Solid State Ionics 32/33 (1989) 789-794
North-Holland, Amsterdam

CVD OF LAMINAR COMPOSITES IN THE SYSTEM $TiN-TiB_2$

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Received 8 June 1988; accepted for publication 4 August 1988

A project has been started in order to develop laminar composites in the system $TiN-TiB_2$, candidate materials for wear-resistant coatings in corrosive atmospheres. The objectives of the project are outlined. TiN layers have been deposited by chemical vapor deposition. The relations between the growth rate and deposition conditions have been determined. The deposition of TiN on molybdenum using $TiCl_4$, N_2 and H_2 is complicated by the presence of HCl in the gas mixture.

1. Introduction

Titanium diboride, TiB_2, has very interesting properties: it is hard and wear resistant, erosion resistant [1], corrosion resistant under reducing circumstances [2], and fairly oxidation resistant because of the formation of a dense oxide skin [3]. The material is being tested for applications in the field of coal liquifaction [4], aluminium refining [5] and the nuclear industry [6]. It is a candidate material for application as wear-resistant coating under severe corrosive conditions.

TiB_2 can be deposited on a substrate by chemical vapor deposition (CVD) using titanium tetrachloride, $TiCl_4$, boron tribromide, BBr_3, and hydrogen, H_2, at temperatures around 1000°C. However, if the substrate contains iron or nickel, as is the case for steel and the binder in certain hard metals, severe boronation of the substrate occurs [7]. Iron and nickel borides are formed, leading to the formation of a weak layer between the coating and the substrate or to extensive crack formation in the substrate.

A diffusion barrier for boron is necessary to avoid this boronation. Titanium nitride, TiN, is a good candidate: it is used in the electronic industry as a diffusion barrier for boron but under much milder conditions than present during CVD [8]. Furthermore TiN is a hard and wear-resistant material itself.

2. The laminar composite $TiN-TiB_2$

The ultimate coating is a laminar composite in the system $TiN-TiB_2$. Several CVD techniques differing in the activation of the reactant gases exist: thermal activation, laser activation (LCVD) [9], and plasma-enhanced CVD (PECVD) [10]. They are being developed because the high substrate temperatures in traditional thermally activated CVD is too high for many practical substrate materials. At present only the high temperature CVD process offers the possibility of forming both TiN and TiB_2. Therefore, this research has been focused on the development of $TiN-TiB_2$ laminar composites using thermally activated CVD with $TiCl_4$, BBr_3, N_2, and H_2 as reactants.

We may distinguish two types of processing. In a two-step process TiN and TiB_2 are deposited separately. This is essentially the deposition of TiB_2 on a TiN substrate. The advantage is that both materials can be deposited with the most optimal technique.

In a one-step process the composition of the reactant gas mixture is changed during deposition. The inherent advantages in the second case are that the interface between TiN and TiB_2 remains clean, and that several morphologies can be expected. The first possibility, schematically depicted in fig. 1a, consists of grains of TiB_2, nucleated between TiN and growing gradually. This type of morphology promises good adhesion between the layers because of mechanical

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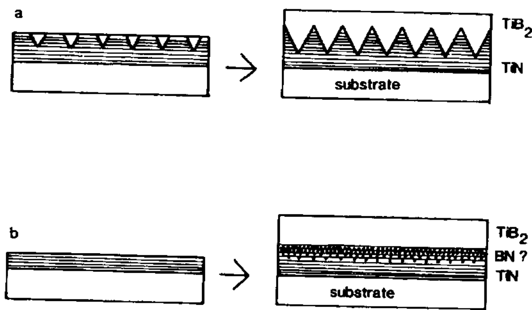


Fig. 1. Possible morphologies resulting from the one-step deposition of a $TiN–TiB_2$ laminar structure. See text for further explanation.

