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TITANIUM NITRIDE COATINGS CREATED BY NITRIDING TITANIUM DIOXIDE COATINGS ON CORUNDUM CUTTING TOOLS

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The TiN coatings on the surface of cutting tools were prepared by nitriding TiO_2 coatings applied by the sol-gel method. The coatings are gold to bronze in colour, electrically conductive and brought about partial improvement of the durability of the cutting tools.

1. INTRODUCTION

Application of a layer of TiN onto the surface of ceramic cutting tools allows their service life to be improved. At present, the TiN coatings are applied above all by chemical vapour deposition (CVD) and physical vapour deposition (PVD). However, both methods require comparatively expensive apparatus and the technology involved is quite demanding.

The present study was concerned with investigating the possibility of creating a TiN layer on cutting ceramics by nitridation of TiO_2 coatings prepared by the sol-gel method.

The sol-gel method is utilized in the preparation of oxidic materials, basically of glass, glass-ceramic and ceramic types. Essentially, solutions of metal alkoxides in alcohol or another non-aqueous solvent are converted, by controlled hydrolysis, to a sol and subsequently to a gel. The use of solutions ensures homogenization on molecular level [1–3].

The layers are mostly prepared by drawing on the substrate from the metal alkoxide solution. In this way, a high degree of uniformity is ensured even with complex shapes [4].

As is known from the literature, TiN can be prepared, apart from direct reaction of titanium with nitrogen at considerably high temperatures, also according to the following stoichiometric equation:

$$6\,TiO_2 + 8\,NH_3 \rightarrow 6\,TiN + 12\,H_2O + N_2 \qquad (1)$$

at temperatures of 900° C and higher [5, 6].

2. EXPERIMENTAL

2.1. Preparation of titanium dioxide layers

The layers of titanium dioxide were prepared by mixing titanium isopropoxide (further on abbreviated to $Ti(i\text{-}PrO)_4$), ethyl alcohol, water and hydrochloric or nitric acid according to the schematic diagram in Fig. 1.

On mixing the starting substances it was necessary to add one substance to the other dropwise so as to avoid formation of turbidity or a gel-like precipitate. The solution prepared in this way was used to coat the specimen by drawing out at a constant rate. The coat thickness depends on the speed of drawing out and on the

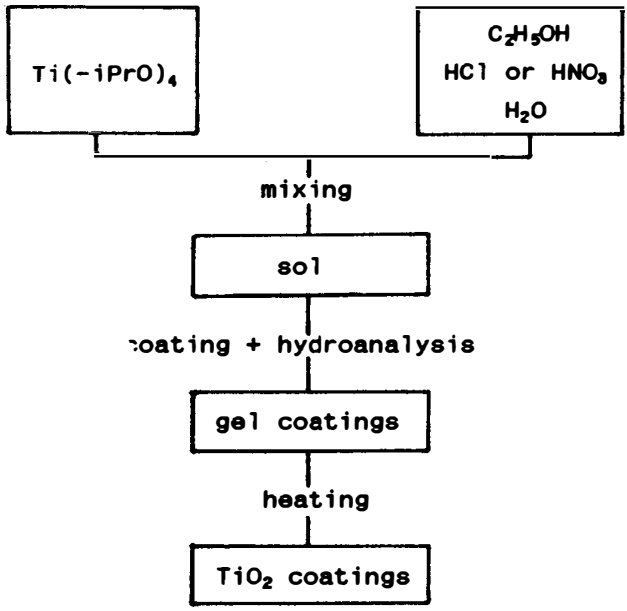

Fig. 1. Schematic diagram of the preparation of TiO_2 coatings by the sol-gel method.

concentration of the solution [7]. The operation can be successfully accomplished within about 48 hours from the time of preparing the solution.

The specimens were converted thermally to TiO_2 with due respect to the sequence of structural conversions of titanium dioxide [8],

$$\text{anatase} \xrightarrow{800^\circ C} \text{brookite} \xrightarrow{1040^\circ C} \text{rutile.}$$

For this reason, the heat treatment of the gel coatings was conducted in the following ways:

a) for 15 minutes at 500° C,

b) for 10 minutes at 1100° C.

