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ARTICLE

# Preparation and Characterization of Ceramic Film on Drilling Pipe Joint

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**Abstract:** A metallic ceramic film consisting of nitrides, carbides and oxides of Ti, Cr and Al was prepared on the surface of a drilling pipe joint by low pressure chemical vapor deposition (LPCVD). The film was characterized by scanning electron microscopy (SEM), energy-dispersive X-ray spectroscopy (EDS) and X-ray diffraction (XRD). The adhesive ability and the corrosion resistance performance were evaluated by scratch test and corrosion test, respectively. The results show that the film is dense and homogeneous with 15 μm in thickness including a 5 μm transition layer. The film presents a good adherence to the substrate with no cracks and no pores. It could decrease electrochemical corrosion and chemical corrosion through separating the harmful atoms or ions from the substrate. Particularly, it could also effectively prevent $H_2S$ and $CO_2$ from contacting the steel, avoiding hydrogen blistering (HB) and hydrogen to induce cracking (HIC). Consequently, the service life of drilling pipe can be greatly improved.

**Key words:** LPCVD; ceramic film; wear resistance; corrosion resistance

With the development of oil and gas exploration, the drilling environment is becoming much severer, especially in oil and gas fields where exist high content $CO_2$, $H_2S$, $Cl^-$ and sulfur. Therefore, corrosion is the main reason for the drilling pipe failure. According to the statistics in drilling industry, almost 60% of the drilling string failure accidents are due to the corrosion in drilling fluid[1]. In general, the surface modification of drilling pipe joint through ceramic film coating technology is one of the effective methods to improve corrosion resistance of the drilling pipe joint. The metallic ceramic film can overcome the brittleness of ceramic and present excellent properties in strength, toughness, hardness, wear resistance and corrosion resistance[2-4]. Therefore, the ceramic film coating technology finds a wide application in anticorrosion fields. For instance, Xue Qi [5] et al. prepared the ceramic film on the surface of down hole tools successfully, and their results showed that the ceramic film had good corrosion resistance. Zhai Yanbo[6] investigated the influence of the current parameters of plasma oxidation ceramic film on its corrosion resistance, and the results revealed that current density and pulse form had great effect on the corrosion resistance of the ceramic coating on the alloy surface. Masao[7]prepared the ceramic film with strong adhesion, uniformity and good corrosion resistance on low carbon steel and stainless steel surfaces successfully. Some other scholars also studied the structure and the properties of nanostructured ceramic film[8-15]. W. C. Ma[16] studied the process of chemical vapor deposition of $TiC/Al_2O_3$ and the performance of cemented carbide blade with coatings. However, there are few studies about the preparation and characterization of the metal ceramic film on the surface of the drilling pipe joint. In this paper, we described the preparation process of the metallic ceramic film and studied the relationship between microstructure and properties of the metal ceramic film. The chemical vapor deposition technology provides a new anticorrosion method for oil-gas field downhole tool materials.

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## 1 Experiment

The substrates used in this study were 37CrMnMo (G105) from the drilling pipe joint and the chemical composition of G105 is shown in Table 1. It contains about 0.37% carbon which ensures its strength, toughness and weld ability and 1.08% Cr and 0.30% Mo which can improve its harden ability, tempering stability and corrosion resistance. The microstructure of 37CrMnMo is a tempered sorbite. Fig.1 illustrates the preparation process of the metal ceramic film. The gas reaction source mainly included $H_2$, $N_2$, $CO_2$, $CH_4$ and $Ar_2$ with the purity of 99.99% among which $H_2$ and $Ar_2$ were shielding gases, while $N_2$ and $CH_4$ were reaction gas. The exhaust gas treatment device consisted of an acid gas spray synthesis system and an exhaust gas absorption system. The acid gas spray synthesis system was used for neutralizing the acid gas formed in the reaction, while the exhaust gas absorption system was used to absorb CO. Vacuum system was a rotary-vane pump. Deposition pressure was $0.5\times133$ Pa (The samples were numbered as follows: JB—the original samples without CVD treatment; JR—the samples with CVD ceramic film treatment).

