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Microstructural study of titanium carbide coating on cemented carbide

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Titanium carbide coating layers on cemented carbide substrates have been investigated by transmission electron microscopy. Microstructural variations within the typically 5 μm thick chemical vapour deposited TiC coatings were found to vary with deposit thickness such that a layer structure could be delineated. Close to the interface further microstructural inhomogeneities were obsered, there being a clear dependence of TiC deposition mechanism on the chemical and crystallographic nature of the upper layers of the multiphase substrate.

1. Introduction

The life of cemented carbide cutting tools is substantially improved by titanium carbide coatings produced by chemical vapour deposition (CVD). In the CVD process, a gaseous mixture of $TiCl_4$, H_2 and CH_4 is passed over the cemented carbide substrate at temperatures of the order of 1000° C. The structure and morphology of the TiC coating, typically 5 μm thick, has been shown by a number of investigations, using optical, scanning and transmission electron microscopy techniques, to be complex [1–5]. Since the mechanism of nucleation and growth of the coating is both substrate and vapour-phase controlled, microstructural variations occur with deposit thickness. Additionally, changes within the upper regions of the substrate occur both as a result of decarburization and diffusion between cemented carbide component phases.

Cemented carbides are basically two-phase materials resulting from the liquid-phase sintering of cobalt and tungsten carbide. The structure is thus of a relatively ductile binder phase of a cobalt-rich solid solution of Co, W and C and a relatively brittle hard phase of angular grains of pure hexagonal WC. Cubic transition metal carbides, referred to as γ-carbides, are often added in small quantities to improve wear resistance. The bulk substrate microstructure so described is subject to surface decarburization during the CVD deposition of TiC coatings. This results primarily in the formation of a brittle carbide of tungsten and cobalt referred to as η-carbide. The composition and thickness of sub-coating layers of η-carbide have been the subject of recent studies [4, 6, 7]. Although the η-carbide layer may be up to 5 μm thick it is generally reduced by pre-carburization [6].

The present transition electron microscope (TEM) study is a detailed examination of the microstructural and crystallographic features of the TiC coating and in particular of the interface between TiC and the cemented carbide substrate. The results are based upon the observation of thin foils taken from within and parallel to the 6 μm thick TiC deposit as well as from cross-sections through the coating.

2. Experimental procedure

All foils for transmission electron microscopy were prepared from commercially available CVD TiC-coated cemented carbides (Sandvik Coromant GC 1025) containing approximately 6 wt% Co, 5 wt% γ-carbides [(Ti, Ta, Nb) C] and 89 wt% WC.

Specimens were sectioned by low-speed diamond sawing and then carefully thinned by diamond polishing to obtain wafers approximately 30 μm thick. Electron transparent specimens were obtained by ion-beaming milling. In order to obtain thin foils within, and parallel to the coating layer, ion-

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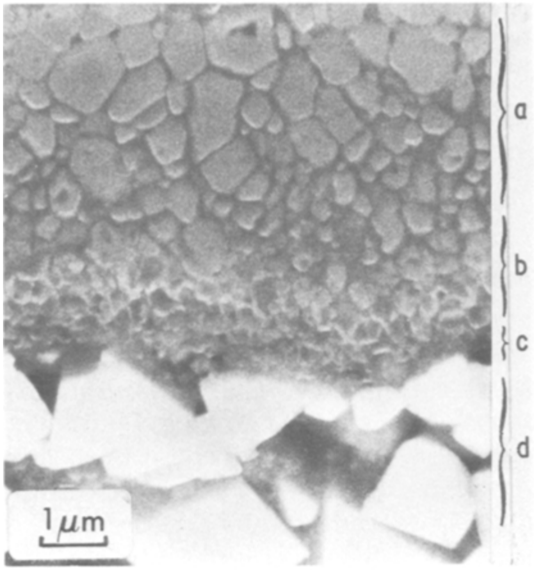

Figure 1 SEM showing TiC coating on cemented carbide substrate. A multi-layer structure may be delineated.

