

Preparation, composition and some properties of codeposited TiB_2 - TiC_x -coatings

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Heterogeneous TiC_x and TiB_2 containing layers have been deposited from the gas phase onto hard metal and tantalum substrates in a cold wall reactor. The process parameters were thermodynamically calculated and verified by experiments. The deposited layers have been characterized regarding the chemical composition, structure, microhardness and abrasion wear. In a large composition range a characteristic layer structure is observed. Microhardness and abrasion wear run in dependence on the layer composition through a peak factor.

1. Introduction

Besides the characteristic material properties the tribological behaviour of hard coatings depends on their structure. For example, it was found by Holleck [1] that alternating sputtered TiC - TiB_2 layers with a large number of coherent phase boundaries have a better wear resistance than the single phase layers due to an enhanced adherence and toughness. A higher bending strength of PVD TiC - TiB_2 multilayers in comparison with single phase layers was also measured by Movchan *et al.* [2]. According to Tkachenko *et al.* [3] as well as Holleck [4] sintered composites containing carbides (TiC , ZrC), borides (TiB_2 , ZrB_2) and other hard materials (SiC , B_4C , Al_2O_3) yield a better wear behaviour to abrasion and more favourable mechanical properties than the sintered single phases. Especially, MeC - MeB_2 samples ($\text{Me} = \text{Ti}$, Zr) of eutectic composition (approximately 60 wt % TiB_2 or 50 wt % ZrB_2) revealed a maximum in the bending and compression strength, whereas the microhardness is characterized by a minimum. Some investigations point to superplastic properties of those samples [3, 5].

Though the development of CVD multilayers, consisting of thin homogeneously composed single layers has been forced in recent years [6, 7], the deposition and investigation of heterogeneous multiphase layers found less interest. In this paper the codeposition of TiB_2 and TiC_x from the gas phase is experimentally investigated and thermodynamically calculated. Furthermore, mixed layers from TiB_2 and TiC_x deposited on hard metal substrates were characterized.

2. Thermodynamics of the system Ti-B-C-Cl-H

Using the method of minimization of free energy the deposition conditions for TiB_2 - TiC_x mixtures were calculated at 1300 K. The ternary system Ti-B-C is qualitatively known at higher temperatures (Fig. 1). There is no ternary compound in this system. The mutual solubilities of TiB_2 and TiC_x at a temperature

of about 1300 K are unknown. According to investigations at higher temperatures [9] they are small and could be neglected. The stoichiometry of TiC_x changes relatively strong in the coexistence range with TiB_2 . Therefore the dependence of free energy of TiC_x on the composition was taken into consideration with the following relation [10]

$$\Delta G_f^0 = -593.366 + 191.056x + 275.064\left(\frac{1}{x}\right) - 42.006\left(\frac{1}{x^2}\right)$$

where ΔG_f^0 is expressed in kJ mol^{-1} . This is related to the reaction $\text{Ti}_s + x\text{C}_s = \text{TiC}_x$. The data of the other considered gaseous and solid species (TiCl_4 , TiCl_3 , TiCl_2 , TiCl , BCl_3 , BHCl_2 , CH_4 , C_2H_2 , H , Cl , Cl_2 , H_2 , HCl , B_g , C_g , Ti_g , TiB_2 , TiB , B_4C , B_s , C_s) were generally taken from thermodynamic tables in [11] except for BHCl_2 and TiB_2 which were derived from [12] and [13], respectively. Some results of the calculations are shown in Figs 2–5, where n is the number of moles, p^{x_0} is the balance pressure of initial state, and x