interlocking. Such morphology can also be obtained by the two-step process, if filling of a rough layer of TiN with TiB_2 occurs. However, it is quite possible, that the presence of BBr_3 in the gas phase disturbs the deposition of TiN resulting in the formation of very fine grained porous material with virtually no cohesion and low mechanical strength. The third possibility is that TiN is not affected at all by the presence of BBr_3 and continues to grow in a dense layer, meanwhile TiB_2 nucleates in the gas phase and the fine, submicron, particles are inserted in the layer as schematically depicted in fig. 1b. This process is called thermo-phoresis-enhanced CVD and results in very fast growing layers [11]. In addition to the variations in morphologies several compounds can be expected. The gas mixture contains both BBr_3 and N_2 and the formation of BN is likely. Furthermore there is uncertainty as to whether Ti(B, N) actually exists. If it does, then a homogeneous layer with gradually changing composition can be formed as occurs in the system TiN–TiC.

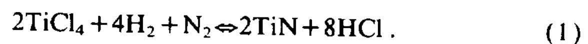
The one-step process is preferred for the formation of the laminar composite, since it opens many possibilities to manipulate the properties of the composite.

3. CVD of TiN

In all cases an initial layer of TiN will be deposited and a dense coating is a prerequisite for obtaining a proper diffusion barrier. Therefore, the properties of TiN, prepared by CVD are studied in depth as a function of the deposition conditions, since the reproducible deposition of a good TiN layer is of utmost importance. Properties of importance are the morphology of the layer (crystal size, porosity, and roughness [12]), the composition, and the interaction with the substrate. Some general trends in the dependence of these properties on the deposition conditions are found in the literature. Smooth layers are formed if reaction at the surface is the rate-determining step. If, however, the reaction is determined by the supply of reactants through the gas phase, rough layers are formed [13]. While these rough layers are commonly very undesirable, they are very useful for the present laminar composites. High substrate temperatures result in coarse grains, while at very low temperatures amorphous layers are formed [10]. Furthermore, chlorine is built in at low temperatures [14]. High nitrogen contents of the gas phase produces superstoichiometric $TiN_{1.04}$ [15]. This paper focuses on the relations between process conditions for CVD of TiN and its properties as a diffusion barrier.

4. Experimental aspects

TiN is deposited using $TiCl_4$, H_2, and N_2 according to



$$2TiCl_4 + 4H_2 + N_2 \Leftrightarrow 2TiN + 8HCl . \quad (1)$$

The reversed reaction is called etching.

The CVD reactor system is schematically depicted in fig. 2. It consists of a gas-dosage system, a hot-wall reactor, and a waste-product trap. Hydrogen, 99.9%,

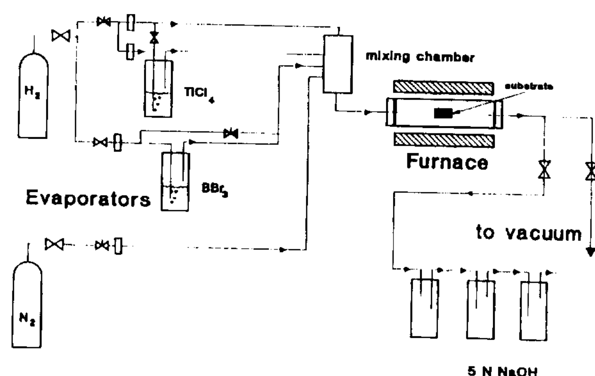


Fig. 2. Schematic drawing of the CVD reactor, used for the deposition of $TiN–TiB_2$ laminar composites.