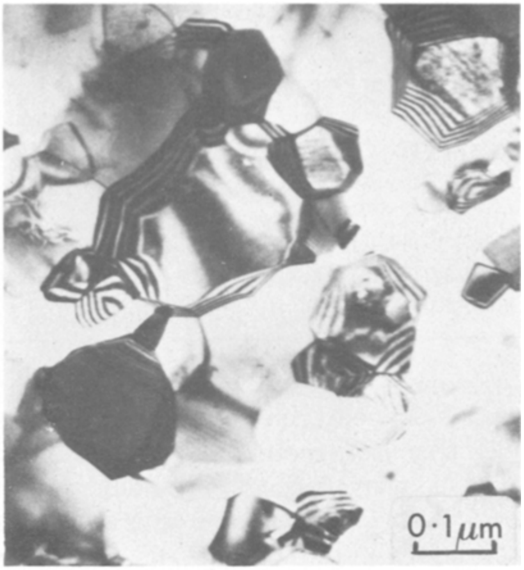

Figure 2 A bright-field transmission electron micrograph of CVD TiC in the "interfacial carbide" layer.

beam milling was predominantly carried out from the polished wafer surface opposite to that covered by the TiC coating. The final stages of thinning were controlled by intermittent observation in the scanning electron microscope (SEM). For cross-sectional specimens, the coating could be preserved during ion-beam milling by mounting two mechanically polished wafers in the ion-beam thinner holder so that the TiC coated surfaces lay edge-to-egde. Transmission electron microscopy was carried out using a JEOL 200 A operating at 200 kV.

3. Microstructural observations

The observations reported here are connected with the microstructural variations within the CVD deposited in the upper region of the hard metal substrate and the details of the TiC–substrate interface.

The results were obtained from electron transparent regions of thin foils containing the TiC–substrate interface or from thin regions entirely within the 6 μm thick TiC coating. Individual TEM micrographs from positions within the coating and interfacial layers are located by reference to SEM observations of perpendicular sections through the coating, see Fig.1.

3.1. The structure of the TiC coating

The TiC coating is composed of two distinct regions. There is thus a layer close to the substrate and extending to a thickness of 1.5 to 2 μm which is composed of fine, equiaxed TiC grains, as shown in Fig. 2. In this "interfacial carbide" layer the average grain size is of the order of 0.1 μm but is by no means uniform. Regions of extremely fine grain size (~ 0.01 μm) could be found, predominantly in close connection with the cobalt areas of the substrate surface (Fig. 3). In the areas of interfacial carbide immediately above γ-carbide grains, the TiC grain size is increased to 0.2 μm to 0.5 μm.

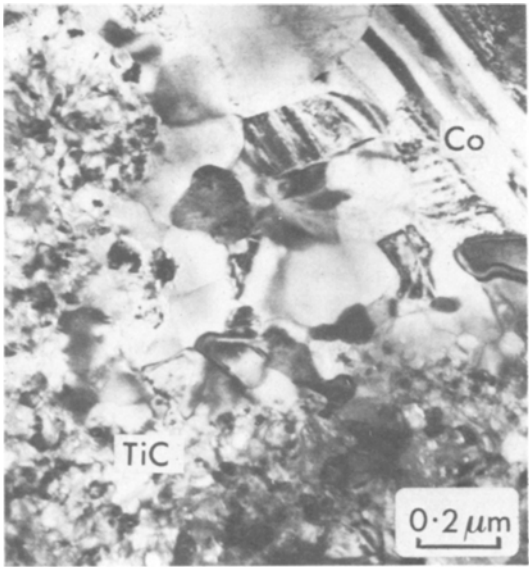

Figure 3 Extremely fine-grained TiC in the vicinity of Co regions at the substrate surface.

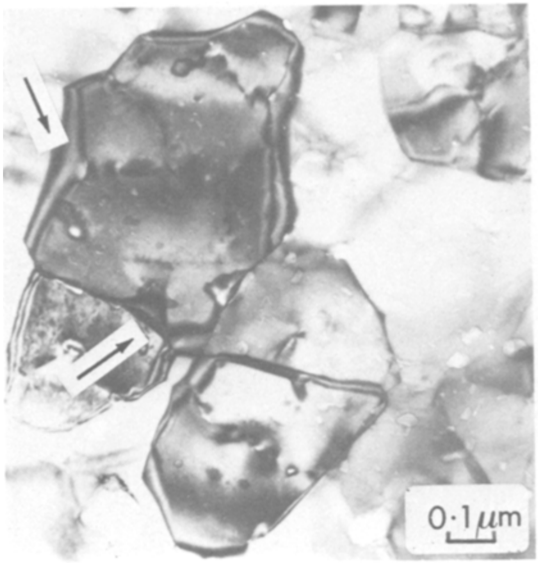

Figure 4 Uppermost region of TiC coating showing large grain size. Many voids can be seen, often pinning grain boundaries (arrowed).

