

Development of Aluminide Coatings for Hydrogen Isotope Permeation Resistance

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Process Development of Aluminide Coatings for Hydrogen Isotope Permeation Resistance

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ABSTRACT

A tube in tube hydrogen isotope separation device required a permeation resistant coating on the internal and external surfaces. The coating characteristics were established and two methods of applying an aluminide permeation reduction coating were evaluated. The details of the coating characteristics and processes are described. A liquid phase slurry coating method was selected based on technical and other considerations.

INTRODUCTION

In order to improve the thermal efficiency of the thermal cycling absorption process (TCAP) which is used to separate hydrogen isotopes, an alternate system was designed. This new system uses a liquid rather than a gaseous (nitrogen) thermal fluid. Liquids in general have superior heat capacity and heat transfer coefficients than gas: The proposed change in the thermal fluid also allowed changes in the overall design that modifies the system footprint as well. This combination of design changes resulted in a small diameter tube concentric in a larger diameter tube and so is called a tube in tube (TNT) TCAP.

The TCAP operates at elevated temperatures that can enhance the mobility of hydrogen isotopes in metals. There is a concern then that tritium, in particular, could permeate the inner wall of the inner tube into the thermal fluid in addition to permeating through the outer wall into the vacuum jacket. If the contamination level can be maintained below XXX curies, then the fluid can be incinerated thereby producing very little waste volume. On the other hand, if the contamination is greater than this, the fluid must be fixed and disposed of as solid waste.

Because of these environmental and waste disposal concerns, it was determined that a permeation barrier

coating was required for the internal surface of the inner tube and the external surface of the external tube. The reason for not having coating on both sides or on the "working" side of the tube is to accommodate other design improvements, including the incorporation of copper foam for increased heat transfer. There was the fear that the coating may be damaged by the foam during post coating processes.

BACKGROUND

Fig. 1 shows a cross-section of the TNT TCAP. The copper foam is placed into the annular space after assembly. Several changes the design resulted in changes to the coating sequence and assembly order. These changes resulted in limits for the allowable temperature during coating and other processing conditions.

Permeability is the product of the diffusivity and the

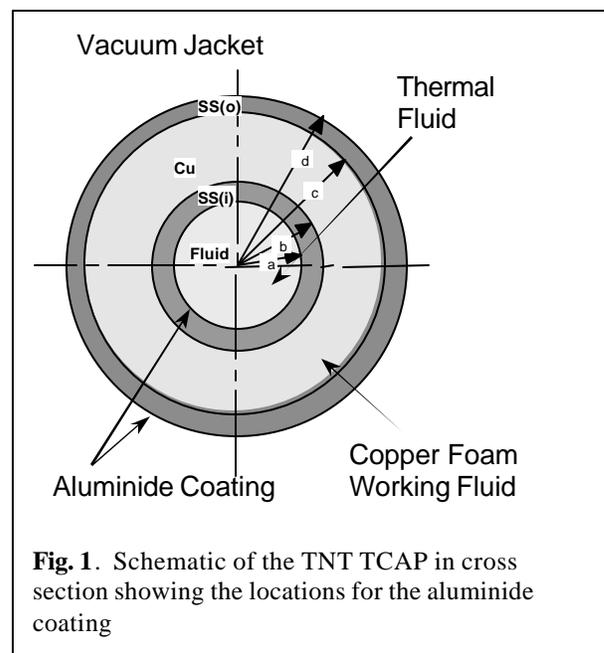


Fig. 1. Schematic of the TNT TCAP in cross section showing the locations for the aluminide coating

solubility of the gas in the material. The general equation for permeability is shown in Eq. 1. Permeation is thermally activated and thus increases exponentially with increasing temperature. The permeability of several metallic coatings is shown in Fig. 2. Permeation through

$$P = DS = DKp^{1/2} = Ap^{1/2}e^{-Q_p/RT} = P_0^* e^{-Q_p/RT} \quad (1)$$

Where: P is permeability; S is solubility; D is diffusivity; K is pre-exponential coefficient; p is gas pressure; A is a coefficient, Q_p is an activation energy for permeation; R is the universal gas constant; and T is the temperature.