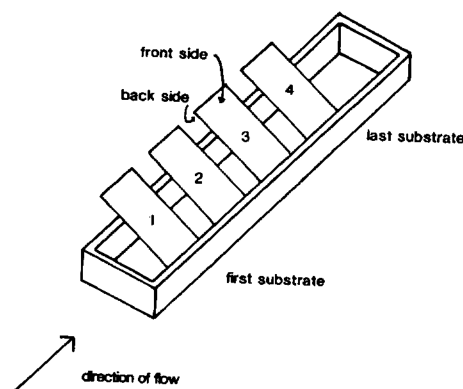


Fig. 3. The position of the four substrates in the alumina susceptor.

is used as a reducing agent and as a carrier gas. It is purified over a BASF palladium catalyst and a Dow A4 zeolite. Part of the hydrogen stream bubbles through liquid $TiCl_4$, where it is saturated with $TiCl_4$ vapor. The vapor pressure of $TiCl_4$ is controlled by its temperature. Nitrogen, 99.9%, is purified over a BASF copper catalyst and Dow A4 zeolite. Next the gas streams are mixed and fed into the reactor. The substrates are positioned in an alumina susceptor, fig. 3. The gases are finally passed through 5 N NaOH to neutralize the acid, and to decompose unreacted $TiCl_4$.

The weight change of the substrates is determined and used as a measure for the average layer thickness. In general the layer is twice as thick on the front side as it is on the back side of the samples. The morphology of the layers is studied with scanning electron microscopy. The composition is checked with X-ray diffraction and X-ray spectroscopy. In a number of cases also cross sections have been studied.

5. Results and discussion

5.1. Deposition of TiN on nickel

The deposition of TiN on nickel is not reproducible. The layers are fairly rough, and sometimes we even have observed the growth of whiskers. There seem to be two competitive processes: the formation of TiN, and the formation of Ti–Ni compounds. In a number of cases only TiN, in a dense, gold colored layer has been formed. In other cases the formation of Ti–Ni layers underneath TiN has been observed, probably due to an open structure of the TiN coating. Occasionally only Ti–Ni compounds are formed. Some nucleation problem seems responsible for these phenomena, but no systematic relation between deposition conditions, substrate conditions and the formation of Ti–Ni compounds could be found.

5.2. The behavior of TiN on nickel as a diffusion barrier for boron

As already mentioned above, TiN is used in the electronic industry as a diffusion barrier for boron. However, the boronation conditions are relatively mild there: i.e. the boron-rich side of the TiN layer contains less than 0.1 at% boron [8]. During CVD of boron or borides the boron content of the gas phase will be much higher than that. In order to test their barrier properties, TiN coatings have been tested under the most severe conditions: reduction of BBr_3 in H_2 at high temperatures thereby depositing pure boron on TiN.

The samples consist of dense TiN layers on nickel, which functions as a good trap for any boron diffusing through the TiN layer. The quantification of the boron content has proven to be difficult, since only a very small amount of boron has been found in the substrate. Therefore only a qualitative picture can be presented. If a 3 μm thick TiN layer on nickel is treated with BBr_3 and H_2 for 3 h at 925°C, only a layer of 0.5 μm very lightly boronized nickel is formed and no nickel borides are found. If an unprotected nickel substrate is treated this way, 120 μm of nickel borides are formed and the substrate shows many cracks. These results show that TiN is indeed a good diffusion barrier for boron, but that there are limits to the acceptable boronising potential of the gas mixture. At high boron activity some boron might diffuse through the TiN coating during the TiB_2 deposition. The maximum allowable boron concentration in the substrate sets the limits of the gas composition and the minimum required TiN layer thickness.

5.3. The deposition of TiN on molybdenum

The relations between the properties of TiN and the deposition conditions are studied more system-

atically with molybdenum substrates. In general the layers on molybdenum are smoother than on nickel. Fig. 4 gives a micrograph of a layer obtained at high temperature and considered to be rough within this series, but generally considered to be fairly smooth. Layers, which have been deposited at lower temperature are smooth, do not show any structure and conform to the substrate surface perfectly. Details on the roughness of the coatings and their determination are reported elsewhere [12]. In all cases studied, the coatings consist of stoichiometric TiN, contain no chlorine and are gold colored. No interlayers are found.

