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CHEMICAL VAPOUR DEPOSITION OF Al-CONTAINING TiC - AND Ti(O,C) - HARD COATINGS

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Abstract - For the Ti-Al-O-C-system it is shown that it is possible to produce good quality deposits of both single-phase TiAlOC or Al₂O₃-layers and heterogeneous layers of TiAlOC and Al₂O₃ under normal pressure-CVD-conditions using a reaction gas mixture of TiCl₄, AlCl₃, H₂ and a CO/CO₂-mixture.

1. Introduction

The preparation of TiC-, TiN-, Ti(C,N)- and Al₂O₃-wear resistant layers as monolayers or in combination with each another is nowadays a technological standard for the CVD-coating of cutting and forming tools.

Both types of layer possess advantages as well as disadvantages. For example, TiC has a good adhesive strength, high hardness and low flank wear, but it has a relatively strong crater wear. Al₂O₃ reveals a good wear resistance and high oxidation resistivity, but a low adhesive strength and high brittleness.

A hard coating is of great importance for instance for the cutting of austenitic steels and there is a need to combine the outstanding properties of TiC and Al₂O₃. It is known from the PVD-technology, that reactively sputtered Ti-Al-N-phases surpass conventional TiC-coatings [1].

The aim of the studies here was to check the possibility for the preparation of Al-containing hard phases in the systems Ti-Al-C-N and Ti-Al-O-C, respectively, as homogeneous or heterogeneous layers using CVD.

The deposition of TiC [2, 3, 4] as well as of Al₂O₃ [5, 6] is known in detail both from thermodynamic calculations and also by experimental investigations. The CVD-process was performed in a hot wall reactor at normal pressure and 1323 K.

2. Results

2.1. Ti-Al-C-N-system

TiN-, TiC-, Ti(C,N)-layers were deposited, using TiCl₄, H₂, benzene or n-heptane as C-carrier and N₂, with additional AlCl₃ for Al-containing deposits, (the Al/Ti-ratio in the gas phase was < 5).

In no case could Ti-Al-hard phases be detected. Microhardness measurements, X-ray phase analyses as well as element analytical investigations by EPMA have shown, that in each case only pure

TiN-, TiC- or Ti(C,N)-layers were obtained. Only mass-spectroscopic analyses yielded an Al-content of 0,2 wt%. Obviously there is a low solubility of aluminium in titanium carbide.

2.2. Ti-Al-O-C-system

In general besides AlCl_3 and H_2 for the Al_2O_3 - deposition, CO_2 is used as an oxygen carrier. An undesirable effect of this process is a homogeneous gas phase reaction of H_2O , formed from CO_2 and H_2 , with AlCl_3 in the reaction zone, forming powdery Al_2O_3 . The consequences are a disturbed layer growth and obstructions in the reactor system. The water formed in the reaction zone is also a great problem for the co-deposition of TiC and Al_2O_3 . Titanium has a higher affinity to oxygen than to carbon, yielding preferably oxygen-rich Ti(O,C)-layers. But for a wear reducing hard coating only titanium-oxycarbide with a low oxygen content can be used, because the microhardness strongly decreases with oxygen incorporation. For these reasons it was not possible to deposit technically useful Al-containing hard coatings.

To overcome these problems mixtures of CO and CO_2 as oxygen sources were used, and they can be prepared easily by passing CO_2 over charcoal giving concentration ratios depending on the charcoal temperature. In this way for the Ti-Al-O-C-system the process succeeded with the deposition of both single-phase layers consisting of the homogeneous phases TiAlOC and Al_2O_3 , respectively, or co-deposits of TiAlOC and Al_2O_3 in any Al/Ti-ratios, thus homogeneous gas phase hydrolysis was avoided.

There is a clear correlation between gas phase concentration and phase composition.

