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TITLE: LOW-TEMPERATURE CHEMICAL-VAPOR DEPOSITION OF TUNGSTEN FROM TUNGSTEN HEXACARBONYL

AUTHOR(S): Gerald J. Vogt

MASTER

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Los Alamos Los Alamos National Laboratory
Los Alamos, New Mexico 87545

LOW-TEMPERATURE CHEMICAL-VAPOR DEPOSITION OF TUNGSTEN FROM TUNGSTEN HEXACARBONYL

Gerald J. Vogt
Los Alamos National Laboratory, Group CMB-6,
Mail Stop 770, Los Alamos, NM 87545

Abstract

Chemical vapor deposition (CVD) of tungsten from $W(CO)_6$ has been investigated below 670 K as an alternate process to WF_6 CVD for coating glass microspheres. The major advantages of $W(CO)_6$ CVD are the elimination of the HF damage to the glass microspheres and potentially a lower deposition temperature for coating DT-filled microspheres. $W(CO)_6$ CVD can be utilized, in principle, to coat the microspheres with 1 to 5 μm of tungsten or to flash coat the microspheres for further coating by WF_6 CVD. Test coatings were deposited in a fluidized-bed reactor with a hydrogen carrier gas. The coatings were found to contain nearly-equal portions of carbon and oxygen, ranging from 16 to 25 at.% for each element. The high carbon and oxygen concentrations are believed to result principally from the physical entrapment of chemisorbed CO molecules at the surface of the growing deposit. The general quality and adhesion of the $W(CO)_6$-derived coatings are unsatisfactory at this time for ICF applications. The poor coating quality may possibly be due to an undesirable design feature in the fluidized-bed reactor.

I. Introduction

A variety of refractory metallic coatings can be successfully deposited on microspheres by chemical vapor deposition (CVD) in a gas-fluidized bed. For inertial confinement fusion (ICF) targets the application of chemical vapor deposition encounters specific process difficulties in addition to the dimensional and material constraints common to all potential coating techniques. The deposition conditions for a desired metallic coating must be chemically compatible, as well as thermally compatible, with bare or previously coated microspheres. Coating microspheres filled with a deuterium-tritium fuel can represent a major problem for retaining the fuel under CVD conditions.

Tungsten deposition by CVD demonstrates the serious nature of the compatibility problem that can occur between the substrate and the deposition conditions. Tungsten coatings are of interest for pusher layers in ICF targets because of their high density and Z number. Typically, CVD tungsten is deposited by the chemical reduction of WF_6 in hydrogen at $\sim$ 725 K. Within a fluidized bed microspheres can readily be coated with a fine grain metal of target quality. However, tungsten coatings cannot be achieved on bare glass microspheres due to the excessive surface damage resulting from HF, a major process by-product. Moreover, the desired deposition temperature of $\sim$ 725 K is generally too high compared to the permeation fill temperature used for bare or coated glass microspheres.

The deposition of tungsten from $W(CO)_6$ is being considered as an alternate process to the WF_6 CVD process for coating glass microspheres and other HF-sensitive substrates. The major advantages to the pyrolysis of $W(CO)_6$ are the presence of a more chemically benign environment and the potential of a lower deposition temperature. The thermal decomposition[1] of $W(CO)_6$ becomes detectable near 500 K, increasing sharply above 525 K. The

$W(CO)_6$ process can be utilized, in principle, to coat glass microspheres with a thin layer (1 to 5 μm) of tungsten or to flash coat a HF-sensitive substrate for further coating by the WF_6 process.

Our study of the low temperature deposition of tungsten from $W(CO)_6$ has concentrated on $W(CO)_6$ pyrolysis in hydrogen below 670 K within a CVD fluidized bed. The oxygen and carbon contents of the coatings were measured to ascertain if any signficant lowering of the mean atomic number occurred. The possible reaction mechanisms for the inclusion of oxygen and carbon within the deposits are discussed. The general quality and adhesion of the low temperature coatings are described for several common substrates.