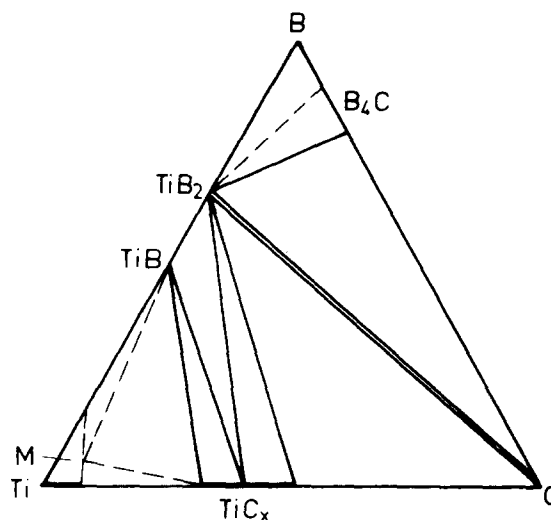


Figure 1 Ternary system Ti-B-C at 2073 K [8].

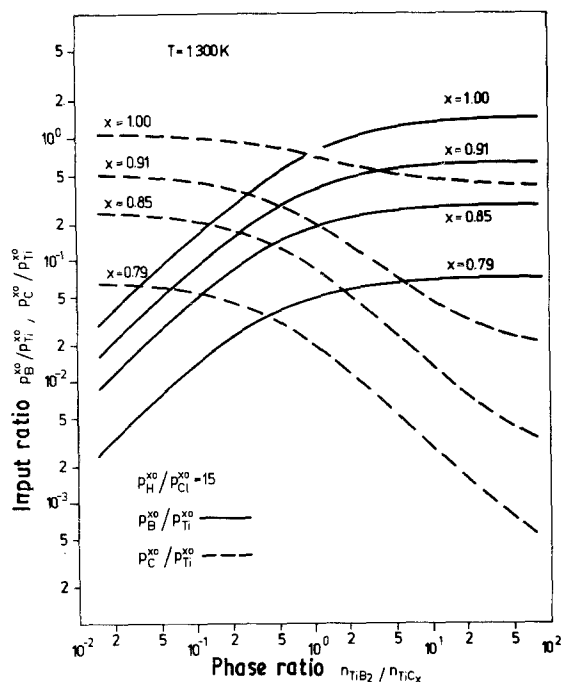


Figure 2 Change of phase ratio in the solid with the gas phase composition.

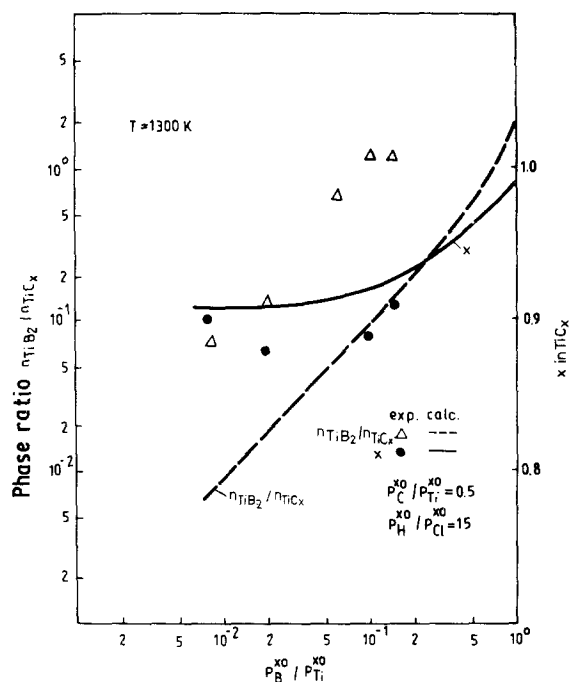


Figure 4 Influence of the B/Ti ratio on the $\text{TiB}_2/\text{TiC}_x$ -phase ratio and the stoichiometry of TiC_x .