As the bonding property between $Al_2O_3$ and substrate is not strong, a layer of TiC or TiN was prepared firstly on the metal surface, which can improve the bonding property of $Al_2O_3$ coating. The thermal expansion coefficient of TiC is closer to the metal substrate than that of TiN, so the residual stress of TiC coating is smaller and the bonding property between TiC and substrate is excellent. Meanwhile, TiC coating can prevent the crack propagation effectively. Therefore, TiC coating was selected as the first layer of the multilayer coating on metal substrate. In this work, the metal ceramic film on the surface of the drilling pipe joint was prepared by LPCVD. The TiC coating was prepared as the first layer, the TiCN coating doped with some Cr was prepared as the middle layer, and the $Al_2O_3$ coating was deposited as the outermost layer.

The reactions of these films formation are shown in the following formula (1) ~ (4):

$$TiCl_4(g)+CH_4(g)+H_2(g)\rightarrow TiC(s)+4HCl(g) \quad (1)$$

$$Ti_xCr(CO)_y(g)+CH_4(g)+H_2(g)\rightarrow TiCrC(s)+CO(g)+H_2(g) \quad (2)$$

$$Ti_xCr(CO)_y(g)+N_2(g)+H_2(g)\rightarrow TiCrN(s)+CO(g)+H_2(g) \quad (3)$$

$$2AlCl_3(g)+3CO_2(g)+3H_2(g)\rightarrow Al_2O_3(s)+6HCl(g)+3CO(g) \quad (4)$$

The morphologies of the ceramic film were examined by scanning electron microscope (SEM, VEGA II XMH). In order to investigate the growth characteristics of the ceramic film, the cross section elements distribution of ceramic film was analyzed by SEM with INCA Energy 350 spectrometer. The element distribution in the cross section was analyzed by line scan. The film thickness was evaluated by the method of metallographic inlaying. Phase analysis of the metal ceramic coating was analyzed by XRD. According to JB/T 8554-1997[17], the bonding strength of ceramic film was measured by MFT-4000 multifunctional material surface performance tester. The ZF-9potentiostat, ZF-4potential sweep generator and ZF-10 data acquisition storer were used for the electrochemical test. The working electrode was G105 drilling pipe steel with working face of 10 mm×10 mm, the reference electrode was saturated calomel electrode and the auxiliary electrode was platinum electrode. The experimental medium was HAc/NaAc buffered solution with pH4. The scanning potential range was ±400 mV of self-corrosion potential. Scan speed was 100 mV/min. The corrosion resistance of ceramic film in the corrosion media containing $H_2S$, $CO_2$ and $Cl^-$ was tested by a self-made autoclave.

## 2 Results and Discussions

**Table 1 Chemical composition of G105 drilling pipe joint material (wt%)**

| Element | Iron | C | Si | Mn | P | S | Cr | Mo | Ni | V | Al | Cu | Ti |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Content | Bal. | 0.37 | 0.25 | 0.93 | 0.011 | 0.0019 | 1.08 | 0.30 | 0.10 | 0.0067 | 0.015 | 0.013 | 0.0039 |

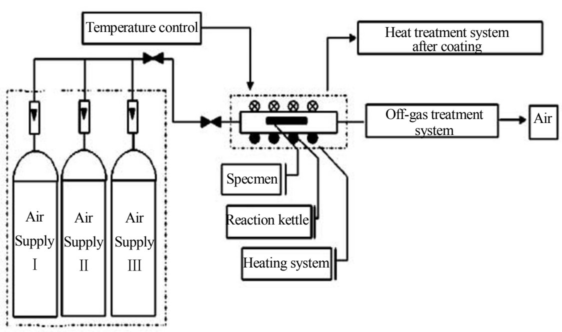


Fig.1 Preparation process flow diagram of the metallic ceramic film

### 2.1 Morphological analysis

Fig.2 shows the surface and cross-sectional morphologies of ceramic film. The ceramic film is compact, no pores and no cracks were observed. Film and metal substrate are bonded closely, which can ensure good wear resistance. At the same time, the ceramic film with a certain thickness could protect the substrate and improve the wear resistance and corrosion resistance effectively.

### 2.2 Chemical composition studies

The typical EDS of ceramic film surface is shown in Fig.3. The ceramic film is mainly composed of Al, O, Ti, and C which make the film have high radiation resistance, wear resistance and high antioxidant properties.

The element distribution in the cross section was