In the case of deposition of several layers, the next coating was applied only after the previous one had been heat treated.

2.2. Preparation of the titanium nitride layers

As has already been mentioned, the TiN layers were prepared by nitriding the TiO_2 layers with gaseous ammonia at temperatures of 900° C and higher. The specimens of ceramic cutting tools coated with titanium dioxide were placed in a tubular furnace where an inert atmosphere was created by introducing dry nitrogen for about 30 minutes. The heating was then switched on at a preset heating rate

and dry ammonia was allowed to pass through the furnace. On attaining the required temperature, the specimens were kept there for a certain dwelling time. After switching off the heating and in the course of cooling down, nitrogen was continuously passed through the tube. The specimens were removed from the furnace only after cooling down to room temperature.

2.3. The apparatus employed

The nitrided coatings were subjected to X-ray analysis on the GON 2 powder diffractometer using CuKα radiation and the Ni filter. The microhardness of the coating was measured with the mhp 160 tester using Vickers indentor, fitted to the Amplival microscope by Carl Zeiss Jena.

3. RESULTS AND DISCUSSION

The properties of the titanium dioxide coating on the surface of the ceramic cutting tool depended on the composition of the coating solution and on the time and temperature of firing. The specimens coated by a solution having a $Ti(i\text{-}PrO)_4 : H_2O : C_2H_5OH : HCl$ ratio of 1 : 4 : 4 : 1 or 1 : 4 : 6 : 1, fired at 500° C, exhibited a porous structure with poor adhesion to the surface. After firing at 1100° C, the structure of the coating became microcrystalline and the adhesion improved considerably. In the case of coatings prepared from dilute solutions with a molar ratio of $Ti(i\text{-}PrO)_4 : H_2O : C_2H_5OH : HNO_3 = 1 : 2.45 : 45.00 : 0.72$, or 1 : 1 : 10 : 0.08, after firing at 500° C the coatings were amorphous with a glassy appearance. After firing at 1100° C they were crystalline, and in both cases showed a satisfactory adhesion to the surface. The properties of the coatings mentioned were retained even in the case of deposition of several layers.

According to the results of X-ray diffractometric analysis, the firing at 1100° C converts the TiO_2 to rutile. This finding allowed the thickness of the coating to be determined according to the difference in the specimen weight before and after firing at 1100° C. The thickness of the coating prepared from the solution having the ratio $Ti(i\text{-}PrO)_4 : H_2O : C_2H_5OH : HCl = 1 : 4 : 4 : 1$ was 0.08 μm. The thickness of the coating fired at 500° C could not be established as the density of the amorphous coating was unknown.

The presence of titanium nitride coatings was indicated visually, by electrical conductivity and with some selected samples also by X-ray analysis. Samples prepared in the following two ways were subjected to the X-ray analysis:

a) Using the basic solution having the ratio $Ti(i\text{-}PrO)_4 : H_2O : C_2H_5OH : HCl = 1 : 4 : 4 : 1$, TiO_2 layers were prepared by firing at 1100° C each layer separately. The TiN layer was prepared in the way described above (samples B2 and B5, where 2 and 5 are the numbers of layers deposited).
b) Using the basic solution having the ratio $Ti(i\text{-}PrO)_4 : H_2O : C_2H_5OH : HNO_3 = 1 : 2.45 : 45 : 0.72$, TiO_2 layers were prepared by firing each layer separately at 500° C. The TiN layer was then prepared in the way described above (sample 4, containing five layers).

The diffraction patterns of these samples (Table I) mostly indicate the presence of α-Al_2O_3 (for example, the No. 4, 6 and 2 peaks) acting as a base material. The presence of TiN is demonstrated by the less distinct diffraction peaks (e. g. Nos. 2a, 3a, 7a). The presence of no other substances was indicated, as shown by Fig. 2 on the diffraction patterns of sample B5.