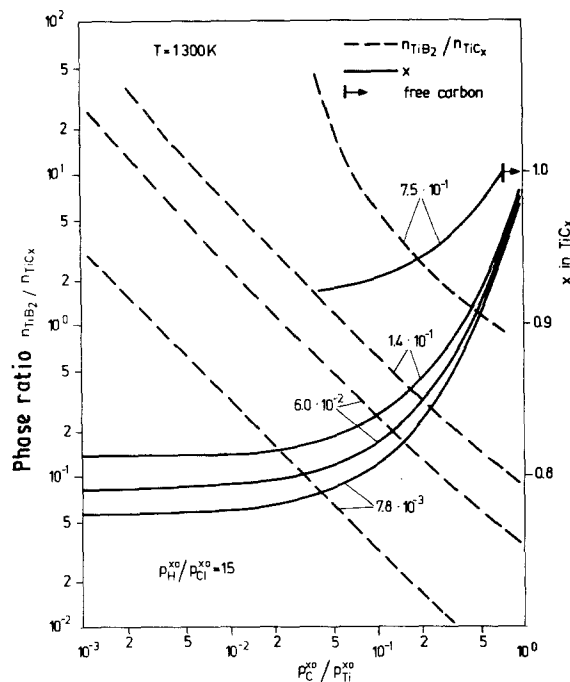


Figure 3 Influence of the C/Ti-ratio on the $\text{TiB}_2/\text{TiC}_x$ -phase ratio and the stoichiometry of TiC_x . The parameter denoted on the curves is the ratio p_B^x/p_Ti^x .

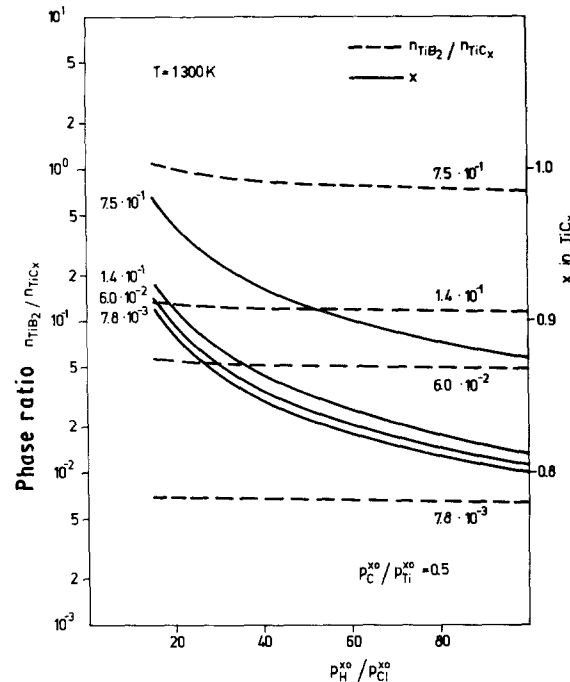


Figure 5 Influence of the H_2 content on the $\text{TiB}_2/\text{TiC}_x$ -phase ratio and the stoichiometry of TiC_x . The parameter denoted on the curves is the ratio p_B^x/p_Ti^x .

is the stoichiometric coefficient of TiC_x . In Fig. 2 the change of composition of the deposited solids in dependence on the initial balance ratios is shown for fixed compositions of TiC_x . With the aid of an iteration procedure the limit composition of TiC_x in coexistence with TiB_2 at 1300 K was found to be $x = 0.75$.

In the Figs 3–5 the influence of the deposition parameters on the composition of the solids (phase ratio and composition of TiC_x) is illustrated more in detail. It is remarkable that the hydrogen content

(Fig. 5) has only a small influence on the phase ratio of the solid. Figs 3 and 4 show that the stoichiometry of TiC_x is growing with the increase of the B/Ti-ratio in the gas phase.

3. Experimental details

Deposition experiments have been performed at 1300 K using an inductively heated cold wall reactor. The starting substances were TiCl_4 , $n\text{-C}_7\text{H}_{16}$, BCl_3 , and H_2 . In some cases benzene and BBR_3 were used

instead of $n\text{-C}_7\text{H}_{16}$ and BCl_3 , respectively. As substrates hard metal cutting plates or Ta sheet were used. The layers deposited on Ta sheet could be easily removed and were investigated by chemical analysis (determination of Ti, B), gas analysis (C, O_2 , and N_2 content), activation analysis (detection of Ta), as well as X-ray diffraction. The coated hard metal substrates have been characterized by metallographic techniques, EPMA, X-ray diffraction, microhardness measurements, and wear tests (turning of cast iron).

