Thermal Stability Improvement of the Silcolloy Coating

Technical Insight

Author

Min Yuan,
R&D Scientist

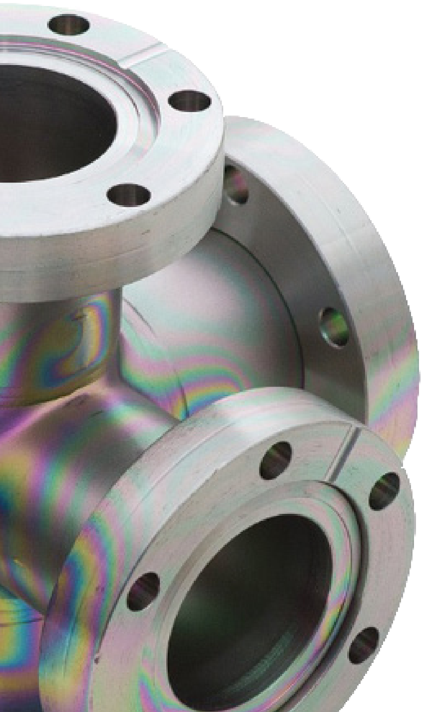
SilcoTek® Corporation

Synopsis

One of the key advantages of SilcoTek's CVD coatings over polymer-based coatings is their ability to be used for high temperature applications. Among our current commercially available coatings, Silcolloy (hydrogenated amorphous silicon) has been the recommendation for most high temperature applications (≥ 450°C). Amorphous silicon (a-Si) transitions to crystalline silicon (c-Si) at around 700°C as part of its intrinsic physical properties, but when in direct contact with a metal substrate, crystallization of a-Si can be catalyzed by the metal and occur at a lower temperature, the degree of which depends on the type of metal. Crystallization causes coating degradation and facilitates outward metal diffusion, which undermines the coating's barrier properties. SilcoTek discovered that by placing a primer layer between the metal and the a-Si coating, this premature crystallization is effectively eliminated, and the thermal stability of the coating is significantly improved up to the testing temperature of around 800°C.

Background

High temperature thermal stability is one of the key advantages of SilcoTek's silicon-based CVD coatings when compared to traditional polymer-based organic coatings. Unlike organic coatings that soften, decompose or melt usually in the 200-300°C temperature range, SilcoTek's coatings can handle at least 400-500°C for coatings that have a surface functionalization chemistry (such as SilcoNert 2000 and Dursan), or 700°C and beyond for coatings that are comprised of one bulk layer with no surface functionalization chemistry (such as Silcolloy and Dursox). In the case of coatings that come with surface functionalization, the functionalization (i.e. the uppermost layer of the coating that is too thin to be measured) starts to decompose in the 400-500°C range, leading to gradual loss of properties such as ultra-inertness and hydrophobicity, yet the bulk of the coating still remains to provide basic barrier protection to the underneath substrate.



Among the current commercially available SilcoTek coatings, Silcolloy has been the go-to recommendation for most high temperature (≥ 450°C) applications. Silcolloy is made purely of hydrogenated amorphous silicon (a-Si) with no additional surface functionalization. As amorphous silicon is an excellent barrier against corrosion, especially oxidation (which is a form of corrosion), Silcolloy seems to have the best chemistry (among SilcoTek products) to handle high temperature applications.

However, Silcolloy does have its Achilles' heel in that amorphous silicon starts to crystallize at around 700°C. This is an intrinsic materials property of amorphous silicon, as shown in our previous TGA-DSC study on a-Si particles. The TGA-DSC experiment investigated stand-alone a-Si particles (not a coating attached to a substrate), therefore the properties measured reflect the inherent attribute of a-Si regardless of any substrate. When a-Si is deposited as a coating on top of a metal substrate, the silicon crystallization may often occur below 700°C because many metals catalyze the silicon crystallization process to trigger the transition before it reaches the intrinsic crystallization temperature. For example, a-Si deposited on aluminum starts to crystallize as early as around 400°C, while for stainless-steel, this transition occurs around 600°C.

Once crystallized, silicon becomes much more susceptible to oxidation, and the transformation from amorphous to crystalline may lead to coating degradation. Therefore, it is important to eliminate the occurrences of such premature crystallization caused by metal, to maximize the potential of a-Si within its materials limits. This TI discusses SilcoTek's recent improvements on this front to deliver a more thermally stable Silcolloy coating.

Experiment and Discussion:

Since metal in direct contact with a-Si is the cause for premature silicon crystallization, the approach we took to eliminate this impact is by adding a primer layer between the metal substrate and the Silcolloy coating. The primer layer must meet the following requirements to be successful:

- It must act as an effective diffusion barrier to isolate the metal from Silcolloy.
- The primer layer itself is immune to metal-catalyzed crystallization below the intrinsic crystallization temperature of Silcolloy.
- It should bond well to both the metal substrate and Silcolloy.
- It can be easily integrated into the current CVD process to be production friendly.

We successfully developed such a primer layer that met all the above criteria, and the Silcolloy coating deposited with such a primer layer will be referred to as "RD15" in the rest of the TI. In comparison, the standard Silcolloy without the primer layer will be referred to as "SOP". Figure 1 below illustrates the difference between these two versions of Silcolloy.