Table I
Diffraction pattern of samples 4, B2, B5 with TiN surface layers

No.	Sample						Attributed to
	4		B2		B5		
	d [nm]	I/I_0 [%]	*d* [nm]	I/I_0 [%]	*d* [nm]	I/I_0 [%]	
1	0.347	42	0.347	38	0.347	33	Al_2O_3
2	0.255	70	0.255	62	0.255	61	Al_2O_3
2a	0.244	4	0.244	10	0.244	27	TiN
3	0.238	34	0.238	29	0.238	30	Al_2O_3
3a	0.212	17	0.212	24	0.212	48	TiN
4	0.2083	100	0.2083	100	0.2083	100	Al_2O_3
5	0.174	52	0.174	46	0.174	52	Al_2O_3
6	0.160	92	0.160	88	0.160	98	Al_2O_3
7	0.1512	10	0.1512	11	0.1512	14	Al_2O_3
	0.1510	11	0.1510	12	0.1510	13	Al_2O_3
7a			0.1499	5	0.1499	19	TiN
8	0.1404	44	0.1404	38	0.1404	48	Al_2O_3
8a	0.1375	48	0.1375	43	0.1375	55	Al_2O_3
9	0.1275	4	0.1275	4	0.1275	9	TiN
10	0.1239	22	0.1239	24	0.1239	22	Al_2O_3
	0.1236	16	0.1236	17	0.1236	17	Al_2O_3
11	0.1189	8	0.1189	9	0.1189	9	Al_2O_3

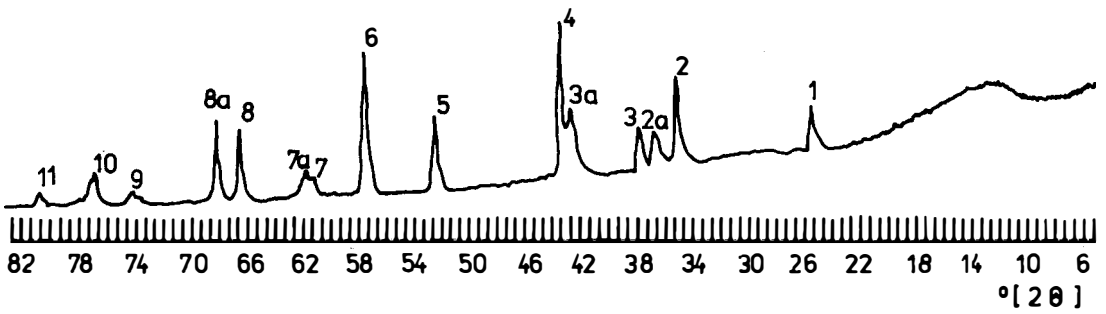

Fig. 2. Diffraction pattern of sample B5.

The diffraction peaks were attributed to the respective compounds according to the JCPDS tables for α-Al_2O_3 (card 10–173), TiN (card 6–642), TiO_2-rutile (card 4–551). The respective values are listed in Table II.

Table II
Diffraction peaks for α-Al_2O_3, TiN, TiO_2-rutile

α-Al_2O_3 (10–173)		TiN (6–642)		TiO_2-rutile (4–551)	
d [nm]	I/I_0 [%]	d [nm]	I/I_0 [%]	d [nm]	I/I_0 [%]
0.4379	75	0.244	77	0.3245	100
0.2552	90	0.212	100	0.2489	41
0.2379	40	0.1496	56	0.2297	7
0.2085	100	0.1277	26	0.2188	22
0.1740	45	0.1223	16	0.2054	9
0.1601	80	0.1059	7	0.1687	50
0.1514	5	0.0972	11	0.1624	16
0.1510	7	0.0948	22	0.1480	8
0.1404	30	0.0865	21	0.1453	6
0.1374	50			0.1360	16
0.1239	15			0.1347	7
0.1234	7			:	:
+32 peaks				0.08196	8
d <0.116; 0.0888>					
I <13;less than 1>					

The diffraction patterns indicate that during the process described, the layers of titanium dioxide are converted completely to titanium nitride.