4. Results

4.1. Interactions in the interface range

In the case of Ta-substrates the interactions between the layer and the tantalum could be neglected at 1300 K, as it was confirmed by low adherence of the layers and by their Ta-content, which was found to be 0.1 wt % or lower. If the coatings were directly deposited on the hard metal substrates, the formation of brittle intermediate layers was observed. An extreme example is given in Fig. 6, where the cross section of a WC/Co substrate coated with TiB_2 is shown. Three intermediate layers are visible. According to the relative X-ray intensities of the elements in the interface region the compounds denoted in the figures subscription seem to be the main components of these layers.

By deposition of intermediate TiC, TiN or TiCN layers of some micrometer thickness the diffusion of B into the substrate and of Co in the direction of the growing layer is decreased. Thus it is possible largely to avoid undesired interaction until about 1273 K at short deposition times.

4.2. Composition and structure of the layers

Both in coatings on hard metal substrates and on Ta-substrates no other phases besides TiB_2 and TiC_x have been detected by X-ray diffraction.

The O_2 content in the layers amounted to 1–3 wt %, the N_2 content to 0.05–0.1 wt %. Assuming that the total B amount is present as TiB_2 we have calculated

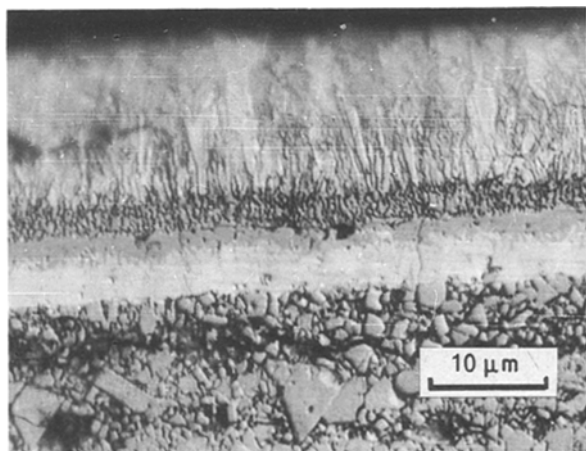


Figure 6 Cross section of a TiB_2 coated WC-Co-substrate. Layer sequence beginning from the top: $\text{TiB}_2\text{-TiC}_x + \text{Co}_x\text{Ti}_y\text{B-zTi(W)C}_x\text{-CoWB}$.

from the analytically determined Ti, B, and C content the molar ratio of TiB_2 to TiC_x and the stoichiometric coefficient x in TiC_x . The medium values which in most cases were obtained from two experiments are shown in Fig. 4. It should be mentioned in this context that the layer composition and the deposition rate are independent of the flow rate of gases in an extended range ($2\text{--}32\text{ cm s}^{-1}$). Figs 7 and 8 show chemically etched ($\text{HF:HNO}_3\text{:H}_2\text{O} = 1:1:1$) metallographic cross-sections of characteristic samples. Layers with a very low TiB_2 content ($< 7\text{ mol \%}$) are deposited in a granular structure.

At higher TiB_2 amounts the coatings exhibit structures, which are composed of numerous thin fine-

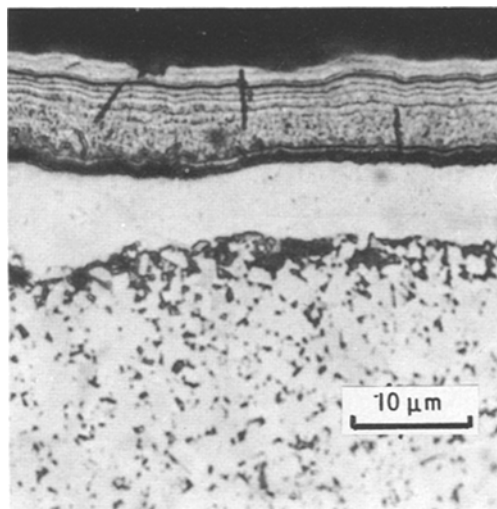


Figure 7 $\text{TiC}_x\text{-TiB}_2$ layer, granular grown in the beginning (inter-layer: TiC_x , substrate: WC/Co).