metallic coatings is limited by bulk diffusion through the entire metal coating thickness. Thus, greater permeation reduction occurs in thicker metallic coatings. Ceramic coatings such as titanium carbide and titanium nitride^{1,2} have been evaluated with mixed success as hydrogen permeation barriers. Aluminide coatings exhibit significantly larger reduction in the permeation of hydrogen isotopes, presumably due to the in-situ formation of an aluminum oxide surface film that develops on the aluminum rich surface, (the permeation reduction is not due to the reduction in diffusion as for metallic coatings). Permeation reduction factors between 10 and 10,000 have been reported for aluminide coatings^{3,4}.

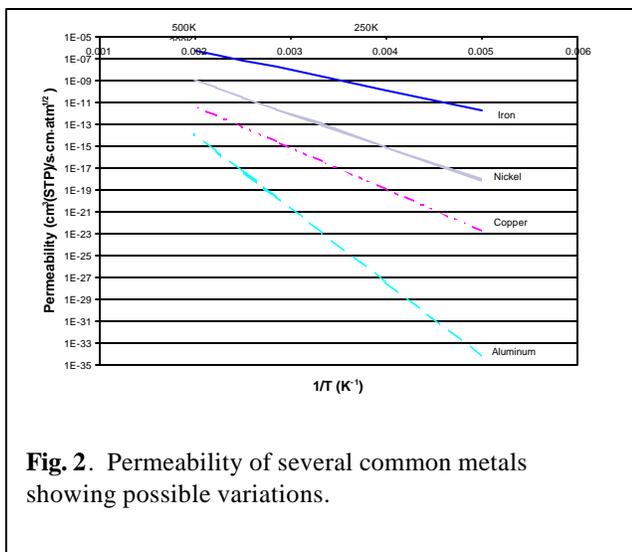


Fig. 2. Permeability of several common metals showing possible variations.

Due to the large possible reduction in tritium permeability, the desire for a thin surface treatment and the use of existing technology it was determined that an aluminide coating process that would permit the coating of internal as well as external surfaces would be best suited for the TNT TCAP application.

Possible Processes

Aluminide coatings are commonly used in the gas turbine industry to apply a high temperature oxidation resistant coating to relatively small components. The techniques for coating both internal passages and external surfaces have been developed. The most common methods to apply aluminide coatings include pack aluminizing, gas phase aluminizing, and slurry coating.

Pack aluminizing: Pack aluminizing is a coating technique that applies aluminum to the surface of the part by loading a large retort with an aluminum source material, an inert material, an activator, e.g., ammonium chloride, and the component. As the retort and contents are heated, the aluminum melts, reacts with the halide to form an aluminum halide gas, the gas contacts the part surface and is reduced and the aluminum reacts to form the aluminide, (iron aluminide in the case of a ferrous component such as that made from stainless steel). The final coating product is determined by the reaction time, temperature, and aluminum activity of the starting powder. There are typically two temperature and time regimes for aluminizing; low (1400-1750°F) for four to 20 hours and high (1800-2100°F) for two to four hours. Low temperature applications tend to produce a coating that is high in aluminum content, has little interdiffusion, and has more additive thickness than high temperature coating applications. Conversely, the high temperature aluminide coating process produces a coating with a lower aluminum content, less additive thickness, and more interdiffusion. In both cases, the aluminum content can be reduced and the coating thickness increased using a post coating heat treatment.

Gas phase aluminizing: There are two types of gas phase aluminizing processes; those that have the aluminum vapor generated in-situ (also called “above-the-pack” or “out-of-pack”) and those generated ex-situ such as chemical vapor deposition (CVD). In the above-the-pack process, pack materials as described for the pack aluminizing process (aluminum source material, activator, and inert filler, if required) are placed into a special multi-chamber retort that has gas flow tubes to interconnect the chambers and to provide aluminum gas to the part. The retort is heated and an aluminum rich gas forms and the balance of the process is essentially the same as for the pack aluminizing method.