In Table 1 three characteristic reaction conditions (the initial number of moles $\cdot \text{h}^{-1}$ $n_{\text{AlCl}_3}^\circ$, $n_{\text{CO}_2}^\circ = \text{constant}$) and metallographical results are given, while in Table 2 element- and phase analytical determinations are shown.

Table 1 Reaction conditions and metallographical results for TiAlOC-deposits ($T = 1323 \text{ K}$)

Sample	$\frac{n_{\text{AlCl}_3}^\circ}{n_{\text{TiCl}_4}^\circ}$	$\frac{n_{\text{CO}}^\circ}{n_{\text{CO}_2}^\circ}$	metallography	EPMA
1	8	350	homogeneous, grey layer HV = 2870 VE	Fig. 1
2	8	2	homogeneous black layer HV = 2350 VE	Fig. 2
3	24	50	homogeneous, darkgrey layer, greater sized, black inclusions HV = 3030 VE	Fig. 3

Fig. 1 EPMA line-scan of sample 1

Fig. 2 EPMA line-scan of sample 2

Fig. 3 EPMA line-scan of sample 3

Table 2 Results of element- and phase analysis of TiAlOC-deposits

Sample	phase components			TEM	element analysis	
	X-ray diffraction TiO_xC_y	$\alpha-Al_2O_3$	$\delta-Al_2O_3$		relative quantities Ti:Al:O:C	phases
1	xxxx			TiO_xC_y qual. Al	12:2:1:1,5 Fig. 4	TiAlOC
2		xx	x	Al_2O_3	6:20:16:1	Al_2O_3 +(TiAlOC)
3	xx		x	$Ti(Al)O_xC_y$ + α -, δ - Al_2O_3 grain size (0,2,um)	10:20:12:1	Al_2O_3 +TiAlOC

For sample 1 a homogeneous grey layer was observed using optical microscopic, and this was characterized by X-ray diffraction as a TiO_xC_y -phase. But by element analysis it was established, that aluminium (11 wt%) was distributed homogeneously in this TiO_xC_y -phase. TEM-investigations of this sample confirmed this result. Fig. 4 shows a very fine-crystalline structure. Only TiC_xO_y could be detected as a phase component by microdiffraction. It was not possible to detect Al_2O_3 in any modification, but aluminium was detected qualitatively by element analysis, i.e. this phase is a TiC_xO_y -phase, in which Al is dissolved (TiAlOC).

Fig. 4 TEM-image of sample 1

The phase components of the samples 2 and 3 were also analyzed. If the CO_2 -content is increased, a darkblack, homogeneous layer (sample 2) is obtained, the main components of which were definitely only aluminium and oxygen. The transmission electron micrographs show a large-grained layer,

and by microdiffraction of these single crystals Al_2O_3 was detected (α -, δ -modifications), confirming the X-ray diffraction results. A cubic TiC_xO_y -phase could not be detected.

If the titanium content is lowered in the gas phase ($\text{Al/Ti} = 24$) (sample 3), layer compositions can be detected at the given CO/CO_2 -ratio, which consist of both Al_2O_3 and TiAlOC in comparable quantities. This two-phase nature could be confirmed by TEM. The deposition of such multiphase layers is proved to be very useful, because the coatings show both an outstanding adhesive strength as for pure TiC -coatings and a high oxidation resistivity as for pure Al_2O_3 .

To test the performance of TiAlOC -layers in comparison to Al_2O_3 layers TiC coated cutting plates were coated with surface layers of about 2 μm thickness.

As demonstrated in Figs. 5 and 6 the performance of a $\text{TiAlOC/Al}_2\text{O}_3$ -surface layer in turning of steel is equivalent to that of an Al_2O_3 -surface layer.

However, there are advantages in preparation of $\text{TiAlOC/Al}_2\text{O}_3$ -coatings.

Fig. 5 cutting time of TiAlOC -coatings in the M10 region (3, 4 coated commercial cutting places)

Fig. 6 cutting time of TiAlOC -coatings in the M20 region

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