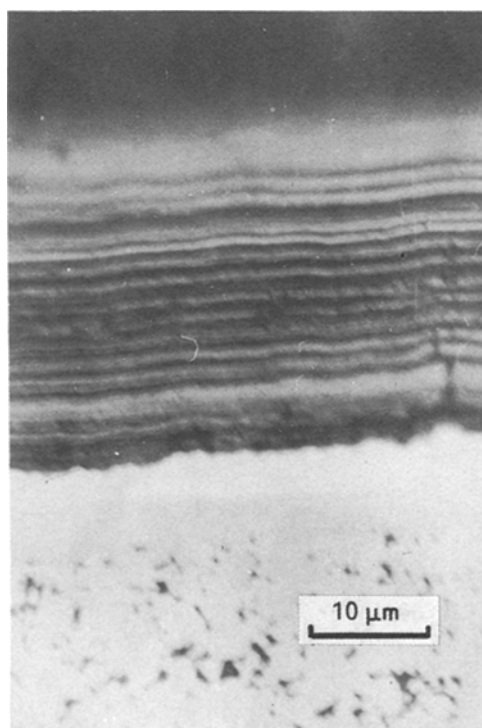


Figure 8 $\text{TiC}_x\text{-TiB}_2$ coating with layer structure (interlayer: TiC_x , substrate: WC/Co).

grained layers. The depth of the single layers amounts to about 1 μm and increases with increasing TiB_2 content. Their fine structure could not be resolved by light microscopy. According to X-ray analysis the layers with about equal portions of phases are especially favoured to form imperfect lattices; for this reason an exact phase-analytical characterization of the layer structures in this composition range was impossible. As was demonstrated by Auger spectroscopic investigations, the B to C ratio in the single layers changes in an alternating way. Furthermore, it was found that the mixed layers exhibited none or only weak textures, whilst single phase TiC_x and TiB_2 -layers form strong growth induced textures.

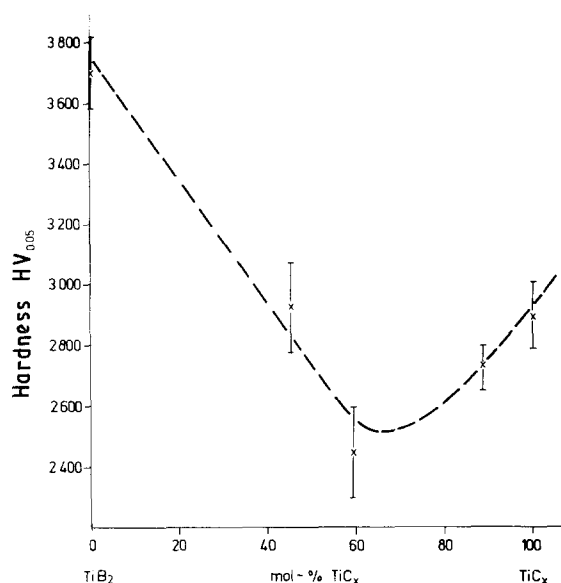


Figure 9 Dependence of the microhardness on the layer composition.

