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OBSERVATIONS
ON
THE PROPERTIES AND BEHAVIOR
OF
EARLY SNAP 8
HYDROGEN PERMEATION BARRIERS
(Title Unclassified)

AEC Research and Development Report

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OBSERVATIONS
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By

H. W. CARPENTER

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ABSTRACT

The purposes of this program were:

- 1) To compare the performance of Solaramic 14-35A and AI 8763D glass hydrogen-barrier coatings at 1400 and 1500°F in hydrogen
- 2) To determine whether chromizing of Hastelloy N is essential to provide a stable coating substrate
- 3) To find which properties influence coating performance, and to recommend a course of action for making the coatings more stable.

Small specimens were aged under the most severe reactor conditions anticipated (1400 and 1500°F at 1 atm of hydrogen) for 50 to 2000 hr. The following observations were made:

- 1) Alkaline oxides in the S14-35A barrier were reduced by the hydrogen atmosphere.
- 2) Chromizing the Hastelloy N substrate before application of the coatings was beneficial in decreasing coating defects and in promoting a more stable interface.
- 3) Significant devitrification of the glass coatings occurred within the first 100 hr.
- 4) The coefficient of thermal expansion changed, but the change was not detrimental to the coatings.
- 5) Coating porosity increased from 8 to 30% in some areas in both coatings.

Based on the results of this program, five recommendations were made for producing a more stable coating:

- 1) Use a formula low in easily reducible oxides.
- 2) Make the frit from calcined, high-purity oxides.
- 3) Quench the molten glass with water-cooled metal rollers and vacuum outgas the frit.
- 4) Crystallize the coating under controlled conditions.
- 5) Refine the chromizing process.

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I. INTRODUCTION

The SNAP 8 reactor is a compact liquid-metal (NaK-78) cooled reactor that utilizes uranium-zirconium hydride as the fuel-moderator material. The fuel-moderator is clad in a nickel-base alloy (Hastelloy N). The equilibrium hydrogen dissociation pressure of the zirconium hydride at reactor operating temperatures is in the range of 1 to 2 atm. In order to assure satisfactory reactor performance, the total loss of hydrogen moderator from the core during the life of the reactor may not exceed 5%. To obtain this degree of hydrogen retention, the fuel cladding is provided with an internal porcelain enamel coating which acts as a hydrogen permeation barrier.

The purpose of this report is to describe some of the results obtained, in the early work, in evaluating the hydrogen permeation barrier materials for the SNAP program reactors. The properties studies, as a part of this program, included visual appearance, microstructural changes, x-ray diffraction pattern changes, coefficient of thermal expansion, and adherence characteristics.

Metals are adequate hydrogen barriers at temperatures below 600°F. Above this temperature, hydrogen loss through metals is so rapid that a much more effective permeation barrier is required. In general, hydrogen diffuses through metals as an atom, or ion, but it diffuses through a ceramic material as a molecule. Permeation rates are therefore found to be lower in ceramics than in metals, by a factor of two or three orders of magnitude.

Only two ceramic hydrogen barriers were available when this program started. The first, Solaramic 14-35A,^{*} was developed for AI by Solar, a division of International Harvester, for use in the SNAP 10A/2 program. This coating performed well at temperatures below 1200°F, but the presence of certain volatile and less stable constituents led to marginal performance at higher temperatures. The second coating, AI 8763D, was developed at AI for use at higher temperatures. The composition of AI 8763D is noted in Table 1.

The objectives of this program were:

- 1) To compare the performance of Solaramic 14-35A and AI 8763D coatings at 1400 and 1500°F in hydrogen

^{*}The formulation of S14-35A is a modification of a Solaramic (trademark) coating developed by John V. Long (US Patent 2,843,507).

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2) To determine whether chromizing the Hastelloy N surface is essential to provide a stable metal-coating interface for coating application and during performance in a hydrogen environment

3) To find which properties influence coating performance, and to recommend a course of action for making a more stable coating.

Subsequent studies, to be reported separately, resulted in the selection of another glass coating developed at AI (SCB-1), for the SNAP 8 application.