The CVD process can be conducted either at low temperatures using organometallic precursors (OM) or at high temperatures using aluminum or aluminum alloys and halide gas activators and a hydrogen carrier gas. The aluminum source for CVD is outside of the coating chamber and is piped in to the retort. At high temperatures, the aluminum-based gas reacts and forms

the aluminide in much the same manner as the pack or gas phase methods. A low temperature OM-CVD process may also be used. In this process, the decomposition and deposition of the aluminum occurs below its melting point and pure elemental aluminum is deposited. The coated part is then heat treated to form the aluminide. The diffusion heat treating time and temperature dictate the coating thickness and chemistry.

Slurry Coatings: Slurry coatings are used to apply aluminum source material by spraying or painting aluminum or an aluminum-alloy on the surface. The coated part ("green part") is cured at a temperature less than 650°C and is then diffusion heat-treated. This method permits coating of large complex shapes that have few blind areas, as it is somewhat a line-of-sight process. Within the slurry coating method either liquid phase or vapor phase transport can occur. The transport mechanism depends on the composition of the slurry and the aluminum source alloy. If a vapor phase method is used, then the slurry contains activators, an aluminum source, and possibly inert fillers much like the pack processes. The coating mechanism is virtually identical to those described above.

If the liquid phase transport is used, then the painted on slurry contains either aluminum or an aluminum- alloy and possibly inert fillers or binders to provide green strength (strength before the part is diffusion heat treated). The part is green coated, the coating cured, and then heat treated by heating above the melting point of aluminum where the iron and aluminum inter-diffuse to form the desired aluminide phase. The resulting coating depends on the aluminum activity of the applied slurry and the diffusion conditions. Under the preferred conditions, the final coating thickness should be independent of the amount of slurry applied once a threshold amount has been exceeded. For this condition, the coating is diffusion limited as opposed to green coat limited. In other words, additional green coating thickness does not increase the diffused coating thickness. From a processing viewpoint, the diffusion heat treatment limited condition promotes a more robust coating process since the amount of green coating on a complex part can vary widely without causing a wide variation in the final coating.

For large complex parts, the high temperature pack process has limitations since it may be difficult to adequately control the coating thickness, especially for thin wall pipes, the low temperature pack process was not pursued due to vendor inaccessibility so OM-CVD and slurry coating techniques were examined for use with the TNT TCAP.

Process and Product Definition

There were both real and arbitrary process and product requirements for the application and performance of the permeation reducing coating. The maximum allowable diffusion temperature was 1037°C, stemming from the possible presence of a copper foam inside the outer tube during the coating operation. The internal surface of the 0.75 inch outside diameter tube required coating to prevent tritium contamination of the fluid, and the external surface of the 1.5 inch tube required coating to prevent contamination of the vacuum jacket. A uniform thickness without cracks, chips, or sharp transitions was desired. The process had to be adaptable to large components from 22 inches in diameter by 20 inches tall to five feet long tubes.

The coating requirements were that it be from 50 to 125 μm thick (including the interdiffusion layer), exhibit high ductility, be crack free, have no free aluminum on the surface, and have an aluminum content from 20 to 40 weight % as measured on the outer fourth of the coating.

RESULTS

Coatings that were produced using OM-CVD and slurry coating techniques were examined. OM-CVD coatings were applied to the internal surface of a U-bend 0.75 inch tube, as shown in Fig. 3. The "green" coating, (undiffused) thickness ranged from 30 μm on the inlet to 20 μm on the outlet. This thickness variation was deemed acceptable and a heat treatment study was undertaken to determine optimal conditions for achieving the desired coating characteristics. Temperatures between 700 and 1000°C were used to develop the coating microstructure and composition. Fig. 4 shows the coating structure for the green coating and after diffusion treatments at 850 and 1000°C. The coating exhibited a uniform thickness and a smoother surface condition after the