II. Experimental

A schematic diagram of the deposition apparatus used to prepare the coatings for chemical analysis is shown in Fig. 1. The reaction vessel, typically used in this laboratory, was constructed of Pyrex glass with a coarse Pyrex frit gas distributor. The coating zone was a 76-mm-high cylindrical section (from the frit to the expansion cone) with a 12-mm i.d. During deposition the fluidized bed was completely contained within the coating zone. The water-cooling jacket on the lower portion of the vessel extended above the coarse frit by ~ 7 mm to prevent plugging during deposition.

Within the coating zone the mean deposition temperature was established by a resistive furnace and was measured by a thermocouple inserted into the center of the substrate bed at middle bed height. The deposition pressure was maintained at 20 or 40 kPa by a servo-metering valve connected to a vacuum pump. Capacitance manometers measured the inlet and exit pressures to the reaction vessel.

The $W(CO)_6$ solid was placed within the inlet section of the reaction vessel, shown in Fig. 1, enclosed by the water-cooling jacket. The $W(CO)_6$ vapor was transported to the coating zone by passing the metered hydrogen carrier gas through the solid reactant. The $W(CO)_6$ partial pressure was controlled by regulating the temperature of the solid with a circulating water bath. Typically, the vaporization temperature was set at a value between 333 and 353 K.

The test coatings were prepared by initially establishing the desired deposition temperature within the substrate bed under a hydrogen flow, while cooling the solid $W(CO)_6$. Actual coating began by rapidly raising the solid $W(CO)_6$ temperature to the required vaporization temperature. During deposition the partial pressure ratio of hydrogen to $W(CO)_6$ was maintained at a constant value, ranging from 100 to 1500. After the desired deposition time, the pyrolysis reaction was quenched by rapidly cooling the solid $W(CO)_6$. The duration of deposition varied from 5 to 7 hours.

The coatings analyzed for their oxygen and carbon contents were deposited upon nickel-alloy microspheres with a 177- to 210-μm-diam range. The quantity of microspheres used for the depositions ranged from 4 to 5 cm^3 in volume. The nickel-alloy microspheres were chosen as the test substrates due to their low oxygen and carbon contents ($\sim$ 2 wt% O and $\sim$ 0.3 wt% C). The oxygen and tungsten concentrations of each coating were determined by neutron activation analysis; the carbon concentration was determined with a LECO low carbon analyzer.

III. Results and Discussion

The chemical composition results for the $W(CO)_6$-derived coatings are given in Table I for deposition temperature ranging from 548 to 659 K. The

estimated analytical uncertainty for the data is ± 10%. The partial pressure ratio of hydrogen to $W(CO)_6$ was computed from the total inlet pressure to the reaction vessel and the known vapor pressure[2] of $W(CO)_6$. The partial pressure ratios of 100 to 200 would typically be used to coat ICF substrates, yielding deposition rates of 0.3 to 0.6 μm/hr.

As evident from Table I, the $W(CO)_6$-derived coatings contain rather high levels of oxygen and carbon, ranging from 16 to 25 at.% for each element. The tungsten content of these coatings is generally not greater than 65 at.%, resulting in a significantly lower mean atomic number than that obtained by the WF_6 process. Interestingly, the oxygen and carbon concentrations are essentially equal with a mean atomic ratio C/O of 1.02 (omitting the data for the two coatings near 650 K). This observation suggests the possibility of a common mechanism for the incorporation of the two elements into the test coatings.

The only major exceptions to the above observations occur for the two coatings obtained near 650 K with partial pressure ratios greater than 900. The reason for the absence of any detectable oxygen in these coatings is presently not known, although the oxygen analyses for these coatings are suspect and require verification by duplicate test coatings. Despite the apparent lack of oxygen, the coatings still possess a relatively high fraction of carbon.

An earlier kinetic study[3] of the pyrolysis of $W(CO)_6$ also found equally large amounts of oxygen and carbon (~ 25 at.% each) in the metallic deposit obtained below 560 K. The large oxygen and carbon concentrations were observed in deposits produced in significant initial partial pressures of argon, helium, and carbon monoxide. In our study the use of the hydrogen carrier gas does not appear to offer any major advantage in the reduction of the incorporated oxygen and carbon in the low temperature coatings.