TABLE 1

AI 8763D FORMULATION

Oxide	wt %	Oxide	wt %
SiO ₂	47.2	CaO	1.5
BaO	31.6	MnO ₂	1.1
TiO ₂	9.9	SrO	1.1
ZrO ₂	5.0	MgO	0.3
Li ₂ O	2.3		

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II. PROCEDURE

A. METHOD

The approach used for this preliminary study was to expose short sections of coated fuel cladding and small massive pieces of coating material under simulated reactor conditions. The environment selected for these tests was (except for irradiation) representative of the most severe conditions expected in the reactor — 1400 and 1500°F in a pressure of 1 atm of hydrogen. The two different coatings, on both chromized and unchromized substrates, were aged together in hydrogen to obtain a direct comparison. Aging tests were also repeated in argon, to determine the effect of hydrogen on property changes in the coatings.

Specimens were aged on stainless steel trays inside quartz or stainless steel retorts that were placed inside a standard resistance-wound tube furnace. A valve, located at one end of the retort, was used for evacuation and introduction of the gases. Samples were removed from the retort at room temperature after being cooled slowly in the furnace, or by purging the retort with argon and removing the specimen without interrupting the test. With the latter procedure, the specimens received a thermal shock from test to ambient temperature. The testing schedule is presented in Table 2.

B. ANALYTICAL TESTS

Most of the tests and observations performed on the coating were standard and need little or no explanation, with one exception. Testing the adherence of a ceramic coating on the inside of a tube, and describing it with objective, quantitative data, is not presently possible. None of the many standard methods of testing and reporting adherence were held to be satisfactory. A substantive or qualitative method, which was adapted for this purpose, simply involved bending back and forth short sections cut from coated tubes. The number of flexures before failure was taken as an index of adherence (Table 3 and Figure 1).

Thermal expansion of the coating materials was measured with an interferometer at the University of Illinois. X-ray analysis of the coating was performed at AI with a Norelco Diffractometer. Metallographic mounts were made with a cold-setting material to minimize coating damage, and microscopic examination was performed with a Bausch and Lomb microscope. Porosity (including

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TABLE 2
SCHEDULE OF ENVIRONMENTAL
TESTING PROGRAM

Furnaces I and II: 1/2-in. long sections of SNAP 8 fuel cladding tubing, coated with S14-35A or AI 8763D, were aged in 1 atm H₂ at 1400 or 1500°F

Aging Time (hr)	Number of Thermal Cycles	Type of Coating Substrate	
		Chromized	Unchromized
77*	1	X	X
500†	1	X	X
500	2	-	X
500	3	X	X
500	4	-	X
500	5	X	X
700	7	-	X
900	8	X	X
1100	9	-	X
1300	10	X	X

Furnace III: 1/2-in. sections of coated unchromized SNAP 8 fuel cladding tubing and massive pieces of S14-35A and AI 8763D were aged in 1 atm H₂ at 1500°F

Time (hr)	Cooling Rate
50	Quenched
170	Quenched
500	Quenched
500	Furnace Cooled
750	Quenched
1000	Quenched
1000	Furnace Cooled
1500	Quenched
1500	Furnace Cooled
2000	Quenched
2000	Furnace Cooled

*At 1500°F only
†At 1400°F only

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TABLE 3
DESCRIPTION OF ADHERENCE TEST

Adherence	Number of 90° Angle Bends Before Coating Broke Off	Substrate
None	Less than 1	Clean
Poor	1 or 2	Clean
Fair	1 to 6	Few adherent glass fragments
Good	6 or more	Many adherent glass fragments
Excellent	Many; usually had to be folded to break coating off	Covered with adherent glass fragments

bubble size, shape, distribution, and coalescence), continuity, crystal development, color, surface morphology, and metal interface characteristics were of primary interest. The fractional void volume was estimated by dividing the flat surface area of voids by the total coating area viewed through a calibrated eyepiece. The average of several locations was taken as the representative void volume.

C. SPECIMEN PREPARATION

Two different types of samples were prepared for testing. Sections of standard coated fuel element cladding assemblies were used for all except thermal expansion tests, where massive pieces of coating material were employed. The latter specimens were made by melting several hundred grams of dried slip in fire clay crucibles at 2300°F for 2 hr, and then cooling slowly. Cladding assemblies were simulated by 15-in. lengths of chromized or unchromized Hastelloy N tubing (0.540 in. OD and 0.010 in. wall thickness), closed at one end. These were sectioned into 1/2-in. lengths with a lathe. The details of the processing variables are noted in Table 4.

Neither coating could be fired on bare Hastelloy N metal in air without formation of large blisters.* This was attributed to the oxidation of molybdenum in the alloy and the resulting formation of MoO_3 gas, which bubbled through the

*With one exception — one cladding assembly, coated with two layers of AI 8763D, had few defects. This feat was not duplicated.