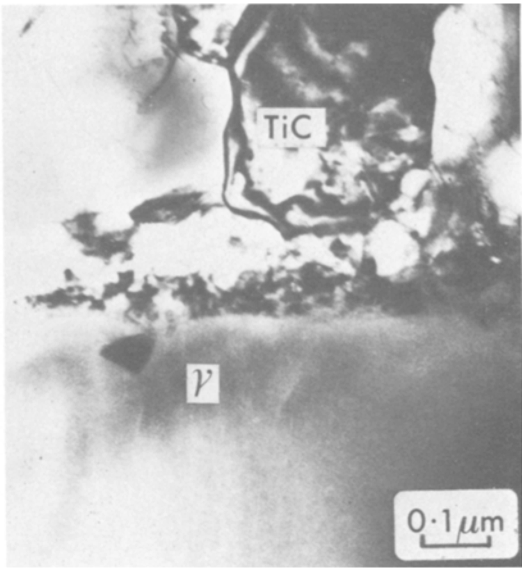

Figure 5 Fine-grained TiC at the γ-carbide–TiC interface.

The uppermost layer of the TiC coating is distinguished from the interfacial region alone by virtue of grain size, there being an order of magnitude increase. This upper layer is typically 2 to 4 μm thick with grain size reaching 1 μm at the top of the coating. (Fig. 4).

Voids were observed in all regions of the TiC coating. The voids occur mainly at the boundaries between TiC grains and appear not to be arranged in any network. Void size ($< 0.1\,\mu$m) and distribution remained largely constant throughout the coating thickness.

Many examples of voids pinning grain boundaries are seen typically in the uppermost part of the coating (as arrowed in Fig. 4).

3.2. The structure of the TiC–substrate interface

The region between the coating and the original hard metal surface is here referred to as the TiC–substrate interface. The multi-phase nature of the substrate results in there being TiC–WC, TiC–binder and TiC–γ-carbide contacts. It has previously been shown by X-ray diffraction analysis that TiC deposition results in binder phase decarburization to form $M_{12}C$, η-carbide in the upper region of the substrate [4]. The interface therefore also contains TiC–$M_{12}C$ contacts. Observations of the grain size variations within the initially deposited TiC coating ("interfacial carbide") are reported above. Additional TiC grain-size changes are found in contact with γ-carbide grains, see Fig. 5. Here, the TiC grains in direct contact with γ-grains have an extremely fine grain size ($< 0.05\,\mu$m). There occurs an abrupt increase however in the TiC grain size in the adjacent regions (in Fig. 5) such that the grain size becomes 0.2 μm to 0.5 μm which is considerably larger than the average "interfacial carbide" grain size of 0.05 μm to 0.1 μm.

A special orientation relationship between TiC grains and substrate could be frequently observed both for TiC–γ and TiC–WC, as indicated by the dark-field micrographs, Figs 6 and 7. The small grains comprising these first layers of deposited TiC on WC and γ grains clearly have a common orientation and appear coherent with the substrate grains. For TiC deposited onto WC there is a $\langle 001\rangle_{TiC}//\langle 1\bar{2}10\rangle_{WC}$ orientation relationship on $\{0001\}_{WC}$. For other WC grain faces and for TiC–γ-carbide the extremely fine TiC grain size complicates the crystallographic analysis considerably such that further experiments are required to determine the distribution of orientation relationships involved.

Fig. 8 shows TiC in connection with both $M_{12}C$, η-carbide and tungsten carbide. Since there is direct TiC–WC contact, concurrent with η-carbide formation, a continuous layer of η-carbide on the original substrate is precluded.

Voids could be found at all interfaces, being clearly facetted at TiC–WC and TiC-γ interfaces.