In Table I the compositions of the coatings deposited near 600 K indicate that, although the $W(CO)_6$ partial pressure can be reduced by more than an order of magnitude, the oxygen and carbon contents remain relatively constant with a marginal decrease at the highest partial pressure ratio $H_2/W(CO)_6$.

The chemical nature of the co-deposited oxygen and carbon from the low temperature pyrolysis of $W(CO)_6$ remains an open question despite the considerable interest in these coatings by Russian researchers.[1,5] The possible formation of oxides and carbides by reactions between tungsten and carbon monoxide appears favorable from thermodynamic analysis;[4] however, the formation of oxides and carbides below 570 K has not been experimentally established[1,5] for the tungsten-carbon monoxide system. Nevertheless, their formation in the pyrolytic deposits cannot be completely dismissed.

The structure of these low temperature deposits from $W(CO)_6$ has recently been examined by x-ray and electron diffraction methods.[5] The investigators concluded that the pyrolysis of $W(CO)_6$ at 573-623 K yields a metastable fcc phase of variable lattice period and composition, that is, an interstitial solid solution, rather than a tungsten carbide. Note that this and all earlier structural studies[5] do not consider or report on the presence of co-deposited oxygen in the test films.

In an attempt to detect the possible formation of oxides and carbides within the coatings, a thin film from $W(CO)_6$ pyrolysis was prepared by suspending a cleaned thin strip of molybdenum in a fluidized bed for coating at ~ 635 K. The thin film (1 to 2 μm) deposited on the molybdenum substrate was then examined by x-ray photoelectron spectroscopy (XPS). The XPS spectrum indicated oxygen and carbon concentrations of roughly 13 and 23 at.%, respectively, with a significantly larger uncertainty in the carbon value than in the oxygen value. The spectrum contains symmetrical

O(1s) and C(1s) peaks centered at binding energies of ∿ 530.5 and ∿ 284.2 ev, respectively. The O(1s) and C(1s) peaks cannot be confidently assigned in our qualitative analysis, although these data may be interpreted as indicating the possible existence of some tungsten oxide with free carbon[6] or of some adsorbed CO[7,8] entrapped within the deposit. The XPS features relating to tungsten in the film appear to be essentially identical to that for tungsten metal.[6,7] The tungsten $4f_{7/2}$ and $4f_{5/2}$ peaks at binding energies of ∿ 31.3 and ∿ 33.4 ev show no clear evidence of any shoulders or broadening to higher binding energies as is expected for tungsten carbides and oxides.[6] On the basis of this analysis of one film one can cautiously speculate that tungsten oxides and carbides probably do not form during the low temperature pyrolysis of $W(CO)_6$.

To gain some chemical insight into the coating reaction, a qualitative analysis of the CVD by-product gas was periodically performed with the quadrupole residual gas analyzer, shown in Fig. 1, sampling downstream from the reaction vessel. The by-product gas consisted principally of H_2 and CO with only rather minor amounts of CO_2 and H_2O which are largely due to outgassing from the CVD apparatus. Other investigators[1,3] have also reported that below 670 K the pyrolysis gas product is mainly CO with a minute amount of CO_2 (< 0.5 vol%). Thermodynamic calculations predict that the by-product gas should be rich in CO_2 via the CO disproportionation reaction, providing a major source for the carbon content of the coatings. The minor concentration of CO_2 in the by-product gas demonstrates that $W(CO)_6$ pyrolysis at low temperatures is clearly a nonequillibrium process. As such, the disproportionation of CO cannot possibly account for the high concentration of carbon found in the low temperature coatings.

Experimental observations from this and other studies are suggestive of a plausible explanation for the high oxygen and carbon impurities in the

low temperature coatings, which had not been seriously considered by earlier workers. The high oxygen and carbon concentrations may likely result from the physical entrapment of chemisorbed CO molecules at the surface of the growing deposit. The β-states[7,8] of adsorbed CO on tungsten are known to be relatively immobile and stable below 600-700 K, gradually desorbing at higher temperatures. Under the high CO partial pressure ($\geq$ 10 Pa) typical for the CVD process these chemisorbed molecules could readily be incorporated into the growing polycrystalline coatings. The physical incorporation of chemisorbed CO is certainly consistent with the observation of nearly-equal concentrations of oxygen and carbon in our low temperature coatings. Moreover, the possible existence of the moderately-bonded CO could account for the seemingly tungsten-like nature[7] of the XPS spectrum and for the formation of an interstitial solid solution. Nevertheless, stronger experimental evidence is needed to critically verify the physical entrapment of chemisorbed CO as a major source for the oxygen and carbon impurities below 670 K.