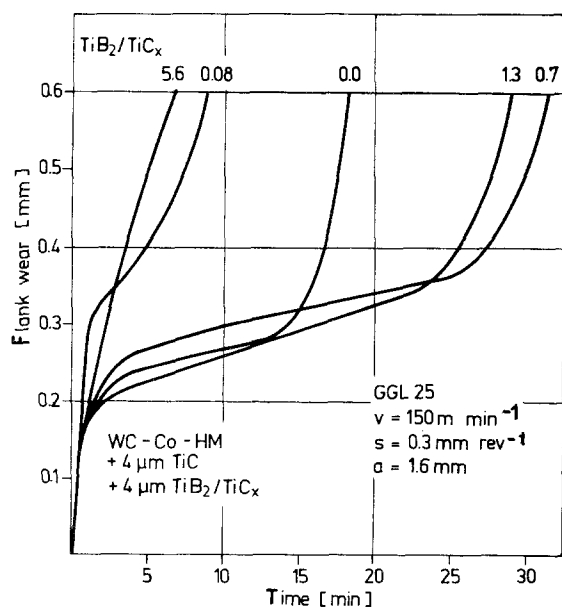


Figure 10 Wear behaviour of differently composed TiB_2 - TiC_x layers.

4.3. Hardness and wear behaviour of the layers

Vickers microhardness measurements have been performed with layers of a different TiC_x to TiB_2 ratio. Even if the scattering of the results is relatively high, a relationship between the hardness and the layer composition is apparent (Fig. 9). At about 60 mol % TiC_x in the layer the hardness reveals a minimum.

In Fig. 10 the results of some turning tests against cast iron are summarized. The best cutting times were found for layers containing TiB_2 and TiC_x in a molar ratio of about 1:1. A low or high TiB_2 content in the mixed layers strongly deteriorate the wear behaviour. Pure TiB_2 is also unsuitable for turning cast iron and steel.

5. Discussion

The intermediate layers observed in the case of direct deposition of boron containing layers on WC/Co substrates, are the result of solid-solid reactions and the diffusion of the elements in the interface range. The arrangement and composition of the observed layers point to a rather quick diffusion of the elements Co, B and C.

As Fig. 4 shows the experimentally determined dependence of chemical layer composition on the deposition conditions is qualitatively in agreement with the calculated one. However, the absolute values of the experimentally determined phase ratios exceed the calculated ratios by about one order of magnitude and the stoichiometric coefficient x does not reach the theoretical values. The difference between the experimental and theoretical values can be explained neither by experimental mistakes (e.g., analytical uncertainties) nor by incorrect thermodynamic data. We assume an insufficient adjustment of equilibrium at the substrate surface to be the reason. In this context we point to the fact, that kinetical effects were also observed by Besman and Spear [14] in the chemical vapour deposition of TiB_2 at temperatures lower than 1373 K. Therefore it is likely, that under the applied experimental conditions both the deposition of TiC_x and TiB_2 are controlled by the kinetics. This assumption is supported by the observed independence of the layer composition as well as deposition rate on the flow rate which presupposes, that the deposition of both phases is kinetically controlled. Because the TiB_2 content of the layers exceeds that thermodynamically expected, a stronger kinetical effect has to be assumed for the TiC_x deposition. Using the less reactive benzene instead of heptane the differences between the deposited and calculated layer compositions were much larger, yet.

We consider also the layered structures with their alternating change of composition to be a result of deposition kinetics. Indeed, it is possible to avoid the layer formation by an increase of deposition temperature by about 100 K.

The results of the microhardness measurements and the wear tests reveal the same tendency as reported for sintered material [1], namely a minimum of hardness and optimum wear properties at about equal phase portions in the layer. Possibly, similar microplastic

processes in the phase boundaries of the fine-grained layered structures exist as in sintered samples.

6. Conclusions

By codeposition from the gas phase heterogeneous TiC_x-TiB_2 layers of any composition are available. The phase ratio of TiC_x to TiB_2 in the deposited layers strongly depends on the gas phase composition. At temperatures of about 1300 K the deposition process performed in a cold wall reactor is kinetically controlled. The thermodynamic calculations are only in a qualitative agreement with the real deposition behaviour. The deposited layers exhibit a layer structure in a wide composition range.

Layers containing about equal concentrations of TiC_x and TiB_2 reveal a minimum of microhardness and a maximum wear resistance (abrasive wear).

The application of heterogeneous CVD-layers for wear protection presupposes a deeper understanding of the correlations between deposition conditions, structure and wear properties.

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