In order to determine the conditions of nitridation, the effect of the heating rate was examined at the rates of 5° C/min., 10° C/min., and 20° C/min. using the same dwell time (2 hrs.) at T = 1000° C. The heating rate was found to have no effect on the nitridation. After nitridation, all samples had a golden or golden-bronze colour.

The effect of temperature and dwell time at a constant heating rate of 20° C/min. on the nitridation of TiO_2 was studied on coatings prepared from a solution having the ratio Ti(i-PrO)$_4$: C_2H_5OH : H_2O : HCl = 1 : 4 : 4 : 1. The specimens with three TiO_2 layers were nitrided for 1, 3 and 5 hours at 900°, 1000° and 1100° C respectively. Table III lists the colours and microhardness of the samples after nitridation.

The table demonstrates that both the nitridation temperature and time influenced the colour of the samples. It also appears, however, that the colour is not related

Table III
The colour and microhardness of TiN following nitridation at various temperatures and for various holding times

Nitridation temperature [°C]	Time [h]	Colour	Microhardness [kp/mm²]
900	1	bronze	1287
	3	bronze	1226
	5	bronze	1498
1000	1	golden	1352
	3	golden	1352
	5	golden	1422
1100	1	golden	1226
	3	golden-bronze	1352
	5	bronze-violet	2403

to the Vickers hardness value (VH). Regardless of the preparation conditions, except for that of 1100° C and 5 hours, the microhardness is more or less identical, showing only a slight increase for nitridation for 5 hours. It is known from the literature [9] that with respect to the values of microhardness for the two materials established by the method in question, the ratio of their presence can be taken to be equal to the ratio of their microhardness. In view of this fact it may be noted that only the value for sample 9 differs from the others. The titanium nitride coating prepared in this way exhibits almost double microhardness compared to the other cases.

The degree to which the effect of nitridation depends on the number of layers was also studied. Specimens with 1, 2, 3, 4 and 5 layers of titanium dioxide were prepared from a solution having the ratio $Ti(i\text{-}PrO)_4 : H_2O : C_2H_5OH : HCl = 1 : 4 : 4 : 1$, and heat treated at 1100° C. Titanium nitride was formed in all the cases. A comparison of diffraction patterns of the specimens with two layers (B2) with those having five layers (B5) shows that the titanium dioxide was completely converted to titanium nitride in both instances. On comparing the intensity of TiN diffraction peaks Nos. 2a and 3a one sees that with samples B2 and B5 their ratio is 1 : 2.7 and 1 : 2 respectively. From this it follows that the ratio of TiN layer thickness for B2 and B5 amounts to approx. 1 : 2.5. This is in full agreement with the number of depositions of TiO_2, which was 2 and 5 respectively for B2 and B5.

The thickness of one TiO_2 coating applied and processed under the given conditions is about 0.08 μm. With the B5 samples having a five-fold layer, the overall thickness of TiO_2 is about 0.4 μm. The diffraction patterns give evidence for a complete conversion of TiO_2 to TiN. It may therefore be concluded that the given way of application, firing at 1000°–1100° C and nitridation for 2 hours produces nitridation of TiO_2 coatings up to 0.4 μm in thickness.

3.1. Testing of the samples

To examine the functional properties of cutting ceramic tools with coatings of titanium nitride, prepared by the procedure described above, a series of commercially produced ceramic tips Disal 100 (made by Dias Turnov) was provided with the respective coatings. The composition of the basic solution, and the number of layers applied were varied. The specimens were tested at the Research Institute of Machine Tools and Machining in Prague by standard durability methods. A roughly 30 % increase in service life was established for specimens on which the TiO_2 coating was deposited twice from a solution having the ratio $Ti(i\text{-}PrO)_4$: : H_2O : C_2H_5OH : HCl = 1 : 4 : 4 : 1, compared to control specimens without any coating. All the other specimens showed no significant change of the service life compared to the standards.

4. CONCLUSION

The present study deals with a procedure for preparing titanium nitride coatings on ceramic cutting tools based on α-Al_2O_3, by nitriding TiO_2 coatings applied by the sol-gel method.