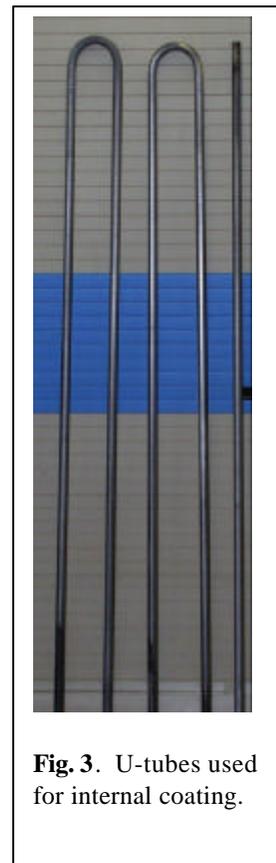
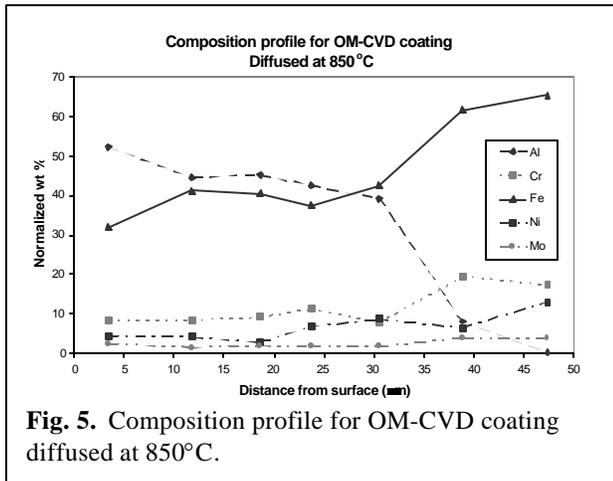
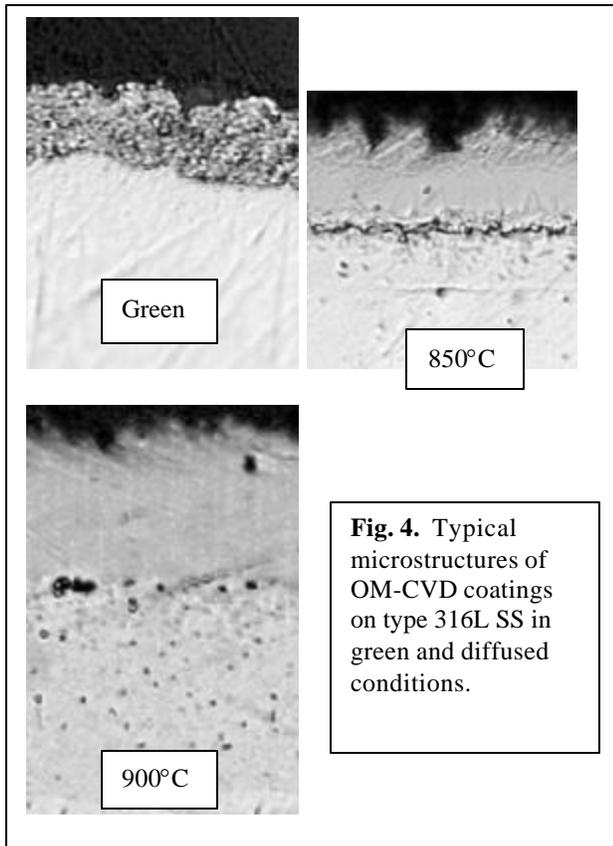


Fig. 3. U-tubes used for internal coating.

