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STEAM CHEMICAL REACTIVITY OF PLASMA-SPRAYED BERYLLIUM

Robert A. Anderl, Robert J. Pawelko and Galen R. Smolik
Idaho National Engineering and Environmental Laboratory
P.O. Box 1625, Idaho Falls, Idaho, 83415-7113
(208) 526-4153

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Richard G. Castro
Los Alamos National Laboratory
Los Alamos, New Mexico 87545
(505) 667-5191

ABSTRACT

Plasma-spraying with the potential for in-situ repair makes beryllium a primary candidate for plasma facing and structural components in experimental magnetic fusion machines. Deposits with good thermal conductivity and resistance to thermal cycling have been produced with low pressure plasma-spraying (LPPS). A concern during a potential accident with steam ingress is the amount of hydrogen produced by the reactions of steam with hot components. In this study we measure the reaction rates of various deposits produced by LPPS with steam from 350°C to above 1000°C. We correlate these reaction rates with measurements of density, open porosity and BET surface areas. We find the reactivity to be largely dependent upon effective surface area. Promising results were obtained below 600°C from a 94% theoretical dense (TD) deposit with a BET specific surface area of 0.085 m²/g. Although reaction rates were higher than those for dense consolidated beryllium they were substantially lower, i.e., about two orders of magnitude, than those obtained from previously tested lower density plasma-sprayed deposits.

I. INTRODUCTION

Most investigations into the plasma spraying of beryllium are those by Union Carbide and the Atomic Weapons Research Laboratory (England) during the 1960-70's [1] and later by Battelle. Historically the quality of plasma-sprayed deposits has been limited by having to spray in an inert gas near atmospheric pressure. Dunmur [1] reported densities (~90%), porosities (10-12%), and gas adsorption surface areas (~0.8 m²/g) for as-sprayed deposits. Deposits produced by Battelle in 1990's for the Fusion Program and used in earlier steam reactivity experiments [2] had densities (86-92%) and open porosities (6-12%). Advances in plasma spray technology allowing spraying under reduced pressures, i.e., less than 400 torr, has contributed to capabilities to produce better quality deposits. The Beryllium Atomization and Thermal Spray Facility (BATSF) at Los Alamos National Laboratory has such capabilities along with a transferred-arc cleaning system. This integrated system using improved powder feed stock and small amounts of hydrogen in the plasma gas has

produced some high quality beryllium deposits. Deposits with good substrate adherence, densities, and desirable crystallographic orientation have been produced with good thermal conductivity and resistance to thermal cycling [3,4]. This system was used to produce the deposits studied in this investigation.

II. SAMPLES AND PROCEDURES

Two types of deposits were prepared in BATSF using a SG100 Miller Thermal torch mounted on an automated X-Y manipulator. The coatings were produced from Brush Wellman spherical atomized powder (-38 μm to +10 μm, 0.36 wt% BeO). Beryllium was used as the substrate for Plate A. The other deposit, Plates B and C, was sprayed onto a CuNiBe alloy. The transferred-arc system shown in fig. 1. was used to clean and preheat the substrates before spraying. Other cleaning and spraying parameters are shown in Table I. The only notable differences are 1) a higher substrate temperature for Plate A (600°C) compared to (450-550°C) for Plates B and C and 2) higher power input into the torch for Plate A (15.8-16.6 kW) compared to 12.8 kW for Plates B and C.

Fig. 1 Negative transferred-arc cleaning system used for plasma spraying beryllium deposits.

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Table 2. Density, porosity, and surface area parameters of plasma-sprayed coupons

Specimen Type	Bulk density (g/cm ³)	% Theoretical Density (%)	Open Porosity (%)	Closed Porosity (%)	Total Porosity (%)	BET SSA (m ² /g)
PS-Bc-A	1.744 +/- 0.009	94.4 +/- 0.5	1.4 +/- 0.6	4.2 +/- 0.8	5.6 +/- 0.5	0.085 +/- 0.009
PS-Bc-B	1.702 +/- 0.003	92.1 +/- 0.2	7.7 +/- 0.2	0.2 +/- 0.3	7.9 +/- 0.2	1.214 +/- 0.097
PS-Bc-C	1.706 +/- 0.008	92.3 +/- 0.4	7.6 +/- 0.4	0.1 +/- 0.6	7.7 +/- 0.4	1.070 +/- 0.054

(a)

(b)

Fig. 3. Microstructures of beryllium plasma sprayed deposits. (a) Plate A. (b) Plate B. Magnification: 300X.

