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A study of CVD growth kinetics and morphological evolution of rhenium from $ReCl_5$

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ABSTRACT

Rhenium was fabricated on molybdenum by chemical vapor deposition (CVD) of $ReCl_5$ in a cold-wall atmospheric pressure reactor at temperature range of 1000 to 1300 °C. To investigate the deposition mechanism, the process was carried out by direct sublimation of $ReCl_5$ powder instead of the commonly used in-situ chlorination of solid rhenium method to supply the precursor. The effects of deposition temperature, $ReCl_5$ partial pressure, and molybdenum substrates on deposition velocity, microstructure were investigated. The deposition was under kinetics control and fitted to a 1.5-power relation versus $ReCl_5$ partial pressure at 1150 to 1250 °C. One reaction pathway has been proposed depending on $ReCl_5$ partial pressure. At deposition temperature below or equal to 1100 °C, the reaction between molybdenum and $ReCl_5$ was calculated and discussed. Evolution of coating microstructure was summarized into a schematic with four typical deposited regions, which provides a simple and efficient way to deposit certain microstructures of rhenium coatings.

1. Introduction

Given its superior high-temperature strength, high ductility, and high corrosion resistance properties, the refractory metal rhenium is applicable for high-temperature circumstances, such as rocket nozzles and rocket thrust divert valves [1–4]. In certain demanding applications, such as fabrication of freestanding complex-shaped rhenium products, rhenium properties can be optimally exploited by adopting chemical vapor deposition (CVD) [5–14].

The most common precursors in rhenium CVD process are ReF_6, $Re_2(CO)_{10}$, and $ReCl_5$. Deposits of rhenium from ReF_6 were produced as thick as 2 mm through hydrogen reduction reaction at 400 to 1500 °C [10]. However, the prepared rhenium from ReF_6 may produce gas-phase precipitation, resulting in much more brittle as-deposited coating than that from $ReCl_5$ or powder metallurgy [14,15]. $Re_2(CO)_{10}$ has also been studied as a precursor to produce rhenium coatings on steel and C/SiC at 350 to 500 °C, with deposit as thick as 3.3 μm to 7.8 μm [11]. However, this precursor would produce carbon impurity which might cause solution strengthening or rhenium embrittlement [16]. In addition, some other rhenium organometallic compounds were rising these years, such as CH_3ReO_3 and $C_2H_5ReO_3$ [17,18]. These reactions took place at lower temperatures (<1000 °C); however, the ReO_x, and ReC_y were normally produced [17,19–22]. Rhenium prepared from pyrolysis of $ReCl_5$ has high purity and corresponding fine mechanical properties [14,15]. Consequently, more studies on CVD of rhenium from $ReCl_5$ have been conducted. According to these reports, two methods have been used to supply $ReCl_5$ for deposition, namely, in-situ chlorination of solid rhenium method for preparing $ReCl_5$ and direct sublimation of $ReCl_5$ [29]. The former method is mostly adopted because $ReCl_5$ is highly reactive with air and water [24].

Glaski et al. [25] investigated rhenium from $ReCl_5$ decomposition. In their research, chlorine gas was fed into a chamber containing rhenium powders heated to 700 to 800 °C. $ReCl_5$ was formed and passed over the 1050 to 1250 °C substrate surfaces, where $ReCl_5$ decomposed into rhenium and coated. Analogously, Harding [26] and Bai [27,28] successfully fabricated rhenium coating on molybdenum and guarded carbon substrates. With a deposition velocity of 20 μm/h to 140 μm/h, Bai also studied the influence of chlorine at 30 ml/min to 120 ml/min and claimed that chlorine increased the deposition velocity. Kim et al. [29] deposited rhenium on molybdenum substrates through pyrolytic

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decomposition of $ReCl_5$, which was supplied by chlorination of rhenium at 800 °C. Unlike former researchers, Kim adopted a cycle system for $ReCl_5$ from in-situ chlorine, which increased the effective use of the precursor and improved the deposition velocity to 200 μm/h at a deposition temperature of 1150 °C.

Powell et al. [23] adopted both methods to fabricate rhenium from $ReCl_5$ and claimed that the best process was the pyrolytic decomposition of $ReCl_5$ prepared by sublimation. King et al. [30] studied the possibility of chemical vapor infiltration of rhenium on C/SiC substrate with $ReCl_5$ precursor, which was either prepared by in-situ chlorination of rhenium metal granules at 760 to 800 °C or sublimation of $ReCl_5$ powder at 67 to 220 °C. Deposition took place at 752 to 1051 °C under atmospheric pressure. According to King, the chlorination method produced thicker deposits, whereas the sublimation method produced finer-grained and more uniform deposits. He also found that higher chlorine flow rates yielded more rhenium deposits.