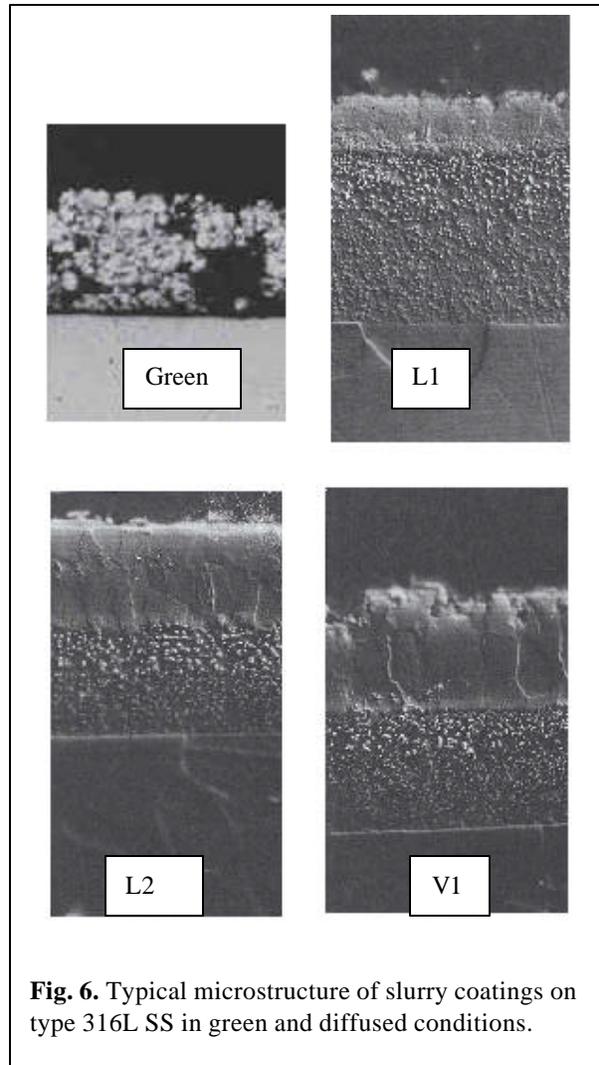
1000°C treatment compared to the 850°C treatment. There was little interdiffusion layer in the 850°C diffused sample and a near single layer aluminide coating. The aluminum content was determined using semi-



quantitative analysis on the scanning electron microscope (SEM). These results revealed a surface content of approximately 50 weight percent or 70 atomic percent. The coating composition varied with distance from the surface as shown in Fig. 5. The peak composition determined for this sample suggests that it contains $FeAl_3$ rather than the desired intermetallic $FeAl$. Increased

diffusion temperature may decrease the surface aluminum content.

Two types of slurry coatings, a vapor phase and liquid phase, were used to determine which type and composition would be most suitable for the TNT TCAP.



In addition, two compositions and viscosities of liquid phase slurries were examined. Heat treatment conditions were varied to determine the effects of temperature on the microstructure and composition of the coatings. The microstructures of the green and diffused coatings are shown in Fig. 6. The green condition is similar for the both types of coatings while the diffused coating thickness and microstructures exhibit significant variability. The liquid phase one (L1) sample exhibits a very thin additive layer and a large interdiffusion zone. The liquid phase two (L2) sample exhibits a thicker additive layer and a smaller interdiffusion zone. The grains are near equiaxed. The vapor phase one (V1) coating exhibits a microstructure similar to the L2 except

the additive layer appears to have nearly fully epitaxial, columnar grains.

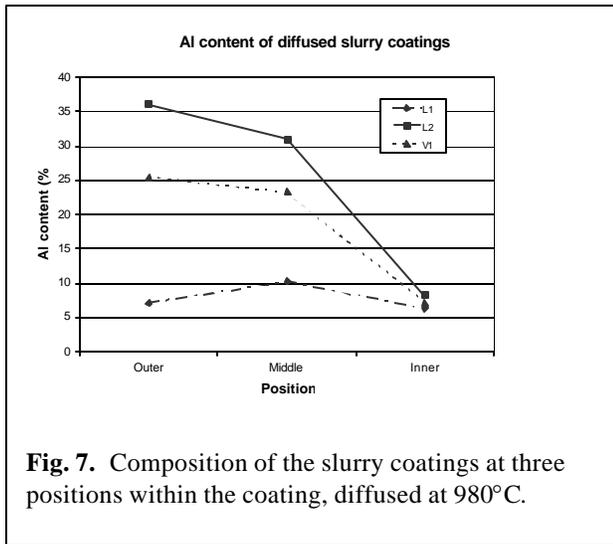


Fig. 7. Composition of the slurry coatings at three positions within the coating, diffused at 980°C.