If we consider the relation between the layer thickness, as determined by weight, and the reaction time, viz. fig. 5, we notice that the growth rate increases after about 30 min. Again this suggests a nucleation barrier. Once a closed TiN layer has been formed, it grows easily.

There is a difference between the first and the last substrate. Clearly TiN shows a smaller growth rate on the last substrate. Increasing concentrations of the waste product HCl further down the reactor, can retard the coating growth rate.

A similar difference between the first and the last substrate is observed in the relation between the layer thickness and the $TiCl_4$ content of the gas mixture

Fig. 4. Scanning electron micrograph of the surface of a titanium nitride layer on molybdenum. The layer is considered to be rough. Deposition conditions: 1100°C, 2% $TiCl_4$, $H_2/N_2 = 1/1$, flow = 17 ℓ/h, time = 2 h. Bar indicates 5 μm.

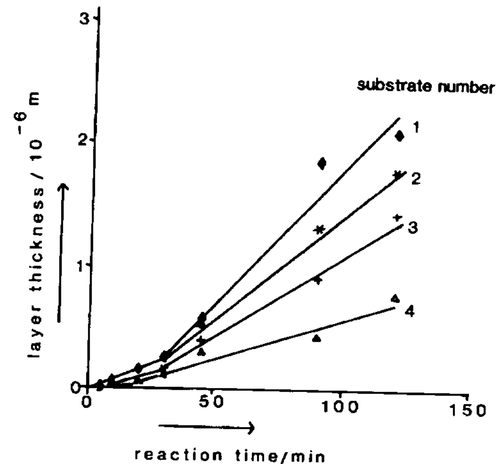


Fig. 5. Thickness of the TiN layer (determined by weight) on molybdenum as a function of deposition time, 900°C, 1% $TiCl_4$, $H_2/N_2 = 1/1$, 17 ℓ/h.

(fig. 6). The first substrate seems to satisfy the square-root relation derived by Jung et al. [16] for a reaction rate limitation with, as a rate-determining step, the reaction between adsorbed nitrogen, and an adsorbed complex of Ti·2HCl. The last substrate, however, shows a linear relation between the layer thickness and the concentration. This means that in this case a different rate determining step occurs. As already pointed out by Jung et al. [16] the presence of HCl in the gas mixture will induce increased ad-

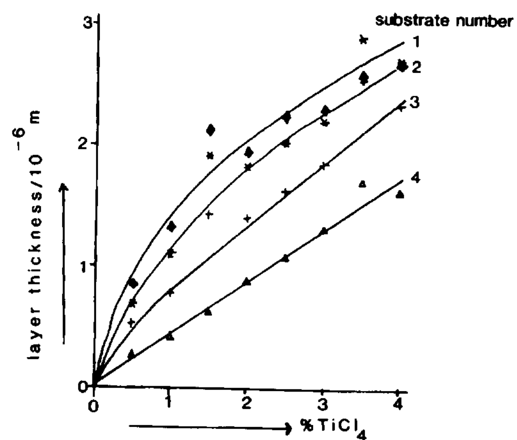


Fig. 6. Thickness of the TiN layer (determined by weight) on molybdenum as a function of the $TiCl_4$ concentration in the gas phase. 900°C, $H_2/N_2 = 1/1$, 2 h, 17 ℓ/h.

sorption of HCl at the surface, thereby shifting other adsorption equilibria and hence changing the reaction rate limiting step. The smoothness of all layers indicates reaction rate control in all cases.

Several models [17] describe the relation between the total flow of reactant (the linear velocity of the gas), and the growth rate. These models are based on transport phenomena in the gas phase and are only valid at low flow rates, for which supply limitation occurs. They are derived in the case of one decomposing reactant, for instance the formation of silicon out of silane. They predict for low flow rates a square-root relation between the flow rate and the growth rate, whereas at high flow rates the growth rate becomes independent of the flow rate. In the latter case reaction limitation occurs. In case of the formation of TiN, following the decomposition of $TiCl_4$, a reaction with nitrogen takes place. Therefore, the abovementioned models cannot describe the supply limitation for this more complicated reaction. Furthermore, it is uncertain how the growth rate depends on the flow rate in case of reaction rate limitation.