The TiO_2 coatings exhibit a satisfactory adhesion to the ceramic base after firing at 1100° C. The coatings prepared in this way can be converted to TiN coatings by treatment with dry ammonia at 900–1100° C for 1 to 5 hours. The α-Al_2O_3 cutting tool tips, on which the TiN layer was created from a TiO_2 layer deposited from a solution having the ratio $Ti(i\text{-}PrO)_4$: H_2O : C_2H_5OH : HCl = 1 : 4 : 4 : 1, exhibited a machining life increase by about 30 % (in the case of a double or triple TiN layer).

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POVLAKY NITRIDU TITANITÉHO NA REZNEJ KERAMIKE VYTVORENÉ NITRIDÁCIOU POVLAKU OXIDU TITANIČITÉHO PRIPRAVENÉHO METÓDOU SÓL–GÉL

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Príprava povlakov TiN na povrchu reznej keramiky na báze α-Al_2O_3 bola realizovaná nitridáciou povlakov TiO_2 vytvorených metódou sól-gél. Povlaky TiO_2 boli vytvárané na povrchu reznej keramiky ponáraním do roztoku pripraveného z izopropoxidu titaničitého, alkoholu, vody a kyseliny chlorovodíkovej. Po vypálení vrstvy pri 500 °C, resp. 1000 °C bolo možné naniesť ďalšiu vrstvu TiO_2, čím boli dosahované požadované hrúbky. Takto vytvorená vrstva TiO_2 bola v prúde suchého NH_3 pri 900 °C až 1000 °C prevedená na TiN vrstvu. Röntgenografickou analýzou bolo dokázané, že dochádza k úplnej konverzii TiO_2 na TiN. Britové doštičky na báze α-Al_2O_3, na ktorých bola TiN vrstva vytvorená z TiO_2 vrstvy pripravenej z roztoku $Ti(i\text{-}PrO)_4 : H_2O : C_2H_5OH : HCl = 1 : 4 : 4 : 1$ 2× a 3× nanesenej vykázali zlepšenie životnosti pri obrábaní cca o 30 %.

Obr. 1. Schéma prípravy TiO_2 povlakov sól-gél metódou.
Obr. 2. Difraktogram vzorky č. B5.

ПОКРЫТИЯ ИЗ НИТРИДА ТРЕХВАЛЕНТНОГО ТИТАНА, ОБРАЗОВАВШИЕСЯ В РЕЗУЛЬТАТЕ АЗОТИРОВАНИЯ ПОКРИТИЙ ИЗ ОКСИДА ЧЕТЫРЕХ ВАЛЕНТНОГО ТИТАНА, НАХОДЯЩЕГОСЯ НА РЕЖУЩЕЙ КОРУНДОВОЙ КЕРАМИКЕ

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Приготовление покрытий TiN на поверхности режущей керамики на основании $\alpha - Al_2O_3$ проводили путем азотирования покрытий TiO_2, полученных методом сол-гел. Покрытия TiO_2 образовались на поверхности режущей керамики погружением в раствор, состоящий из изопропоксида четырехвалентного титана, алкоголя, воды и хлороводородной кислоты. После обжига слоя при температуре 500°C, или 1000°C можно было наносить дальнейший слой TiO_2 с целью достижения требующей толщины. Полученный таким образом слой TiO_2 в потоке сухого NH_3 при температуре 900–1000° C переводили в слой TiN. С помощью рентгенографического метода было доказано, что протекает полная конверсия TiO_2 в TiN. Режущие пластинки на основании $\alpha - Al_2O_3$ со слоем TiN, образовавшимся из слоя TiO_2, полученного из раствора $Ti(i\text{–}PrO)_4 : C_2O : C_2H_5OH : HCl = 1 : 4 : 4 : 1$ и дважды и трижды нанесенного, обладали лучшей жизнеспособностью при обработке приблизительно на 30 %.

Рис. 1. Схема приготовления TiO_2 покрытый методом сол–гел.
Рис. 2. Дифрактограмма образца N° V5.