and separations between individual splats. The large amount of void space revealed by the cross section in fig. 3(b) and the SEM image of the EDM surface in fig. 2(b) indicates high permeability for Deposits B and C. The high total porosity and low closed porosity measurements in Table 2 confirm this. The micrograph for Deposit A shows far fewer unmelted particles, more isolated pores, and very obscure boundaries at splat interfaces. We would expect

this from a higher energy input that would provide higher temperature, more fluid particles. The evidence of the

isolated porosity agrees with data in Table 2 showing that most of the porosity for this deposit is closed porosity. These observations show why access of Kr gas and resultant BET SSA was lower for Deposit A compared to B and C.

The samples were tested in the Steam-Reactivity Measurements System (SRMS) shown in fig. 4 and described in detail elsewhere [5,6]. Typical operating parameters were as follows; line pressure (675-685 torr), Ar carrier-gas flow rate (100 std cc/min), steam flow rate (2500 std-cc/min for a water throughput of 2 cc/min), steam-generator temperature (350°C). The reaction-chamber tube furnace can operate between 25°C to 1200°C. The system response time for these conditions is about 6 minutes and H₂ detection sensitivity with the quadrupole mass spectrometer (QMS) is about 3 ppm of H₂ in Ar. This allowed us to detect hydrogen release from the steam reaction with the plasma sprayed samples down to 350°C. Oxidation rates were also confirmed by measurements of mass change. Specimens were suspended near the center of the hot zone in the sample furnace via a platinum hanger attached to a quartz support rod. Specimen temperatures were based on prior calibration between a Type-K thermocouple (TC) at the sample position and the furnace controlling TC.

III. EXPERIMENTAL RESULTS

Only samples from Plates A and B were tested due to the very similar nature of the plasma-sprayed deposits on Plates B and C. Hydrogen and weight gain measurements for these tests are summarized in Table 3. In general there was very good agreement between the amounts of hydrogen measured with the QMS and those calculated from mass change. There were some differences for samples heated to 600°C and higher. Some of these samples underwent temperature excursions due to the exothermic energy generated from the steam reaction. Oxide formed on these specimens was very loose and friable resulting in non-recoverable amounts during weighing. Data in Table 3 show that a significant portion of these samples reacted.

Table I. Spraying parameters for beryllium deposits

	Plate A	Plate B	Plate C
Spraying Parameters			
Arc gas – argon (slm)	40	40	40
Secondary gas- hydrogen (slm)	1	1	1
Powder gas – argon (slm)	1	1	1
Powder feed rate (g/min)	7.6	7.6	7.6
Spray distance (cm)	9.53	9.53	9.53
Volts	35	32	32
Current (A)	450-475	400	400
Chamber pressure (torr)	450	450	450
Substrate temperature (°C)	600	450-500	450-550
Substrate	Beryllium	CuNiBe	CuNiBe
Transferred-arc cleaning			
Peak amps	40	40	40
Background amps	40	40	40
Power supply (amps)	150	150	150

The as-sprayed deposits of nominal 50-mm widths were 8-mm, 10-mm and 12-mm thick for Plates A, B, and C, respectively. Milling was used to remove the substrates and provide flat parallel surfaces. Electro-discharge machining (EDM) was then used to remove oxidation coupons that were nominally 15-mm wide x 15-mm long x 3-mm thick. The milled surfaces on the back of the coupons had a finish of 63 micro-inch while front surfaces of the coupons underwent erosion from EDM. Illustrations of both types of surfaces as revealed by SEM at 800X are shown in fig. 2.

Immersion density methods were used to measure the bulk densities and open porosities for the various deposits. Measurements on bulk sections of the deposits and on individual coupons provided essentially the same results. Average values for the density and porosity parameters obtained from the eight to ten coupons from each condition are summarized in Table 2. Theoretical density is considered as 1.85 g/cm³. Surface areas were measured using a Micromeritic ASAP 2010 gas-adsorption system with Kr gas. One coupon from each plate was split into two sections. Average BET specific surface areas obtained from several measurements from each section are included in Table 2.

Metallographic sections were prepared from each of the plasma-sprayed conditions. Light microscopy using both bright-field and polarized light at 100X provided information about grain size, porosity and crystallographic orientation. Porosity levels determined by image analyses of 4.0% for A, 5.5% for B, and 6.2% for C are in general agreement with the total porosities reported in Table 2. Bright field images at higher magnification (400X) are shown for Deposits A and B in fig. 3. The micrograph for B shows a significant number of unmelted particles, porosity,

(a)

(b)

Fig. 2. Surfaces of oxidation coupons. (a) Milled surface on the back of a Type A coupon. (b) EDM surface on the front of a Type C coupon. Magnification: 800X.