NO ADHERENCE

5552-2-1

POOR ADHERENCE

5552-4-1

FAIR ADHERENCE

5552-1-1

GOOD ADHERENCE

5552-5-1

EXCELLENT ADHERENCE
(Note sharp bend angle re-
quired to break off coating)

5552-3-1

Figure 1. Representative Adherence Test Specimens
(Figure Unclassified)

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TABLE 4
SPECIMEN DESCRIPTION

Metallizing Treatment	Coating	Coating History			
		Number of Coats	Firing Temperature (°F)	Firing Time Each Coat (min)	Firing Atmosphere
Chromized	S14-35A	3	1800	12	Air
None	S14-35A	3	1800	12	26 parts argon 3 parts air
Chromized	AI 8763D	3	1900	12	Air
None	AI 8763D	3	1900	12	10% air-argon
None	AI 8763D	2	1900	First Coat 20	10% air-argon
				Second Coat 13	Air 10% air-argon
None	AI 8763D	2	1900	8	Air

molten coating during firing. Chromizing the Hastelloy N surface, prior to coating, suppressed the formation of coating defects and provided a more stable interface in a hydrogen environment. Chromizing was done by a pack-diffusion technique. Another method, used to suppress the formation of defects, was to fire the coating on Hastelloy N in an argon-10% air mixture. The small quantity of involved air was necessary, to promote enough metal oxide formation at the metal-ceramic interface to induce the ceramic coating to wet the metal.

a. Unaged

2507-5

b. Aged 2000 hr in 1 atm H_2
at 1500°F

2507-3

Figure 2. Massive Specimens of Al 8763D

III. RESULTS

A. HYDROGEN AGING

1. Macroscopic Changes

Several changes were observed on the coated specimen after exposure to hydrogen at elevated temperatures. In general, the color became darker, the surface changed from a glossy to a matte finish, discolored spots appeared on the coating after 500 hr, and star-shaped defects formed. The defects generally penetrated to the metal substrate, and averaged 1 mm across. No significant differences were noted between samples aged at 1400 and 1500°F on chromized or unchromized substrates.

An obvious difference between thermally aged specimens of the two hydrogen permeation barrier materials (Figures 2 and 3) lay in the greater physical and chemical stability of the AI 8763D material. Broken edges were still sharp, and the bottom sides (resting on a wire screen) were unchanged even after 2000 hr. The S14-35A specimens, by contrast, softened and reacted with hydrogen. The sharp broken edges became rounded, and imprints of the wire screen supports were clearly visible on all specimens. Moreover, a porous, dark blue, 1-mm thick rind formed over the entire specimen within 50 hr. The rind thickness increased with time; and, after 2000 hr, the thickness was 3 mm. Many reaction pockets also penetrated into the center of the specimens. A blue-green glass formed concurrently after 50 hr on the surface of the porous rind. The glass layer continued to develop with time; and, after 500 hr at 1500°F, it completely enclosed the specimen.

2. Microscopic Changes

Changes were observed in the characteristics of both the AI 8763D and the S14-35A coatings after aging in hydrogen at 1400 and 1500°F. This observation included crystalline content, porosity (including bubble size, shape, distribution, and coalescence), continuity, surface topology, and the ceramic-metal interface features. Similar changes were observed for both coatings, and for both chromized and unchromized substrates.

a. Unaged

2507-2

b. Cross Section, Aged
50 hr in 1 atm H_2 at
1500°F

2507-1

Figure 3. Massive Specimens of S14-35A

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a. Devitrification

Because of the small size of crystallites which formed early in the devitrification process, crystallization of glass barrier coatings was detected by indirect techniques. First, the clear glass coating became opaque as crystalline phases precipitated. Secondly, crystallization distorted the smooth surface of bubbles within the coatings. Both phenomena began within the first 77 hr of aging, as illustrated in Figure 4.

