PROPERTIES AND PRACTICAL RESULTS OF TUNGSTEN CARBIDE COATING PRODUCED BY LOW TEMPERATURE CVD PROCESS

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Abstract – In forming tungsten carbide layer by low temperature and vacuum CVD, uniformity of film thickness, adhesion and gloss achieved when the effective zone of coating set is increased to $\phi 450 \times 1,100\text{mm}$ is described. Characteristics of tungsten carbide layer are evaluated and compared with other materials. Some practical applications to the mechanical parts of plastic injection molding machines are introduced.

1 Introduction

The technology of forming a tungsten carbide layer, at low temperature by the vacuum CVD, was developed by Archer et al (1-5). The advantages of this tungsten carbide layer forming process are summarized in the following two points.

- (1) In the conventional high temperature CVD, the reaction temperature is high, and thermal distortion is caused by heat treatment of the base metal after coating. Vacuum CVD is capable of coating at a temperature lower than the tempering temperature of steel and does not require subsequent heat treatment, thus thermal distortion does not occur.
- (2) In both the plasma CVD process and PVD, while it is possible to treat at low temperatures, the throwing power is poor for complicated shapes or for the inner wall of a long hole because the plasma generation region is limited. However in vacuum CVD the throwing power is as good as the conventional high temperature CVD process.

We have been continuing research into this process since 1985 with the purpose of enlarging the reaction volume and making this process practicable. This paper describes the quality achieved when the reaction volume is increased, the results of evaluation of characteristics of tungsten carbide layers, and the results of practical applications.

2 Increase of Reaction Volume and Quality Achieved

To use the technique of vacuum CVD in mass production, it was necessary to improve the profitability by increasing the reaction volume. We attempted to make the quality uniform, with the target of an effective coating zone of $\phi 450 \times 1,100\text{mm}$.

The apparatus is schematically shown in Figure 1.

The material gases were WF_6 (99.99%), C_6H_6 (99.9%), and H_2 (99.999%), and Ar (99.99%). Ar gas was used as carrier of C_6H_6 . In the reactor, in principle, the following reactions take place.

Fig.1 Schematic diagram of tungsten carbide coating apparatus

Depending on the reaction temperature, W_2C or W_3C is produced. And the reaction temperature is effected by the pressure in the reactor, the feed gas volume, and the gas mixing ratio. We studied the method of uniformly producing W_3C , which is formed at the lower reaction temperature, for the purpose of preventing thermal distortion.

Table 1 shows the quality evaluation the targets, and the achieved results.

For evaluation of gloss distribution, 150 test pieces of $\phi 30 \times 80\text{mm}$ (AISI-1045) were uniformly arranged in a $\phi 450 \times 1,100\text{mm}$ zone, together with 9 test pieces of $\phi 50 \times 10\text{mm}$ (AISI-M2), for evaluation of distribution of film thickness and adhesion. All test pieces were processed to surface roughness of $R_{\text{max}} 0.4\mu\text{m}$ or less, and were coated with $4\mu\text{m}$ electroless Ni-P plating.

Table 1 Quality evaluation

Evaluation items	Method of evaluation	Quality targets	Present status of 10 batches
Distribution of film thickness	Thickness on 9 test pieces of $\phi 50 \times 10\text{mm}$ inserted uniformly in $\phi 450 \times 1100\text{mm}$ zone were measured by ball tester.	$8 \pm 2 \mu\text{m}$	Average ($\bar{x}$) 7.7 μm Scatter (σ_{n-1}) 0.7 μm max 8.5 μm min 6.7 μm
Distribution of gloss	Gloss of 150 test pieces of $\phi 30 \times 80\text{mm}$ inserted uniformly in $\phi 450 \times 1100\text{mm}$ zone were judged visually compared with A-H gloss standard.	Defect rate of D-H (matte) 3% or less	Defect rate of D-H (matte) 0%
Distribution of adhesion	Adhesion of the above 9 test pieces of $\phi 50 \times 10$ were measured by scratch tester.	35N or more	Average ($\bar{x}$) 39.8N Scatter (σ_{n-1}) 2.4N max 43.0N min 37.5N

The gloss corresponded very well to the morphology (grain size) of the tungsten carbide layer film as shown in Figure 2, and therefore, the gloss was evaluated as a measure of morphology. Photo 1, shows the surface structure of the tungsten carbide layer, observed in the

Photo 1 Various surface appearances of tungsten carbide layer

Fig.2 Relation between the grain size and the gloss

Photo 2 Surface appearance of the tungsten carbide layer of the achieved quality

process of achieving uniformity. The surface picture of the tungsten carbide layer of the achieved quality is given in Photo 2, a sectional picture in Photo 3, and the X-ray diffraction pattern in Figure 3.

