SilcoTek Coatings in a Venusian (Pure Supercritical CO_2) Atmosphere*

Technical Insight

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Please see last page for a full citation of this work.

Background

Over the past twenty years, NASA's planetary exploration efforts have been focused on Earth's neighbor, Mars. Due to its relatively benign atmospheric conditions, engineering of spacecrafts and rovers are one of the biggest hurdles to the exploration of Mars, as common materials such as steel can survive in its atmosphere. Earth's other planetary neighbor, Venus, is not nearly as friendly to common materials for space exploration. The atmosphere consists mainly of supercritical CO_2 along with other gases such as SO_2, H_2O, CO, OCS, HCl, HF, and H_2S. Because of this, material science must take a front seat to find solutions for such harsh conditions.

The interaction between pure supercritical CO_2 and common metal alloys has been studied extensively in the past 40 years, due to the use of supercritical CO_2 as a coolant in nuclear power plants. Many steel alloys tend to oxidize as well as be subjected to increase carbon content in the formation of insoluble chromium carbides at the grain boundaries when exposed to supercritical CO_2. These reactions can lead to cracking and failure of the steel. To create the next generation of probes to explore Venus's surface, an understanding of how common spacecraft materials interact with the harsh atmosphere is necessary. NASA has started to explore coating options such as SilcoTek's Dursan® and SilcoNert® 1040 (a SilcoNert 2000 derivative) on these metal alloys.

Goal:

Quote taken from NASA's report:

"The goal of this work is to study the chemistry, structure, microstructure, and kinetics of metallic composition and temperature and pressure conditions of the Venus atmosphere (96.5% CO2, 3.5% N2, 30 ppm H2O, 150 ppm SO2, 28 ppm CO, 15 ppm OCS, 3 ppm H2S, 0.5 ppm HCl, and 5 ppb HF at 92 bar (1330 psi) and 467°C (873°F)."

The NASA report covered a wide variety of materials, including:

-Bare metals such as steels, nickel-based alloys, and gold

-Coatings including Dursan, SilcoNert 1040, yttria-stabilized zirconia (YSZ), and porcelain

-Ceramics such as alumina, fused quartz, SiC, and Si_3N_4

For brevity, this Technical Insight will focus on the coatings that were tested and how they compare to the bare substrate in the Venusian atmosphere. For reference, all four of the ceramics survived the conditions with no detectible reactions from the spectroscopic and microscopic techniques used in the report; however, due to the materials limitation of ceramics such as their fragile nature, they may not be the best choice in all parts of a Venusian probe.

Results and Discussion

Bare and coated metal samples were placed in the Glenn Extreme Environments Rig (GEER) and were exposed to the atmosphere described above for 10 and 42 days to investigate the difference in weight and elemental composition between a “short” and “long” exposure. The Dursan and SilcoNert 1040 coupons were also subjected to a 21-day exposure specifically for XPS analysis. Coupons were monitored via weight gain/loss, XPS, AES, and XRD. Summary of results are below:

• Bare steel

Figure 1 shows the weight change in all of the bare metal alloys. The carbon steel (1018) shows the worst performance, followed by the three grades of stainless steel (316, 310, and 304). The nickel alloys and gold will not be discussed here as they were not coated for testing; however it is worth noting that the results of the SilcoTek coatings were on par with the specialty nickel alloys.