Fig. 4. System for measuring the chemical reactivity of plasma sprayed beryllium samples in steam.

Table 3. Summary of weight gains and hydrogen generation

Specimen ID / mass(g)	Temperature (°C)	Steam Exposure Time (min)	Weight Gain (mg)	H ₂ (cc) from Weight-Gain Data	H ₂ (cc) from Mass-Spec. Data	H ₂ Ratio (WG/MS)	Quantity of Be Reacted (mg)	(%) of Specimen Reacted
A-I / 1.153	350	406	----	----	0.32	----	(0.1)	(0.01)
A-H / 1.142	400	1510	1.0	1.4	1.44	0.97	0.6	0.05
A-E / 1.152	450	686	1.6	2.24	2.14	1.05	0.9	0.08
A-D / 1.152	500	398	5.8	9.52	9.4	1.01	3.8	0.33
A-B / 1.131	600	291	81.6	114	131	0.87	45.9	4.0
A-I / 1.153	600	(285) [#]	467	654	806	0.81	26.3	22.8
A-H / 1.142	700-1050	(65) [#] (12) [*]	1362	1906	3275	0.58	766	67.0
A-G / 1.145	800-934 <880>	(64) [#] (40) [*]	215	2822	3544	0.80	1133	99.0
A-F / 1.163	890-1010 <950>	(45) [#] (36) [*]	1423	1992	2624	0.80	800	68.8
B-F / 1.100	350	400	1.3	1.82	2.25	0.81	0.7	0.07
B-D / 1.137	400	373	5.0	8.4	8.58	0.98	3.4	0.3
B-E / 1.139	450	405	17.6	24.6	25.7	0.96	9.9	0.87
B-C / 1.134	500	400	143	200	219	0.91	80.4	7.09
B-B / 1.108	600->1000	(50) [#] (14) [*]	1847	2586	4077	0.54	1040	93.8

Approximate steam exposure time

& Approximate reaction time for high-temperature tests during which a large percentage of the sample reacts.

We observed different types of oxidation kinetics depending on temperature as shown in fig. 5. Parabolic kinetics persisted during the duration of the tests of A and B samples at 350, 400, and 450°C typical of the example in fig. 5(a). Parabolic behavior for beryllium at these low temperatures is associated with a protective oxide layer controlled by the outward diffusion of Be^{++} ions. The sample of Type A deposit tested at 500°C, i.e., Specimen A-D, showed a nearly linear rate after an initial parabolic region, fig. 5(b). An accelerating oxidation behavior was shown by Sample B-C at 500°C and Samples A-B and A-I at 600°C, fig. 5(c). This behavior occurs when the oxide scale cracks and the oxidant penetrates along grain boundaries. Volumetric expansion associated with the newly formed oxide causes additional cracking and a continual increases in the effective surface area. The oxidation behavior of all other samples was characterized by rapidly increasing temperatures, high hydrogen release rates, and substantial sample consumption as shown by fig. 5(d). Time resolved plots of hydrogen release allowed us to calculate hydrogen generation rates from the tests that underwent temperature excursions. In

addition, oxidation rates for tests exhibiting parabolic and accelerating behavior are approximated with linear oxidation rates ($\ell/\text{m}^2\text{-h}$). This approximation is used since the duration of our tests was within the times anticipated in accident scenarios. The linear rates obtained for all of the plasma sprayed samples based on initial geometric surface areas of the specimens are listed in Table 4.

The approximated linear oxidation rates from Table 4 are plotted with respect to inverse temperature in fig. 6. The plot includes data from several previous investigations on dense, porous and plasma-sprayed beryllium [7,8]. Figure 6 shows fairly linear Arrhenius relationships for the plasma sprayed materials for temperatures below 600°C. Higher temperature tests of plasma-sprayed material in fig. 6 are rates obtained during temperature excursions. These rates plotted at and above 900°C converge with reaction rates obtained from other product types. At lower temperatures the oxidation rates for the Type A plasma sprayed product is higher than those for the dense consolidated powder

(a)

(b)

(c)

(d)

Fig. 5. Hydrogen generation kinetics at different temperatures in steam. (a), (b) and (c), parabolic, parabolic, and accelerating behavior, respectively, - Hydrogen generation rate (left axis) and cumulative hydrogen (right axis). (d) autocatalytic behavior - Cumulative hydrogen (left axis) and temperature (right axis).