What was most important in creating uniformity, was matching the feed rate of the reaction gas to the an reaction rate on the substrate surface (6,7).

Photo 3 Cross section of the tungsten carbide layer of the achieved quality

Fig.3 X-ray diffraction pattern of tungsten carbide

3 Characteristic Evaluation Test Results of Tungsten Carbide Layer

3-1 Hardness At Elevated Temperature

The hardness at elevated temperature in vacuum is compared with other materials in Figure 4.

3-2 Oxidation Resistance

Figure 5 shows the comparison of the oxidation rate when heated in air with TiC coating.

Fig.4 Comparison of hardness at elevated temperature with other hard materials.

Fig.5 Progress rate of oxidation of TiC and W3C layer

3-3 Wear Resistance

Figure 6 shows a comparison of the coefficient of friction and wear rate with other materials using the pin and disk friction and wear test.

Test condition	
	condition
Material of Pin	AISI-52100
Load	500g
Sliding speed	10mm/sec
Lubricant	no
Total number of revolution	15,916
Total distance of friction	1,000m

Fig 6. Comparison of wear resistance by Pin-Disk tester with other materials

3-4 Corrosion Resistance

Figure 7 and 8 show the comparative results of weight loss due to corrosion with other materials, when immersed in 15% HCl aqueous solution, and 15% H₂SO₄ aqueous solution, respectively.

Fig.7 Comparison of corrosion resistance in 15% HCl solution with other materials

Fig.8 Comparison of corrosion resistance in 15% H₂SO₄ solution with other materials

3-5 Parting Property

Pellets of polycarbonate put on a substrate were heated at 330°C in N₂ atmosphere, melted, and cooled at room temperature. The load required to separate them from the coated substrate was measured by a simple method. Photo 4 shows the polycarbonate melted and cooled on the coated substrate. Figure 9 gives a Schematic diagram of the measuring apparatus, and Figure 10 shows the results when compared with other materials.

Fig.9 Schematic diagram of parting test apparatus

Fig.10 Comparison of parting property with other materials

Photo 4 Polycarbonate melted and cooled on coated substrate

4 Results of Practical Use

Recently there has been an increasing demand for engineering plastics, and super-engineering plastics. Therefore wear resistance, corrosion resistance and parting properties are required in the mechanical parts molding them by injection or ejection.

Making use of these characteristics of tungsten carbide coating, as well its low distortion and high throwing power, we can achieve successful results when applied to these parts. Some of the examples are given below.

4-1 Cylinder (Photo 5)

In the case of cylinders fabricated in an injection molding machine, using a mixture of 40% glass fiber in PPS at 300-330°C, the nitrided cylinder had to be replaced after about 8 months, and the alloy-lined cylinder after about 12 months due to wear. However, the cylinder having the inner surface coated with tungsten carbide could be used for about 2.5 years.

4-2 Screw (Photo 6)

In the case of screws fabricated in injection molding machine, using fluoroplastians (PFA) at 350-360°C, the hard chrome plated screw must be polished to remove surface deposits which cause contamination and degeneration once every three or four days. Pitting was also caused by HF in the course of use and contamination was further increased. By contrast, the tungsten carbide coated screw was free from contamination or pitting corrosion after several months of use.

4-3 Cylinder Head, Intermediate Nozzle, Nozzle (Photo 7)

Screw Head, Counterflow Preventive Ring, Seal Ring (Photo 8)

In these parts, too, excellent results were achieved, such as, wear resistance to resin mixed with glass fiber, corrosion resistance and contamination resistance to resin generating corrosive gases and contamination resistance to polycarbonate or transparent resins.

Photo 5 Cylinder

Photo 6 Screw

Photo 7 Cylinder head, intermediate nozzle, nozzle

Photo 8 Screw head, counterflow preventive ring, seal ring

4-4 Grained Die (Photo 9)

In the case of a grained die, for an injection molding machine using phenol resin at 75-150°C, an untreated steel die is normally used. Using this material, however, parting of the molded products was poor, and many defective pieces were produced. In addition, after repeated use, the graining pattern disappeared due to wear.

In the case of the grained die coated with tungsten carbide, the parting performance is smooth, defective formed pieces are eliminated, and wear of the graining surface is hardly noticed.

Photo 9 Grained die

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