The general quality and adhesion of the $W(CO)_6$-derived coatings have proven to be unsatisfactory at this stage of our study. Figures 2(a) and 2(b) show typical SEM photomicrographs of the difficulties that have been encountered in coating the nickel-alloy microspheres. Both coatings are highly cracked and contain large surface nodules. Similar coating defects are also found for coatings on WF_6/tungsten-coated microspheres and bare glass microspheres. At a higher mean deposition temperature the quality of the coatings appears to improve, as evident by the SEM photomicrograph in Fig. 2(c). These coatings are relatively crack-free, although the outer surface still possesses defects of several μm in size.

At this time we believe that the rather poor quality of the $W(CO)_6$-derived coatings may be primarily a temperature effect resulting from the

design of the reaction vessel. The proximity of the water-cooling jacket to the coating zone, as shown in Fig. 1, produces a major temperature gradient, ranging from the $W(CO)_6$ vaporization temperature to the deposition temperature, in the lower portion of the coating zone. Several deposition experiments with thin molybdenum strips suspended in the fluidized bed confirm that the poorly adhering and cracked coatings do originate from deposition in roughly the lower quarter of the fluidized bed. Consequently, a new reaction vessel design appears to be necessary if the quality of the low temperature coatings are to improve.

IV. Summary

The CVD coatings from the pyrolysis of $W(CO)_6$ below 670 K contain some 16 to 25 at.% of both oxygen and carbon in nearly-equal portions. The chemical nature of the oxygen and carbon impurities has yet to be clearly determined. A feasible reaction mechanism for the high oxygen and carbon contents of these coatings is proposed for future consideration. The physical entrapment of chemisorbed CO at the coating surface into the bulk of the deposit appears to be qualitatively consistent with the experimental observations for the low temperature coatings. The general quality of the obtained coatings is currently unsatisfactory for ICF applications and will require further study to refine the deposition conditions.

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Fig. 1 Diagram of the CVD fluidized-bed apparatus for coating microspheres.

Fig. 2 SEM photomicrographs of $W(CO)_6$-derived coatings deposited at mean temperatures of (a) 548 K, (b) 598 K, and (c) 631 K.

Table I. Chemical composition of CVD coatings from $W(CO)_6$ pyrolysis.