Table 4. Hydrogen generation rates for the plasma-sprayed samples in steam.

Specimen ID	Temperature [@] (°C)	Inverse Temperature (10,000/K)	Steam Exposure Time (min)	H ₂ Rate from Weight Gain (l/m ² -s)	H ₂ Rate from Mass-Spec (l/m ² -s)	Be Reaction Rate (g/m ² -s)
A-I	350	16.05	406	-----	2.08E-5	(8.4E-6)
A-H	400	14.86	1510	2.45E-5	2.52E-5	9.8E-6
A-E	450	13.83	686	8.64E-5	8.25E-5	3.5E-5
A-D	500	12.94	398	6.33E-4	6.25E-4	2.5E-4
A-B	600	11.45	291	1.04E-2	1.19E-2	4.2E-3
A-I	600	11.45	(285) [#]	6.07E-2	7.5E-2	2.4E-2
A-H	700-1050 (1000 +/- 50)	10.28-7.283 (7.856)	(65) [#] (12) ^{&}	4.2 [*]	7.6E-2 ^x 5.6 ^x	(3.0E-2) 1.7
A-G	800-934 <880>	9.320-8.285 <8.673>	(64) [#] (40) ^{&}	1.9 [*]	----- 2.1 [*]	----- 0.8
A-F	890-1010 <990> (950 +/- 50)	8.600-7.794 <7.918> (8.177)	(45) [#] (36) ^{&}	----- 1.5 [*]	----- 2.3 [*]	----- 0.6
B-F	350	16.05	400	1.2E-4	1.48E-4	4.8E-5
B-D	400	14.86	373	5.96E-4	6.09E-4	2.4E-4
B-E	450	13.83	405	1.61E-3	1.68E-3	6.5E-4
B-C	500	12.94	400	1.32E-2	1.44E-2	5.3E-3
B-B	600->1000 (1000 +/- 50)	11.45-<7.856 (7.856)	(50) [#] (14) ^{&}	----- 4.9 [*]	----- 8.2 [*]	----- 2.0

@ For experiments at high temperatures, different specimen temperatures are identified. Temperature in brackets, <>, is an average value that applies to the H₂ rate values in the same row. Temperature in parenthesis, (), is a temperature range that applies to the H₂ rate values in the same row.

Approximate steam exposure time.

& Approximate reaction time for high-temperature tests during which a large percentage of the specimen reacts.

* Rate is based on using the approximate reaction time.

x Rate value is based on analysis of mass-spec cumulative plot.

Fig. 6. Plots of hydrogen generation rates of various product forms based on initial geometric area of the specimens.

Fig. 7. Hydrogen generation rates based on areas measured by BET gas adsorption methods.

metallurgy product. However, the rates for this product are notably lower than Battelle plasma sprayed material, the 88% T.D. powder metallurgy product, and the Type B plasma-sprayed deposit. Data in Table 4 show that the oxidation rates of Type A are 20 to 25 times lower than Type B between 400 and 500°C. These ratios are similar to the ratio of the BET SSA for these two materials given in Table 2. This prompted us to re-calculate oxidation rates based upon effective surface areas obtained from BET surface area analyses. The hydrogen generation rates expressed in this manner are plotted with respect to inverse temperature in fig. 7. This approach resulted in data from all product types below 700°C converging to values near those of dense beryllium. This shows that oxidation rates of the beryllium specimens in steam are largely dependent upon the effective surface area of the material.

IV. CONCLUSIONS

This investigation has shown that at temperatures below 700°C the chemical reactivity of plasma sprayed beryllium is largely dependent on the initial BET specific surface area. Deposits currently produced by LPPS are substantially improved over those previously prepared in the early 1990s by spraying in higher-pressure environments. This study has also shown that a LPPS deposit having only 94% TD has 15 to 20 times lower effective surface area than samples

from 92% TD material. This shows that a threshold density to restrict Kr gas (during gas adsorption measurements) and steam (during reactivity tests) penetration is near 94% TD. A fully dense condition of near TD, e.g., 98% TD, may not be required to achieve substantially reduced reaction rates. This study reflects a marked improvement toward the optimization of the various properties critical to the use of plasma-sprayed deposits for fusion applications.

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