Agglomerates of grains, less than 1μ across, were observed in AI 8763D coating in the as-fired specimens, and in those specimens that were aged for 50 and 77 hr. After 170 hr at 1400°F , however, these crystals disappeared. Smaller crystals, $<1\mu$ in diameter, then appeared; at this time, the coatings became opaque.

b. Porosity

Porosity of the barrier coatings increased significantly with time; but, due to specimen-to-specimen variations, a significant increase was not measurable as a function of temperature (refer to Figure 4). The quantity of bubbles increased, raising the porosity from about 8 vol % to as high as 30 vol % in the worst areas, after 1300 hr at 1400 and 1500°F (Figure 5). The size of the bubbles also increased, until some bubble diameters were one-third the thickness of the coating. Bubbles were generally located in belts near the center of the coating thickness, or near, but never touching the metal. Due to the high concentration of bubbles after 500 hr of aging, they sometimes joined together and formed even larger networks of voids in the coating.

c. Continuity

Coating continuity was affected by increased porosity. When a zone of coalesced bubbles was present, the coating was weakened and circumferential cracks resulted (as illustrated in the last photomicrograph in Figure 4).

d. Surface

As-fired coating surfaces were smooth and flat; but, after aging, they gradually became uneven in some specimens. A few bubbles broke through the surface after 500 hr of aging.

S14-35A COATING

2465-3

2465-8

2545-3

2639-9

2465-2

2465-6

2545-4

2656-1

Al 8763D COATING

Figure 4. Coatings Aged in 1 atm H₂ at 1500°F

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e. Interface

The coating-metal interface became more uneven; and a narrow diffusion zone, less than 1μ in thickness, usually developed upon aging. However, neither of these changes could be related to adherence.

3. X-Ray Diffraction Analysis

An analysis of x-ray diffraction patterns obtained from coatings that were aged in hydrogen demonstrated that both coatings devitrified; moreover, they devitrified in a relatively short time. Only three very weak crystal peaks appeared in the x-ray pattern of unaged specimens, whereas many peaks appeared in the patterns of aged materials. All specimens aged over 170 hr exhibited complex and intense patterns. In a single specimen aged for a shorter time (50 hr), a complex, but less intense, pattern was observed. It also appeared that the crystalline phases were unstable; because some peaks shifted or faded, from specimen to specimen, without any apparent cause. Therefore, quantitative analysis of the data was impossible.

Table 5 shows the major crystalline phases present in aged specimens. BaTi_2O_5 was suspected in AI 8763D, but its similarity to BaSi_2O_5 precluded positive identification. Positive identification of these phases, or of other phases that may have been present, was difficult, because of the complex and shifting x-ray patterns. That these patterns behaved in this manner is not surprising, when the coating compositions are considered. S14-35A and AI 8763D coatings contain 14 and 11 different oxides, respectively, and the formation of several dozen compounds is possible. The three major components alone (SiO_2 , BaO , TiO_2) are capable of forming six barium silicates, five barium titanates, and four barium-titanium silicates. Also, the minor components probably entered into interstitial and substitutional solid solution formation with existing phases, to further complicate x-ray interpretation.

No significant differences were noted between quenched and annealed specimens.

4. Thermal Expansion Analysis

Thermal expansion data of unaged and hydrogen-aged S14-35A and AI 8763D materials are tabulated in the Appendix. The values range from one-half to two-thirds that of Hastelloy N. Because the expansion of the coating is smaller,

Figure 5. High-Porosity Area of S14-35A Aged 1100 hr in
1 atm H₂ at 1400°F

2639-7

TABLE 5
CRYSTALLINE PHASES IDENTIFIED IN HYDROGEN
BARRIER MATERIALS AGED IN
1 atm H₂ AT 1500°F

Material	Type of Specimen	Crystalline Phases
S14-35A	Massive	α and β BaSi ₂ O ₅
S14-35A	3-mil coating	
AI 8763D	Massive	β BaSi ₂ O ₅ and Ba ₂ Si ₃ O ₈
AI 8763D	3-mil coating	

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and because the coating is on the inside of a tube, it is placed in compression upon cooling. This general relationship between the coefficients of thermal expansion for the coating and cladding is important, in order to take advantage of the fact that the strength of glass in compression is approximately ten times its strength in tension.

The coefficient of thermal expansion of both coatings changed with aging time (refer to Figure 6). The coefficient for S14-35A increased slightly, while the coefficient for AI 8763D decreased. AI 8763D coating had a higher initial value, however, particularly for the quenched specimen. The differences in expansion coefficients between quenched and annealed materials was small, and was believed to be caused by stress relief during expansion determination.

A significant factor, shown by this data, is the increase in the softening point upon aging. Expansion curves for unaged AI 8763D and for S14-35A materials showed an inversion point at 1250°F, where the material slumped under the weight of the test equipment. Upon aging, however, this inversion point was greater than 1300°F, the upper limit of operation for the expansion measurement equipment.