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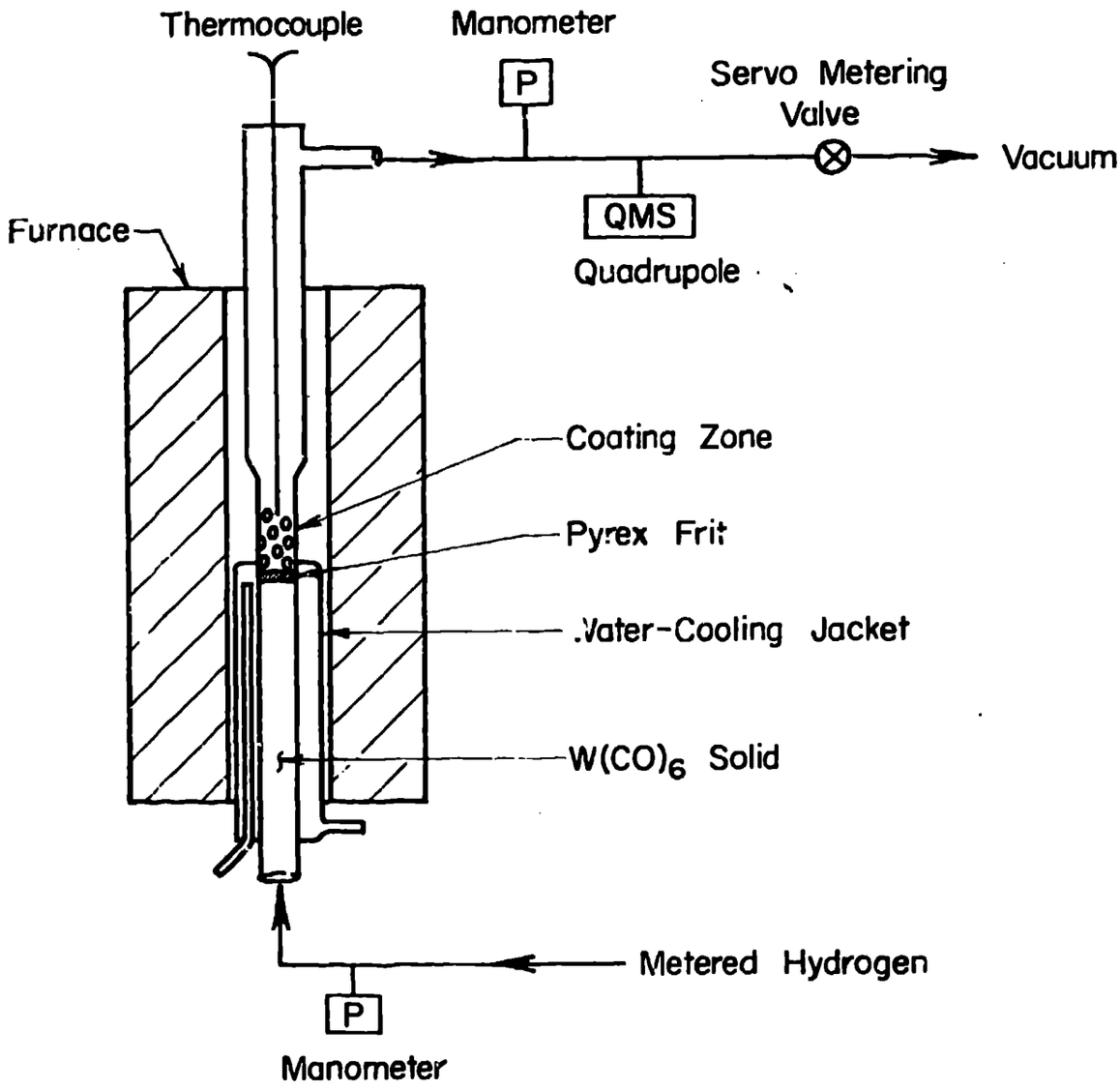

Thermocouple
Manometer
P
Servo Metering Valve
Vacuum
QMS
Quadrupole
Furnace
Coating Zone
Pyrex Frit
Water-Cooling Jacket
W(CO)6 Solid
Metered Hydrogen
P
Manometer

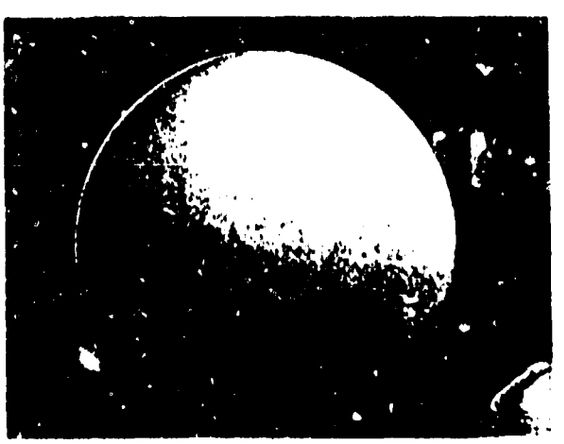
(a)

20μm

(b)

100 μm

(c)



25μm

Mean deposition temperature (°K)	Partial pressure ratio $H_2/W(CO)_6$ used in deposition	Chemical composition (at. %)			Average coating thickness (μm)
		W	O	C	
548	110	54	26	20	2.7
572	200	57	22	21	2.2
604	1400	67	17	16	$\leq$0.2
598	1300	60	22	18	0.5
598	830	62	18	20	$\leq$0.3
598	100	56	22	22	3.1
631	200	59	19	22	1.6
651	1500	74	<.1	26	$\leq$.1
649	1000	75	<.1	25	$\leq$.1
659	200	59	18	23	1.7