The aluminum content of the three coatings was measured using semi-quantitative analysis on the SEM with the results shown in Fig. 7. It is obvious that the L1 sample did not meet the coating requirements with respect to the target aluminum content while the L2 and V1 samples did.

Table 1. Coating thickness and aluminum content for L2 slurry coated type 316L SS, associated micrographs are in Fig. 8.

	Thickness (μm)		wt % Al
	ID	OD	ID
850°C	42	55	42
900°C	45	57	34
980°C	--	109	36

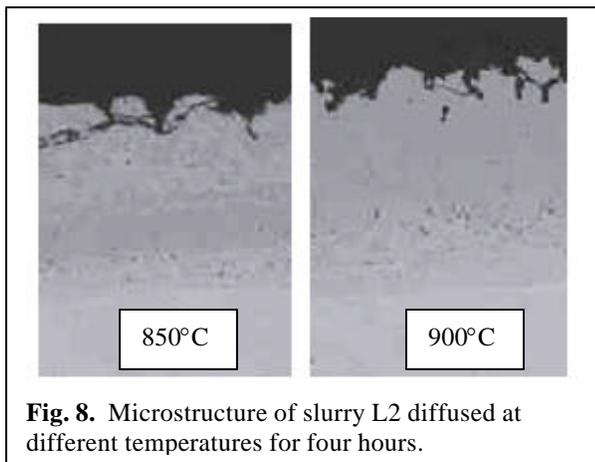


Fig. 8. Microstructure of slurry L2 diffused at different temperatures for four hours.

A number of heat treatments, from 850 to 980°C, were used to modify the coating microstructure, thickness, and chemistry. The minimum heat treat

temperature was determined to be 900°C to ensure acceptable coating characteristics. The coating thickness was slightly greater for 900°C compared to 850°C while the aluminum content was slightly greater for the lower diffusion temperature. These results are consistent with those from the OM-CVD coatings.

NOMENCLATURE

ID internal tube diameter
 OD external tube diameter
 HT high temperature
 LT low temperature

SUMMARY

The preferred method for apply aluminide permeation barrier coatings to the TNT TCAP internal and external surfaces were was selected based on technical and other reasons. Both the OM-CVD and L2 slurry coatings produced acceptable coatings. However, the slurry coating was selected. The target permeation reduction factor was achieved. The heat treatment conditions can be used to modify the coating characteristics.

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REFERENCES

1. Tazhibaeva, I.L., Klepikov, A.Kh., Romanenko, O.G., Shestakov, V.P., "Hydrogen permeation through steels and alloys with different protective coatings", *Fusion Engineering and Design* Vol. 51–52, pp. 199–205, 2000.
2. Shan, C. et al., "The Behavior of Diffusion and Permeation of Tritium Through 316L Stainless Steel with Coating of TiC and TiN/TiC", *Journal of Nuclear Materials*, Vol. 191-194, pp. 221-225, 1992.
3. Gilbert, E.R., Allen R. P., Baldwin, D. L., Bell, R. D., Brimhall, J. L., Clemmer, R. G., Marschman, S. C., McKinnon, M. A., Page, R. E., Powers, H. G., Chalk, S. G., "Tritium Permeation and Related Studies on Barrier Treated 316 Stainless Steel", *Fusion Technology*, Vol. 21., pp. 739-744, 1992.
4. Hollenburg, G. W., Simonen, E. P., Kalinin, G., Terlain, A., "Tritium/Hydrogen Barrier Development", *Fusion Engineering and Design*, Vol. 28, pp. 190-208, 1995.