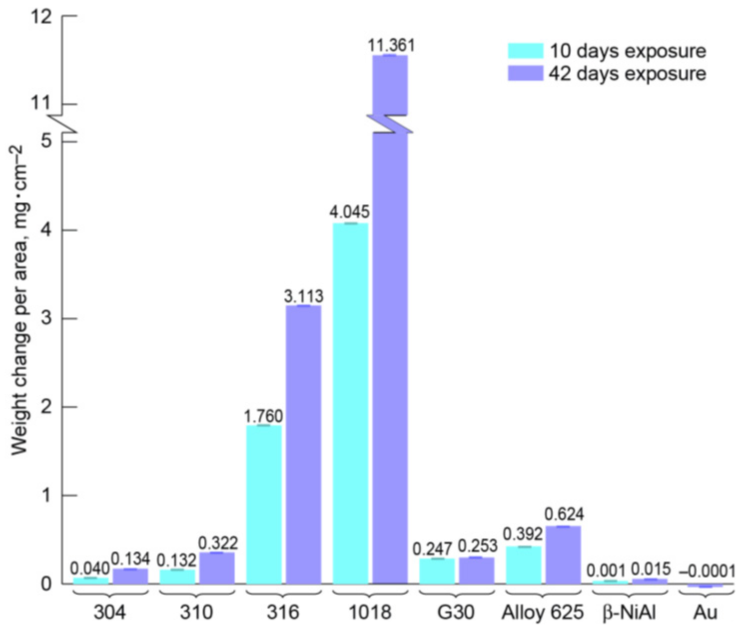
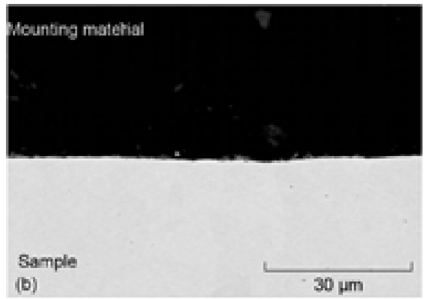


Figure 1: Weight change per area of various metal coupons placed in the GEER and exposed to the Venusian atmosphere.

The bare stainless-steel coupons developed a double layer exterior in which the outer layer is mostly magnetite (Fe_3O_4) and the inner layer is a nickel sulfide. These are formed from the exposure at both 10 and 42 days in the GEER. Figure 2 shows cross sections of the 316 stainless steel before and after exposure. Other oxides were found in the steels as well, but they were much less abundant. Carbon steel was found to have layers that were rich in iron, sulfur, and oxygen. This was largely from the formation of iron sulfide and a multitude of oxide phases. Both layers are not well bonded to each other and are porous which can potentially cause flaking issues. The sulfide formation can be attributed to the SO_2 reaction with the steels, and the oxide is similar to that which is found in previous studies of supercritical CO_2 and its interaction with steels.



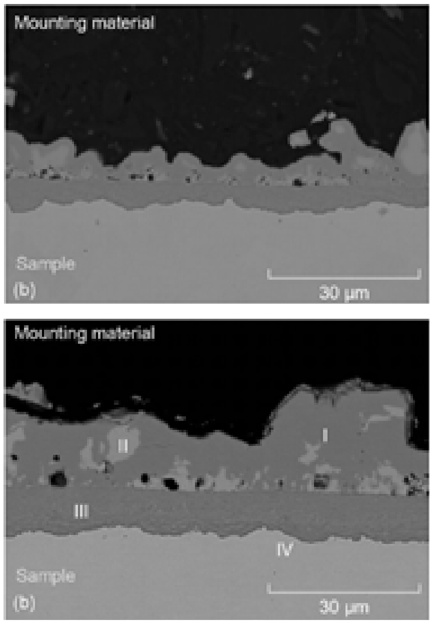


Figure 2: Backscatter electron images of 316 stainless steel coupon cross-section with 0,10, and 42 days of exposure to the Venusian atmosphere.

• Coated steel

Figure 3 shows the weight change for the Dursan and SilcoNert 1040 along with the YSZ and a porcelain coating after exposure in the GEER. YSZ was shown to be a semi-porous coating, as the supercritical CO_2 was able to penetrate through to the steel surface to start the oxidation process. The YSZ simply slowed this oxidation. NASA ranked the coatings as SilcoNert 1040>porcelain>Dursan>YSZ in terms of weight gain observations.