5. Adherence

No significant trends in the adherence data were noted. The results are shown in Table 6.

B. ARGON AGING

1. Macroscopic Changes

The change in the appearance of both coatings after aging in argon was similar to that of the hydrogen-aged samples. The color darkened slightly, the glossy surface became a matte surface, and the AI 8763D coating exhibited a mottled appearance in some instances.

2. Microscopic Changes

a. Devitrification

Indications of devitrification (opacity and distorted bubble surfaces) were the same for specimens that were aged in argon as for specimens that were aged in hydrogen.

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a. AI 8763D

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b. S14-35A

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Figure 6. Thermal Expansion of Hydrogen Barrier Material as a Function of Aging in 1 atm H_2 at 1500°F

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TABLE 6
ADHERENCE TEST RESULTS FOR HYDROGEN-AGED
BARRIER MATERIALS

Aging Time (hr)	Thermal Cycles	Adherence Data From Furnace I: 1400°F				Adherence Data From Furnace II: 1500°F			
		S14-35A Coating On		AI 8763D Coating On		S14-35A Coating On		AI 8763D Coating On	
		Hastelloy N	Chromized Hastelloy N	Hastelloy N	Chromized Hastelloy N	Hastelloy N	Chromized Hastelloy N	Hastelloy N	Chromized Hastelloy N
0	0	F*	P	G	G	F	P	G	G
500	1	F	F	G	F	F†	F†	-	F
500	2	-	-	G	-	-	-	F	-
500	3	F	F	G	F	F	F	F	F
500	4	-	-	G	-	-	-	G	-
500	5	F	F	G	F	F	F	F	F
700	7	G	-	G	-	F	-	F	-
900	8	F	F	G	G	F	F	G	-
1100	9	G	-	G	-	G	-	E	-
1300	10	E	G	E	E	F	F	F	F
2000§	11	-	-	-	-	G	G	E	F

Aging Time (hr)	Thermal Cycles	Cooling Rate	Adherence Data From Furnace III: 1500°F		
			S14-35A On Hastelloy N	AI 8763D On	
				Hastelloy N**	Hastelloy N††
0	0	-	F	F	G
50	1	Quenched	P	P	G
170	1	Quenched	P	F	G
500	1	Quenched	P	P	G
500	1	Slow	P	P	G
750	2	Quenched	P	P	G
1000	2	Quenched	P	P	G
1000	2	Slow	P	N	F
1500	3	Quenched	P	N	F
1500	3	Slow	P	N	F
2000§§	4	Quenched	F	N	F
2000§§	4	Slow	F	-	-

*N = None, P = Poor, F = Fair, G = Good, E = Excellent (Refer to Table 3)

†Aged 77 hr

§The temperature decreased to 1450°F in this zone between 1300 and 2000 hr

**Coating was fired in air-argon atmosphere

††Coating was fired in air

§§Temperature increased to 1500°F

b. Porosity

The porosity increased with time; but, in general, not to the extent that was observed in hydrogen-aged specimens. The change was smaller in the AI 8763D material than in the S14-35A material.

3. Adherence

No significant trends in the adherence data were noted. Table 7 shows the adherence data for specimens that were aged in argon.

TABLE 7
ADHERENCE TEST RESULTS FOR ARGON-AGED
BARRIER MATERIALS

Aging Time (hr)	Thermal Cycles	Aging Temperature (°F)	Adherence				
			S14-35A Coating On		AI 8763D Coating On		
			Hastelloy N†	Chromized Hastelloy N	Hastelloy N*	Hastelloy N†	Chromized Hastelloy N
0	0	1500	F§	P	G	G	G
500	1	1500	P	N	E	E	F
500	5	1500	P	P	G	-	G
1000	6	1500	G	P	-	E	F

*Coating fired in argon - 10% air atmosphere

†Coating fired in air

§N = None, P = Poor, F = Fair, G = Good, E = Excellent (Refer to Table 3)

IV. DISCUSSION

A. PROPERTY CHANGES

1. Crystallization

Both S14-35A and AI 8763D coatings crystallized extensively within 100 hr at 1500°F in a hydrogen environment. X-ray diffraction patterns disclosed that the major part of the change occurred within 50 hr. Surfaces of the coatings changed from a glossy to a matte finish within the same 50-hr period, and surfaces of bubbles in the coating were distorted by crystal growth.