The experimental findings are presented in fig. 7. All the substrates show a linear relation between growth rate and flow rates. No change of slope, possibly indicating the change from reactant gas supply limitation to reaction rate limitation can be observed. The smoothness of the layers, however, suggests that in the whole concentration range reaction rate limitation occurs. The facts, that the slope of the last substrate is again quite different and that all lines, except for the first substrate, intersect the abscissa, show that the actual concentration of the reactants and the side products still influence the reaction rate in this complicated reaction, although reaction rate limitation occurs.

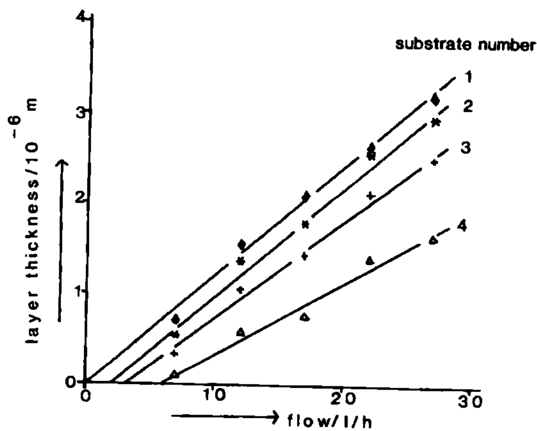


Fig. 7. Thickness of the TiN layer (determined by weight) on molybdenum as a function of the total flow rate.

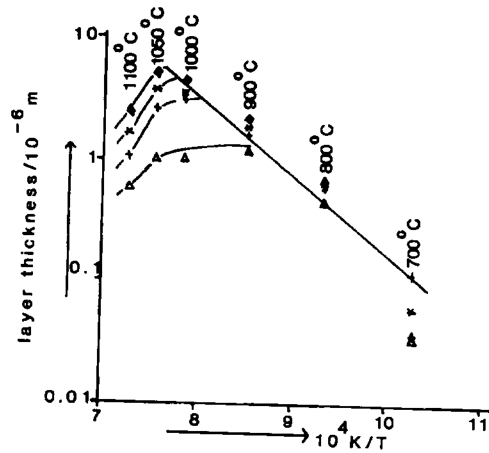


Fig. 8. Thickness of the TiN layer (determined by weight) on molybdenum as a function of the reciprocal temperature. 2% $TiCl_4$, $H_2/N_2 = 1/1$, 17 ℓ/h, 2 h.

With an Arrhenius plot as given in fig. 8, where the logarithm of layer thickness is plotted as a function of the reciprocal temperature, the effective activation energy of the reaction can be determined, if straight lines occur. Again a great difference between the first and the last substrate can be observed. At high temperatures the growth rates are retarded: at 1100°C for the first substrate and already at 1000°C for the last one. This retardation may be due to the presence of HCl, possibly etching the substrate. But more likely is that the presence of HCl shifts the position of the equilibrium of reaction (1).

The data are too limited at present to decide as to whether a different activation energy, indicating another rate-determining step, has to be taken into account for the last substrate at low temperatures.

6. Conclusions

TiN can be prepared reproducibly on molybdenum but not on nickel with CVD using $TiCl_4$, N_2 and H_2. The reaction mechanism is very complex, not

only because there are three reactants, but also because the waste product HCl seems to play a very important role. The dense coatings can be applied as diffusion barriers for boron under CVD conditions.

Acknowledgement

These investigations have been financed by the Dutch Ministry of Economic Affairs in the framework of the Innovation Directed Research Programs (IOP).

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