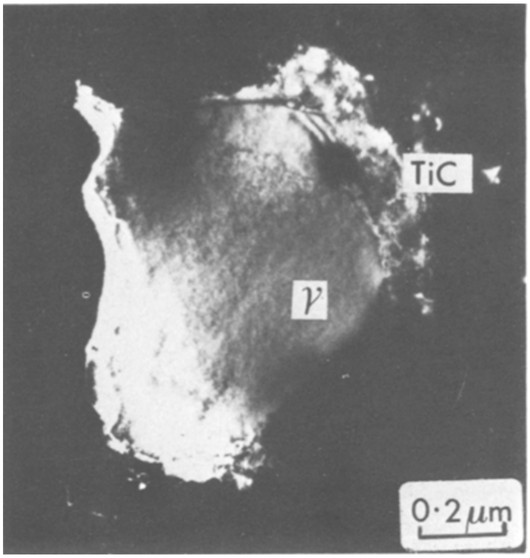

Figure 6 Coherency of the first layer of TiC grains on γ-carbide, (centred dark-field micrograph).

Void size and density were significantly reduced in the vicinity of cobalt binder and $M_{12}C$ phases.

4. Discussion

The microstructure of CVD-coated hard metal substrates may be seen as a complicated multilayer structure which may be directly related to the diffusion and transformation processes occurring during high-temperature deposition. The broadly parallel layers may be delineated from the scanning electron micrograph in Fig. 1.

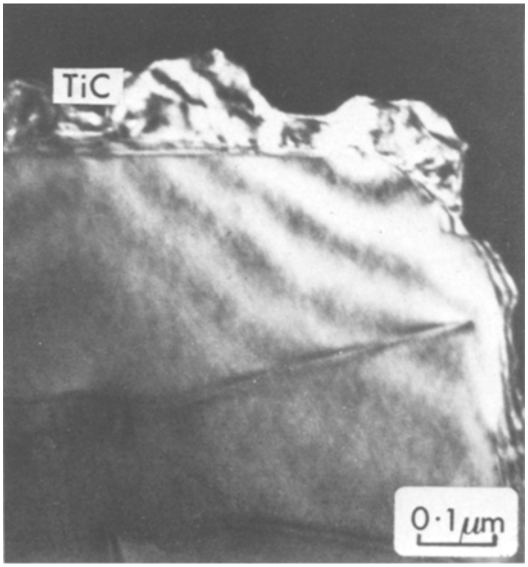

Figure 7 Coherency of the first layer of TiC grains on a WC grain, (centred dark-field micrograph).

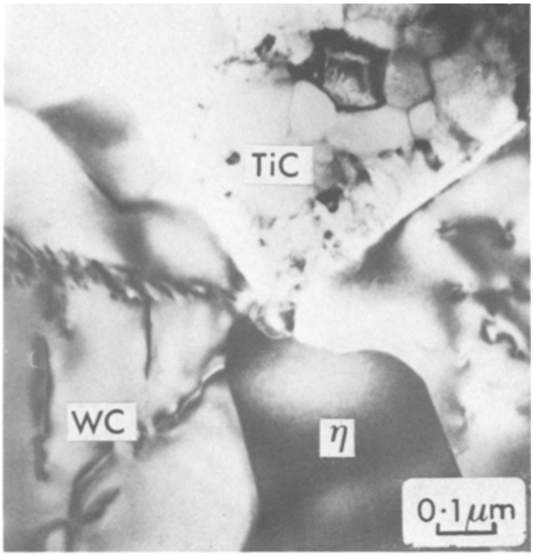

Figure 8 Direct TiC–WC interface in the presence of η-carbide formation shows directly that η-carbide is not in the form of a continuous layer.

The layers are (a) upper part of coating, (b) interfacial carbide layer, (c) TiC–substrate interface, (d) upper part of substrate and bulk substrate.

4.1. The TiC coating

The upper part of the TiC coating is distinguished from the interfacial carbide layer principally in terms of grain size. It has been previously shown that both nucleation [1] and growth rate [8] occur rapidly close to the substrate. It is thus clear that the fine-grained interfacial carbide layer is associated with TiC deposition with carbon diffusion from the substrate. As the coating layer increases in thickness it hinders the supply of carbon from the substrate and carbon supply from the vapour becomes dominant with a consequent drop in growth rate and an increase in TiC grain size. In addition to this variation between upper TiC coating and interfacial carbide, a clear result of the present study is that further microstructural variations occur within the interfacial carbide layer. Interfacial carbide is thus strongly influenced by the inhomogeneous nature of the substrate.