2. Thermal Expansion

Changes in the coefficient of thermal expansion that resulted from aging in hydrogen can be caused by compositional changes, phase changes, or stress relief in the material. Compositional changes, in this case, were caused by the reduction of unstable oxides in a hydrogen environment. However, only S14-35A was subject to reduction, because this material contains about 10 wt % reducible oxides. Phase changes resulted from devitrification of the glass during aging. Thermal expansion coefficients of the resultant crystalline materials are, in many cases, unknown; but most of their effect should have been observed within 100 hr, the time period over which most of the devitrification occurred (refer to Section IV-A-1). Thermal expansion effects due to stress relief are shown by comparing the results from specimens that were cooled at different rates after aging (i. e., quenched or slow cooled). The difference in expansion between quenched and slow cooled specimens was minor, and accounts for only a small part of the total change. This may not be true for AI 8763D samples that were aged less than 500 hr, where data are not adequate for a reliable interpretation.

These observations, together with crystal structure evaluations made by x-ray diffraction methods, suggest that long-term changes in the crystalline phases present may account for the observed coefficient of thermal expansion behavior of the material.

The expansion coefficients of both S14-35A and AI 8763D coatings were always less than that of Hastelloy N. This meant that the coatings were always placed

in compression upon cooling. Since the ceramic coating is strongest in compression, it is believed that the changes in the coefficient of thermal expansion were, in general, not detrimental.

3. Coating Porosity

Increases in porosity and changes in bubble structure, as a result of long-time high-temperature aging, were the most important findings of the program. Bubbles in both coatings grew in size and in number with aging at 1400°F, as well as at 1500°F. Incipient bubble coalescence was observed in some areas after 500 hr of aging. After aging for 1300 hr, both coatings exhibited areas with 30% porosity. Whether significant porosity changes occur with further aging was not determined. Since it has been found that membranes coated with AI 8763D perform well for periods longer than 1300 hr,⁽²⁾ it must be assumed that changes that result from very long-time aging are relatively unimportant.

The increasing bubble size in the coatings is believed to be due to entrapped or regurgitated gas. It has been reported⁽³⁾ that gaseous impurities can be absorbed during the enameling process in quantities as large as 1.5 cc(STP)/g of glass.⁽⁴⁾ Since the solubility for gases is significantly smaller for crystalline materials than for glassy materials, the rejection of gases from the solid would be expected, during the devitrification process. Thus, the devitrification process can act as the driving force for both nucleation and growth of bubbles in the coatings.

In addition to the gases that may be rejected from the glass during devitrification, some components, such as Na_2O , may be reduced in a hydrogen atmosphere and contribute large volumes of water vapor. Solaramic S14-35A contains approximately 10 wt % of reducible oxides, whereas AI 8763D contains <1 wt % as impurities.

Gases dissolved in the metal substrate are not believed to contribute significantly to bubble growth in the coating. Two important factors supporting this hypothesis are: (1) the increasing solubility limits for hydrogen in nickel with increasing temperature,^(5,6) and (2) the fact that bubble formation was not observed at the metal-ceramic interface.

Increases in porosity in the coating would be expected to degrade the effectiveness of the coatings as hydrogen permeation barriers. However, test results

indicate that this effect is not as large as the variation in behavior of the test equipment. In fact, in some fuel assemblies, no significant change in hydrogen permeation rate was found, even when much of the coating spalled.⁽⁷⁾ It is hypothesized that the coating spalled at high porosity strata, or belts, leaving the layer of coating adjacent to the metal intact. Bubble stratification of this nature is illustrated in Figure 5.

4. Appearance Changes

Factors that can cause changes in the visible appearance of the barrier coatings include devitrification of the glass and decomposition of one or more constituents during aging. Since the index of refraction for crystals is, in general, different from that for glasses, it is not surprising that devitrification of the coatings, which results in a dispersion of microcrystals in the glass, caused a matte finish appearance, rather than the usual glossy appearance. This effect is routinely utilized in the porcelain enameling industry for control of the appearance of enamels.⁽⁸⁾ In addition, a mottled appearance was obtained when devitrification was not uniform over the surface. Color changes were observed to occur when the alkaline oxides or TiO_2 were reduced by the hydrogen test environment. TiO_2 is not reduced completely, but rather forms an oxygen-deficient lattice in a reducing atmosphere.

