni-Fe binders using the ICME approach and we compared the results to previous published works. The simplified model developed for Co based systems is used [4,5]. The model describes if the gradient is predictable by a

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difference in activity, phase fraction and time, but it does not account for differences in diffusivities or mobilities to mention some limitations. To gain more understanding more sophisticated models like Dictra should be used. Despite its limitations it is a rather rapid tool to use as a first approach in systems where a lot of data is lacking or uncertain; keeping in mind that the level of uncertainty is probably high.

2. Experimental

2.1. Material and gradient design

The carbon activity was $a_C = 0.6$ in the liquid for all experiments. This is a rather high carbon activity for gradient cemented carbides but was selected to ensure that the Ni-rich systems are in the WC + γ + liquid region at 1410 °C but still have a carbon content high/low enough to avoid η-phase or graphite formation at lower temperatures during cooling.

2.1.1. First series pure binders
With the aim of investigating if it is possible to predict the gradient thickness by the known gradient controlling parameters three simple cemented carbides were made of Co, Ni and Fe using only Ti as γ-phase former. The Thermocalc software and the TCFE7 database were used, despite it is not developed for Ni binders [13]. The simplified model by Gustafson and Östlund [5] was used to modeled the gradient zone, Eq. 1:

$$Gradient\ zone = C\frac{f^{liq}}{f^\gamma}\sqrt{\Delta aN\bullet t}\tag{1}$$

where f^{liq} is the fraction liquid and f^γ is the fraction of γ-phase, $\Delta a_N = a_{NSample} - a_{Nfurnace}$ is the nitrogen activity difference, C is a constant and t is the time at liquid phase sintering.

The alloys were designed setting the conditions of Eq. 1 so that the amount of Ti was fixed to 6.5 at.-% thereby giving the f^γ; f^{liq} = was set to 0.135, the nitrogen content in the carbide was set to reach an activity of 0.13 using N_2 gas as reference state and the carbon activity was fixed to 0.6 using graphite as reference state, since the carbon activity will influence the nitrogen activity. Finally, one mole of atoms, ambient pressure (101,325 Pa) and temperature of 1410 °C was set to determine the system per Gibbs phase rule. The resulting calculated compositions of the alloys are given in Table 1. The calculated solubilities of N and Ti in the liquid at 1410 and 1450 °C are given in Table 2. At 1450 °C the nitrogen activity is 0.23–0.24 and the carbon activity increases to 0.62–0.63 keeping the compositions calculated at 1410 °C constant. The nitrogen activity in the furnace were set to 0 in all calculations.

2.1.2. Second series mixed binders
In the second part a pure Co alloy and an alloy with a Ni-Fe binder phase were compared (Table 3). The conditions were here equally set to a temperature of 1410 °C, the mole fraction liquid was set to 0.135, the amount of Ti, Ta and Nb was set equal in at-% for the two alloys, the carbon activity (using graphite as reference state) was 0.6, the nitrogen gas activity was 0.13 (using N_2 gas as reference state). Then the Fe and Ni contents were optimized in the calculation as to target an alloy that has the same content of N and Ti in the liquid as the Co-based alloy. The final composition reached was 85w.-% Ni and 15w.-% Fe at a sintering

temperature of 1410 °C. Therefore, if Eq. (1) is also valid in these mixed alloy systems, the gradient thicknesses should be equal for these two cemented carbides after sintering at 1410 °C for a constant time (in this case 1 h).

2.2. Powder processing and sintering

Samples were produced by powder metallurgical routes using the same WC raw material, Co raw material (Freeport), Ni-Fe (H.C. Starck) and cubic carbides Ti(C,N), NbC, TaC (Treibacher). Additional carbon was added to compensate for the carbon loss during sintering. The powders were milled in 0.25 l mills for 8 h and pan dried. Powders were uniaxial pressed (ISO SNUN geometry) and vacuum sintered for 1 h at 1410 °C and 1450 °C using 25 mbar CO + 25 mbar Ar. No nitrogen gas was added in the furnace. After sintering samples were cut, grinded and polished using diamond paste. Light optical microscopy (LOM) images were taken on Murakami etched surfaces.

3. Results and discussion

3.1. First series single binders- Co vs Ni vs Fe

After sintering at 1410 °C the gradient thickness for the cemented carbides with pure Co, Ni and Fe gave gradient thicknesses of 27, 28 and 0 μm respectively. Equal gradient thickness for Co and Ni binders were produced. The Fe-based carbide ended up in the η-phase region due to the very narrow carbon window using Fe [14], see Fig. 1-C. Sintering at 1450 °C gave thicker gradients of 33 μm, 42 μm and 8 μm for the Co, Ni and Fe based respectively (here the carbon content had been increased for the Fe-variant), see Fig. 2. As expected and already observed in the mixed Ni-Fe and Co-Fe systems [10] as well as in the pure Co system, higher temperatures increase the gradient thickness, since the gradient formation is diffusion-controlled process. Due to the high N content in these samples no cone was observed at the corners, indicating that the process is controlled by N rather than by Ti-solubility in this case; compare Figs. 3 and 4.

3.2. Second series mixed binders

The W-C-Co-Ti-Ta-Nb-N is a seven and Fe-Ni an eight-component system. Hence, at a given P and T, the Gibbs phase rule gives that there are 9 and 10 degrees of freedom. The Co-based system was calculated for one mole (n = 1), P = 101,325 Pa, T = 1410 °C and with constant conditions of Δa_C, Δa_{N2}, f^{liq} as well as given atomic percentages of Ti, Ta and Nb which impacts the f^γ. As mentioned the Ni and Fe contents were optimized to match or come as close as possible to the content of Ti and N at 1410 °C in the Co based system, (both cannot be set as it would make the system overdetermined). Fig. 5 displays the gradient thickness, far away from the corner (6 mm), for the alternative binder and reference they are equal or within experimental errors after sintering at 1410 °C for 1 h (Table 4). Hence, the gradient thickness can be tailored also for these systems. In this series, the inserts have a cone at the corners for both the alternative binder and reference at both 1410 °C (Fig. 6) and at 1450 °C. In Figs. 5 and 6 it can also be observed that the Ni-Fe insert has macro pores (black) and binder lakes (white) indicating that this temperature is too low for this composition to be of practical importance. No regard has been taken to the porosity in this study which of course might be a source of error.

3.3. Discussion

In this work the carbon loss during sintering was compensated by adding carbon to the powder. However, the N-loss during the open porosity of the sintering stage was not accounted for and assumed to be the same for all alloys. This is probably not the case as they would reach closed porosity at different temperatures and need to be investigated in

Table 1
Composition of the cemented carbides.

Binder	at.% Ti	at.% Co/Ni/Fe	at.% C	at.% N	at.% W (balance)
Co	6.50	10.93	40.79	3.84	37.95
Ni	6.50	11.25	40.54	3.73	37.98
Fe	6.50	10.24	41.79	3.85	37.63