The interfacial carbide deposition may be directly related to the various components within the substrate. In carbon-rich regions, i.e. binder and η-carbide, very fine TiC grains are observed being a result of the simple diffusion of carbon from these phases. Adjacent to WC and γ-carbides, however, decomposition or stoichiometry changes are required before carbon can be supplied to the growing TiC layer. Since WC is highly stoichiometric it is less able to act as a carbon donor, as has been proposed for γ-carbides [3]. The increased growth rate results in large (0.2–0.5 μm) TiC grains in the vicinity of γ-carbide grains.

It is apparent that the upper region of the substrate undergoes microstructural changes which are largely due to decarburization during TiC formation. The dominant transformation here is the formation of the $M_{12}C$-type η-carbide due to carbon loss from the cobalt binder phase [Co (W, C)]. The present observation of large, substrate related, microstructural changes within the interfacial carbide layer indicates that η-carbide does not occur as a continuous layer on the substrate during the early stages of deposition as has been previously suggested. Rather, as is seen directly in the micrograph, Fig. 8, η-carbide is non-continuous on the substrate surface.

4.2. The interface

The true nature of the interface between hard metal substrate and TiC coating is here identified as being a three-dimensional combination of altogether seven sub-interfaces reaching a thickness of 0.5 μm. The sub-interfaces can be divided into three groups: the interfaces between TiC and the substrate directly (a, b, c), the interface between TiC and the $M_{12}C$-type η-carbide (d) and interfaces between $M_{12}C$ and the substrate (e, f, g). The interfaces are as follows (a) WC–TiC (b) Co–TiC (c) γ–TiC (d) $M_{12}C$–TiC (e) $M_{12}C$–WC (f) $M_{12}C$–Co and (g) $M_{12}C$–γ. The structure and distribution of these sub-interfaces is naturally important in determining adherence and wear properties of the TiC coating as well as being of particular importance during the nucleation and growth of the TiC layer.

The results of the present investigation clearly demonstrate that nucleation differences on the cemented carbide substrate are due to both the chemical and crystallographic differences of the phases comprising the substrate. Special orientation relationships of the TiC–WC and TiC–γ carbide interfaces have thereby been observed. Local differences in growth rate at the interface, within the deposited TiC layer, are seen to be determined by chemical differences, principally the supply of carbon from the substrate. Away from the interface, growth rate appears more uniform and not substrate dependent.

Voids were frequently observed at all sub-interfaces as well as TiC–TiC grain boundaries. Rather fewer voids were observed in the fine grain regions due to the TiC–Co and TiC–$M_{12}C$ carbide interfaces which suggests a close dependence of void formation on the general process of vapour deposition nucleation and growth. Facetted voids were frequently observed at the TiC–WC interfaces, being an indication both of the high annealing temperatures undergone during deposition and the orientation relationship at this interface.

5. Conclusions

(a) The CVD TiC coating is composed of a fine grained region close to the interface and an upper, large grained region. This layer structure is associated with carbon supply, being initially controlled by diffusion from the substrate and thereafter by the vapour-phase reaction. In addition to the layer structure (which may be readily seen in the optical and scanning electron microscopes) finer scale variations may be seen within the interfacial carbide layer. Such grain size and morphology changes within this layer appear directly related to the chemical and structural differences of the substrate component phases.

It is suggested that these inhomogeneities may be explained with reference to the ease of carbon supply from the component substrate phases. TiC microstructure near the interface therefore depends on the phase onto which, or near to which, it nucleates and grows. Changes in substrate composition or in the distribution of the substrate phases are therefore expected to result in microstructural changes in this first layer of deposited TiC.

(b) The true nature of the TiC–cemented carbide interface has been emphasized, it being composed of a total of seven sub-interfaces. Important crystallographic differences between these interfaces are apparent. Special TiC–WC and TiC–γ-carbide orientation relationships are preferred during TiC deposition.

(c) Defects in the deposited TiC coating consisted generally of few isolated dislocations. Voids were observed at all sub-interfaces as well as TiC–TiC grain boundaries.

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