5. Chemical Stability

The standard free energies of formation for several of the important oxides present in the coatings studied in this program are plotted as a function of temperature in Figure 7.⁽⁹⁾ The data for water are included for reference. From these data, it may be observed that some of the important constituents of S14-35A coating, which contains approximately 10 wt % Na_2O , K_2O , and ZnO , are subject to reduction in a hydrogen atmosphere. Thus, it would be expected that the formation of water vapor could contribute significantly to the formation and growth of bubbles when S14-35A coating is heated in a hydrogen environment at 1400°F . However, no conclusions can be drawn relative to the kinetics of such reactions.

Evaporation of sodium and zinc has been observed at Solar, when samples of S14-35A coating material were heated at 1400°F .⁽¹⁰⁾ The presence of these materials as a condensate in the colder end of the furnace retort was confirmed by

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Figure 7. Standard Free Energies of Formation of Important Oxides in Al 8763D and S14-35A Coating Materials

x-ray diffraction techniques. Also, visual proof of chemical reduction was obvious in the hydrogen-aged S14-35A material, as illustrated in Figure 3b.

6. Adherence

Over 500 technical reports have been written during the past 50 years on the adherence of glass to metals.⁽¹¹⁾ Most of these reports attempt to develop a theory to explain the data. The diverse theories can be broadly categorized into four groups.

1) "Mechanical" theories explain adherence as the result of physically roughening the metal surface, prior to coating application. The rough metal surface actually "holds" the ceramic.

2) "Electrolytic" theories explain adherence as the result of galvanic corrosion of the metal substrate, which allows the glass to penetrate and "lock onto" the metal. Galvanic reactions are caused by variable-valence cations in the molten glass that transport oxygen from the glass surface to the metal surface. This oxygen then corrodes the metal surface.

3) "Dendritic" theories explain adherence as the result of metal dendrites, growing from the metal surface into the glass. These "fingers" hold the glass to the metal.

4) "Chemical Bond" theories attribute adherence to the electron sharing between the metal and glass materials.

Although the theories expounded in these reports differ, the authors agree on one fact: porcelain enamel - metal alloy systems are very complex, and the fact that many theories have been provided to explain adherence is not surprising.

The most recent and generally accepted papers^(12, 15) approach the subject in a more fundamental way, and support the Chemical Bond theory. The authors, in general, reached the same conclusions. First, mechanical or dendritic bonding is not necessary for adherence, and provides only a small contribution to adherence bonds. Adherence results from a chemical bond [or a Van der Waals Bond⁽¹⁵⁾]. Secondly, to develop this chemical bond, there must be a "thermodynamic balance"^(11, 13) at the metal-ceramic interface. This "thermodynamic balance" results from the presence of an adherent oxide on the metal, and a saturated condition of this oxide (or an oxide with similar qualities) in the glass touching the interface. Further, this oxide must be stable in the system (i. e., it must not be reduced by other constituents in the metal or the ceramic). In practical terms, adherence of SNAP 8 ceramic coatings resulting from a chemical bond would depend on the amount, stability, adherence, and solubility in the glass of the oxide formed on the metal substrate during coating application.

The data obtained in this program do not uniquely support any of the metal-ceramic bonding theories enumerated previously. No evidence was observed in the microstructure of any specimen in this program that would lend support to the Mechanical, Electrolytic, or Dendritic bonding theories. However, this lack of evidence lends indirect support to the Chemical bond theory for the adherence behavior.

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Figure 8. Standard Free Energies of Formation of Oxides Found at the Metal-Ceramic Interface

B. COOLING RATE AND COATING FAILURE

Sommer⁽¹⁶⁾ reported that SNAP 8 hydrogen barrier coatings failed when cooled slowly, but not when quenched. Significant property changes were sought, in this program, to explain this type of failure. Cooling rates had no effect on the properties that might cause catastrophic failure (i. e., crystalline or other changes in microstructure). Also, cooling rates had only a slight effect on changes in thermal expansion coefficients. This slight difference in expansion coefficients is not sufficient to cause catastrophic behavior. The causes for the coating failures were not identified in the present study.

C. COMPARING AI 8763D AND S14-35A

Hydrogen permeation rates for the two coatings that were studied are similar. However, catastrophic failure of S14-35A at temperatures of 1400 and 1500°F has been reported.⁽¹⁶⁾ This correlates with the results of the present study, which demonstrate that S14-35A is unstable in hydrogen in this temperature range. For this reason, AI 8763D, rather than S14-35A, is recommended for use at 1400 or 1500°F.