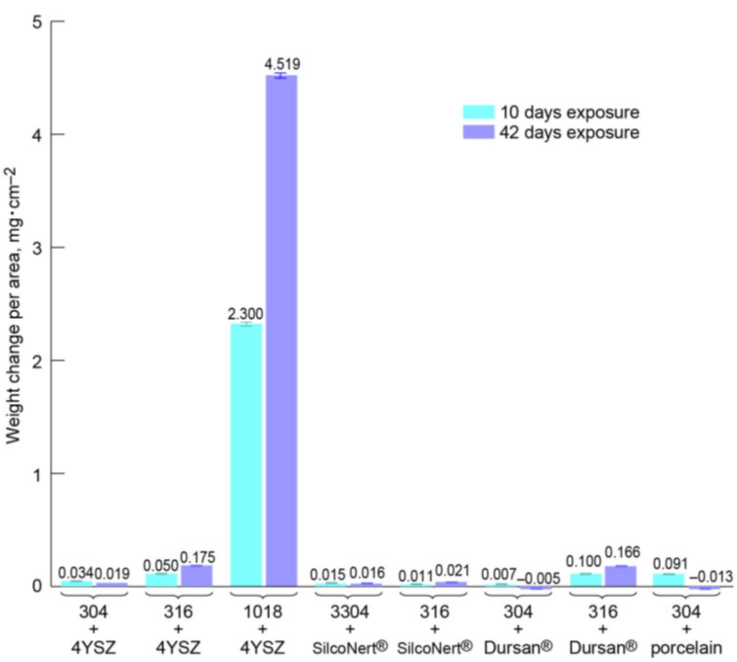


Figure 3: Weight change per area of various coated metal coupons placed in the GEER and exposed to the Venusian atmosphere.

XRD analysis of the coupons before and after exposure shows that the SilcoNert 1040 worked well to stop any corrosion of the stainless steel surfaces. Prior to exposure, only austenite and ferrite were detected. The SilcoNert coating is amorphous, which would result in a very broad peak in the XRD; however, due to the very thin nature of this coating, it was not detectable in NASA's setup. After exposure, these coupons showed iron silicide phases along with the austenite and ferrite suggesting that there was some sort of reaction between the steel substrate and the coating. According to XPS analysis, it was still effective in protecting the steel as there was no evidence of Venus gas penetrating into the bulk of the coating or substrate. Figure 4 is a good illustration of the protective qualities of SilcoNert 1040. After 42 days of exposure to the Venusian atmosphere, the 316 stainless steel has not been attacked like what is seen in Figure 2.

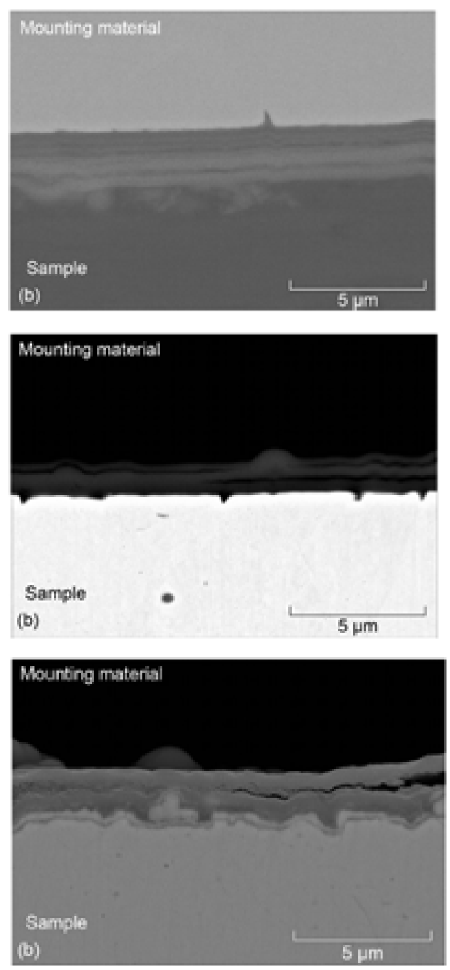


Figure 4: Backscatter electron images of the cross-section of 316 stainless steel with the SilcoNert 1040 coating. From top to bottom, exposure days are 0, 10, and 42.

XPS analysis of the SilcoNert 1040 coating, seen in Figure 5, shows that while there was some reaction of the silicon from the coating with the iron and chromium of the steel at the interface, none of the Venusian gas was able to penetrate into the bulk of the coating, nor the 316 steel substrate.