All great progress in rhenium CVD was made for the process and final products. However, distinctive differences are obvious between reported deposition velocities and growth qualities. Therefore, elucidating the mechanism during the deposition process is necessary for preparation of high-quality rhenium coatings from $ReCl_5$ at high deposition velocity. However, in the former reports, given that unreacted chlorine was inlet into the reactor as both carrier gas and reactant of $ReCl_5$, this process seemed much more complex. In the present research, an elegant way to use $ReCl_5$ precursor and Ar carrier gas was set up. Growth kinetics and microstructures of rhenium CVD films deposited at growth temperatures of 1000 to 1300 °C were described; a growth process was proposed to account for the formation of rhenium deposited from $ReCl_5$. Efforts were made to explain the relationship between deposition qualities and process conditions from the $ReCl_5$ pyrolysis.

2. Experimental

The experimental setup for the reaction studies is sketched in Fig. 1. The reaction apparatus is made of quartz and Teflon, which can resist corrosion of chlorine gas from the decomposition of $ReCl_5$.

The precursor $ReCl_5$ is air-sensitive and volatile; thus, $ReCl_5$ powder was weighed and packed into a glass reservoir equipped with Teflon valves in protective atmosphere of Ar right after the precursor was made. The precursor flux, which was controlled by oven temperature, was measured by the weight loss; the stability of the precursor supply was tested. Fig. 2 shows that the evaporation capacity is stable within 120 min at 220–390 °C and at least 40 min at 395 °C. Therefore, deposition time was chosen within this range, which could guarantee a steady supply of $ReCl_5$ when ~100 μm thick coatings were produced.

The substrate chosen was powder metallurgical molybdenum cut into a vertical cylinder (250 mm high; 6 mm in diameter). All molybdenum substrates were annealed at 1000 °C for 1 h to avoid machine stress. The substrate was sand blasted with Al_2O_3 particles and cleaned in liquid degreaser and deionized water sequentially for 5 min each before deposition.

All experiments were carried out under the conditions summarized in Table 1, unless stated otherwise. Samples will be represented in the following way: a sample deposited at a °C, b × 104 Pa will be named as Sample a/b. Therefore, the sample named as 1200/0.8 was obtained at the deposition temperature of 1200 °C, with the $ReCl_5$ partial pressure of 0.8×10^4 Pa. Deposition time was sufficient to generate coating with thickness of ~100 μm, as measured using cross-sectional metalloscopy.

The substrate was vertically suspended in the reactor and heated by a high-frequency induction heating (Xi'an Tianfeng, IGPS-30KW-200KHz). The substrate temperature was measured using an infrared thermometer (Xi'an Innocent, ATS). The flow rate of argon (99.999 wt.%) was determined using an electronic mass-flow meter (Beijing Sevenstar D07). The composition of the coating was examined by an energy dispersive spectroscopy (EDS, IE250X-Max50). Surface morphology was studied by field-emission scanning electron microscopy (SEM, Hitachi S4800), with 15 keV accelerating voltage utilized for collection of SEM images. Structures were characterized by X-ray diffraction (XRD, Panalytical X'Pert PRO MPD), using a copper source anode operated at 20 kW. Metallurgical structures were studied with a metallographic microscope (OM, Leica DM4000M).

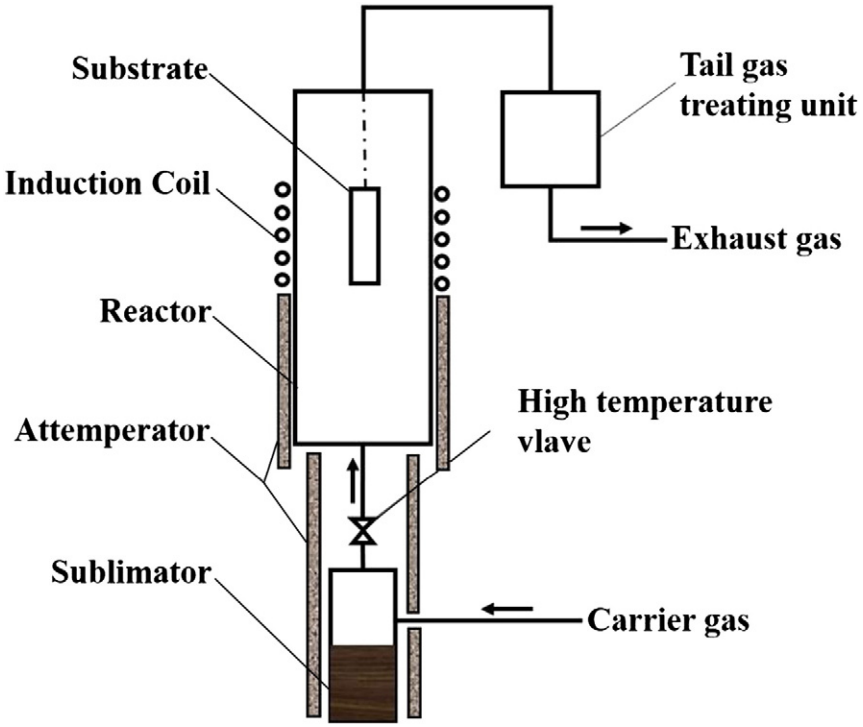

Fig. 1. Experimental setup of Re CVD from $ReCl_5$.