D. EVALUATION OF CHROMIZED HASTELLOY N AS A COATING SUBSTRATE

Use of the chromizing process on all coating substrates has several disadvantages: (1) it causes time delays, (2) it is expensive, (3) it is not uniform in composition or in thickness, and (4) it introduces occluded hydrogen in the metal. However, these objections are offset by two essential advantages. First, a chromized substrate reduces pit and blister defects in the coating that are common with unchromized Hastelloy N substrates. These defects can be prevented by firing in an air-argon mixture, but good adherence of the coating to the metal is retarded under these conditions. Also, wetting of one layer of the coating by the next becomes a problem. Secondly, chromizing increases the chemical stability of the metal-coating interface in a hydrogen environment. The chromized interface is more stable, because additional Cr_2O_3 is formed when the coating is fired. Without a chromizing substrate, NiO is predominant. NiO is unstable in hydrogen at 1400 or 1500°F, whereas Cr_2O_3 is stable (refer to Figure 8). Therefore, it is clear that, at the present time, the advantages of using a chromized substrate outweigh the disadvantages.

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V. RECOMMENDATIONS FOR STABILIZING THE SNAP 8 HYDROGEN BARRIER COATINGS

Two recommendations, based on the results of this program, can be made for increasing SNAP 8 hydrogen barrier coating stability:

1) Eliminate gas impurities in the coating that contribute to porosity formation. This can be done in several ways:

- a) Use high purity oxides as raw materials.
- b) Calcine the raw materials before they melt and form a glass.
- c) Quench between water-cooled rollers, instead of in water.
- d) Vacuum outgas the frit just below the crystallization temperature before making the slip.
- e) Fire the coating on the metal in a vacuum.

2) Take steps to stabilize the metal-coating interface or find a better substrate than "chromizing."

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VI. SUMMARY

The following observations were made in the study of AI 8763D and S14-35A hydrogen barrier coatings when they were aged in 1 atm of hydrogen at 1400 and 1500°F.

- 1) The glass coating crystallized extensively within 100 hr.
- 2) Bubbles present in the as-fired coatings grew larger and more numerous with aging. By 500 hr, the bubbles started to coalesce; and, after 1300 hr, some of the worst areas in the coatings had a fractional porosity of 30%.
- 3) Thermal expansion coefficients changed, as a result of aging, but these changes were not detrimental to the coatings.
- 4) No clear interdependence between aging and adherence of the coatings to the metal substrates was found.
- 5) AI 8763D coating was chemically stable; S14-35A was not.

Chromizing Hastelloy N substrates before coating is necessary, to facilitate coating application. It is also believed that the long term stability of the interface between the coating and the Hastelloy N is enhanced as a result of the chromizing.

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APPENDIX THERMAL EXPANSION DATA

Coating	AI 8763D								S14-35A					
Aging Time (hr)*	0	50	170	500		1000		2000	0	50	170	500	1000	
Cooling Rate†	SC	AQ	AQ	AQ	SC	AQ	SC	SC	SC	AQ	AQ	SC	AQ	SC
Linear Coefficient of Thermal Expansion (x 10 ⁷) Temperature Range (°C)														
20 - 100	77.237	91.488	88.500	68.370	61.58	48.82	58.36	52.592	59.258	66.686	77.266	85.54	77.05	81.92
20 - 200	102.753	121.189	114.156	70.768	68.76	54.36	62.07	56.586	63.276	72.306	100.928	102.93	91.81	97.58
20 - 300	98.936	126.007	115.634	71.673	69.81	57.90	65.43	60.190	65.564	73.229	95.201	94.26	79.92	90.78
20 - 400	94.947	114.319	109.400	72.029	71.36	60.35	68.18	63.676	68.510	74.858	90.592	89.25	77.62	86.19
20 - 500	94.275	106.291	103.576	72.611	74.48	62.91	72.40	68.584	72.118	75.490	85.247	86.95	75.50	85.02
20 - 600	96.418	111.988	110.180	80.410	77.88	66.36	73.04	71.036	77.843	78.474	89.396	98.66	84.23	95.75
20 - 700	-	138.306	153.676	77.965	73.74	65.38	70.07	68.743	-	90.273	121.049	113.08	113.47	106.62

*In 1 atm H₂ at 1500°F

†SC = Slow cool
AQ = Air quench

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