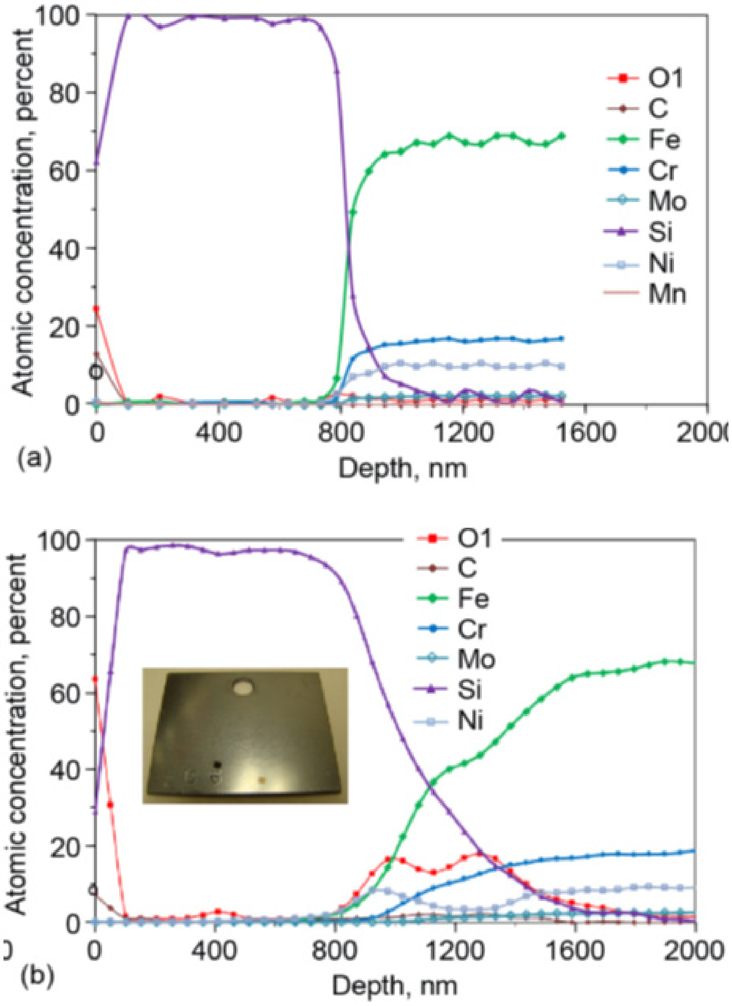


Figure 5: XPS depth profile of a 316 stainless steel coupon before (a) and after (b) exposure to the Venusian atmosphere for 21 days.

The Dursan-coated stainless steel also showed only austenite and ferrite prior to exposure. After the exposure, iron silicon oxide and iron nickel silicide phases were detected suggesting that, like SilcoNert, the Dursan and the substrate underwent some sort of reaction. Figure 6 shows the cross-section of a Dursan-coated coupon, and it appears to be very similar to SilcoNert, where it provided adequate protection of the steel.

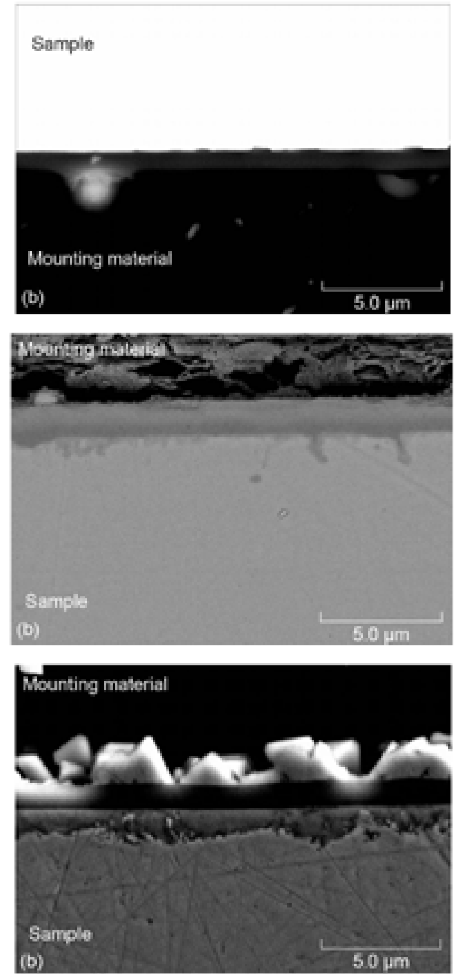


Figure 6: Backscatter electron images of the cross-section of 316 stainless steel with the Dursan coating. From top to bottom, exposure days are 0, 10, and 42 (note that day 0 is upside down compared to all other cross sections).

Unlike the SilcoNert coating, XPS depth profiling showed evidence of a metal sulfide at the interface between the coating and steel suggesting that some amount of the Venusian gas was able to penetrate through the Dursan coating. This can be seen in Figure 7, which shows a before and after XPS of a 316 stainless steel coupon.

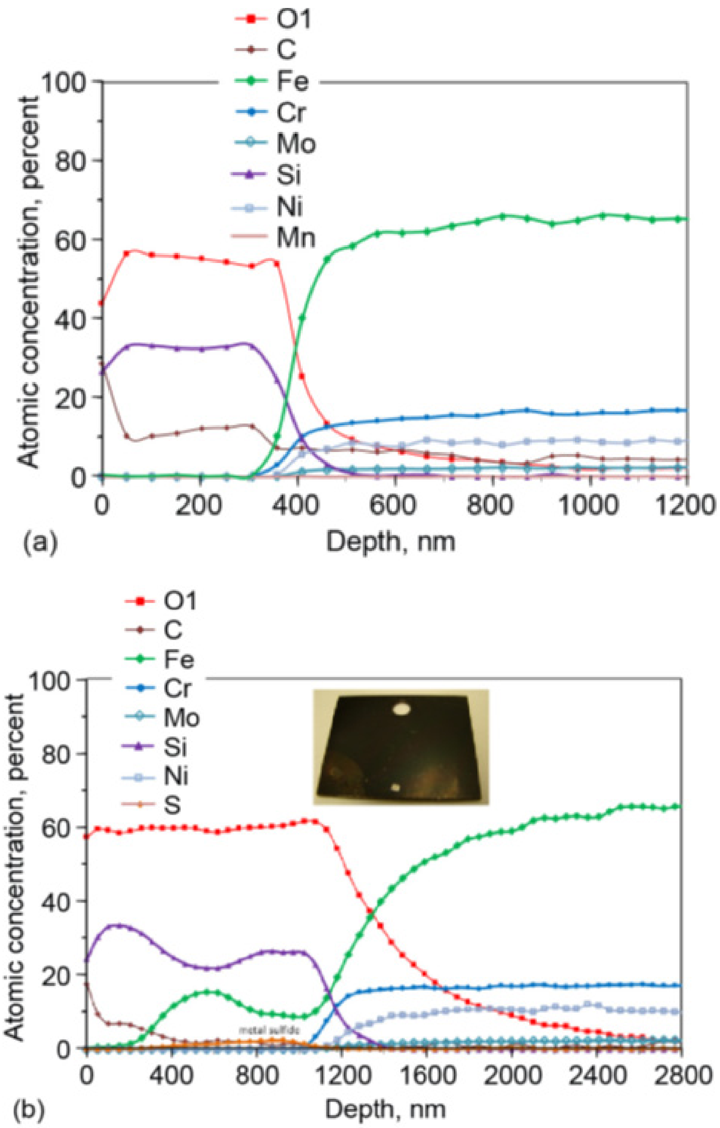


Figure 7: XPS depth profile of 316 stainless steel before (a) and after (b) 21 days of exposure to the Venusian atmosphere.

Conclusion

The study concluded that SilcoNert® 1040 was the most promising coating that NASA tested in the Venusian atmosphere. This sub-micron thick coating not only outperformed SilcoTek's Dursan® coating, but it also out performed a 140 µm thick YSZ coating and a 200 µm thick porcelain coating. NASA will continue testing both SilcoNert and Dursan in the future, and with the knowledge gained from this study, we can now confidently recommend Silconert 1040 as protection against an atmosphere that is pure supercritical CO2, such as that which is found in nuclear powerplants, or in a Venusian atmosphere.

*Thank you to the authors for providing SilcoTek® with this valuable research.

Costa, G.C.C., Jacobson, N.S., Hunter, G.W., Nakley, L., Radoman-Shaw, B.G., Lukco, D., Harvey, R.P. "Chemical and Microstructural Changes in Metallic and Ceramic Materials Exposed to Venusian Surface Conditions" June 1, 2017 Technical Report. NASA Glenn Research Center; Cleveland, OH.

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