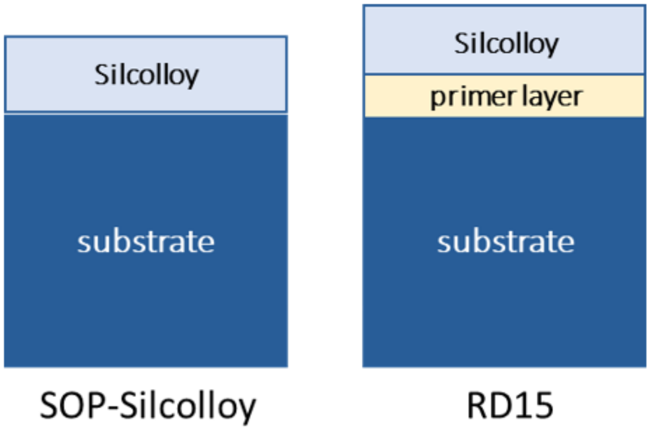


Figure 1: Coating structures of SOP-Silcolloy vs. RD15

To assess the effectiveness of the primer layer, 316L stainless-steel coupons coated with SOP-Silcolloy (SOP) and RD15 were exposed to 600°C in air for six hours. Raman spectra (using 488 nm laser) were collected on the coupons before and after the thermal exposure, as Raman is an excellent tool for identifying amorphous and crystalline silicon phases. Figure 2 shows that RD15 maintained the amorphous silicon nature after this thermal exposure, whereas SOP experienced the amorphous-to-crystalline transition and subsequent silicon oxidation as illustrated by the sharp and intense c-Si peak at 522 cm-1 and the broad Si-O peak near 1000 cm-1. This experiment confirmed that the primer layer is indeed effective at preventing the premature silicon crystallization issue discussed above.

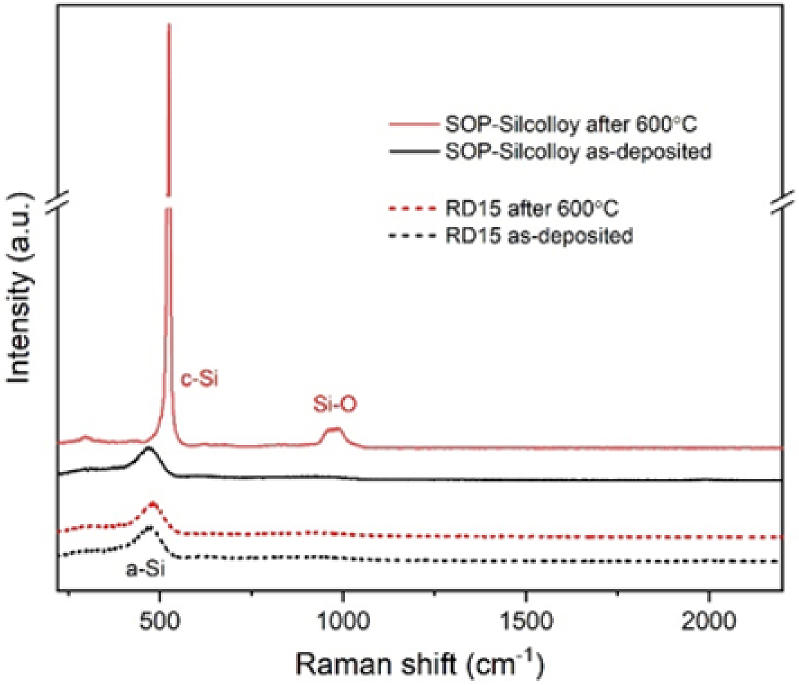


Figure 2: Raman spectra comparison after 600°C thermal exposure

It was mentioned earlier that the intrinsic crystallization temperature for silicon is about 700°C, and this is an inherent materials property that will not be impacted by a primer layer. To confirm this, we repeated the same Raman experiment but raised the thermal exposure temperature to 700°C, while keeping all other parameters the same. Figure 3 (left) shows that both SOP and RD15 turned crystalline after the 700°C thermal exposure, as expected, but a closer look revealed a blue shift (from 522 in SOP to 527 cm-1 in RD15) for the c-Si peak. Similar Raman peak blue shifts in c-Si has been reported in the literature as an indication of stress for c-Si. One study of Si/SiO2 superlattice films described such a Raman blue shift (Figure 3 right).1,2 The superlattice films contain silicon grains embedded in a solid SiO2 film matrix. A laser irradiation is used to melt the silicon grains, which then quickly crystallize to form silicon nanocrystals, resulting in a volume increase of the embedded silicon and a consequent compressive stress about 3 GPa. This stress can be relieved with a lower power laser anneal, and the relaxed structure exhibited a Raman peak characteristic of freestanding crystalline silicon (521 cm-1), as shown in Figure 3 right.

The similarity between the peak shift we observed and what was reported in the literature seems to suggest a similar mechanism. We speculate that in the SOP film, the crystallized silicon grains experience no stress because they are not structurally constrained; in the RD15 film, on the contrary, the primer layer acts as a matrix in which the silicon crystallites are embedded, similar to the Si/SiO2 superlattice, and that constriction provides the source of the stress. SEM images taken on sample coupons after thermal exposure seem to provide supporting evidence, which will be discussed later in this TI.

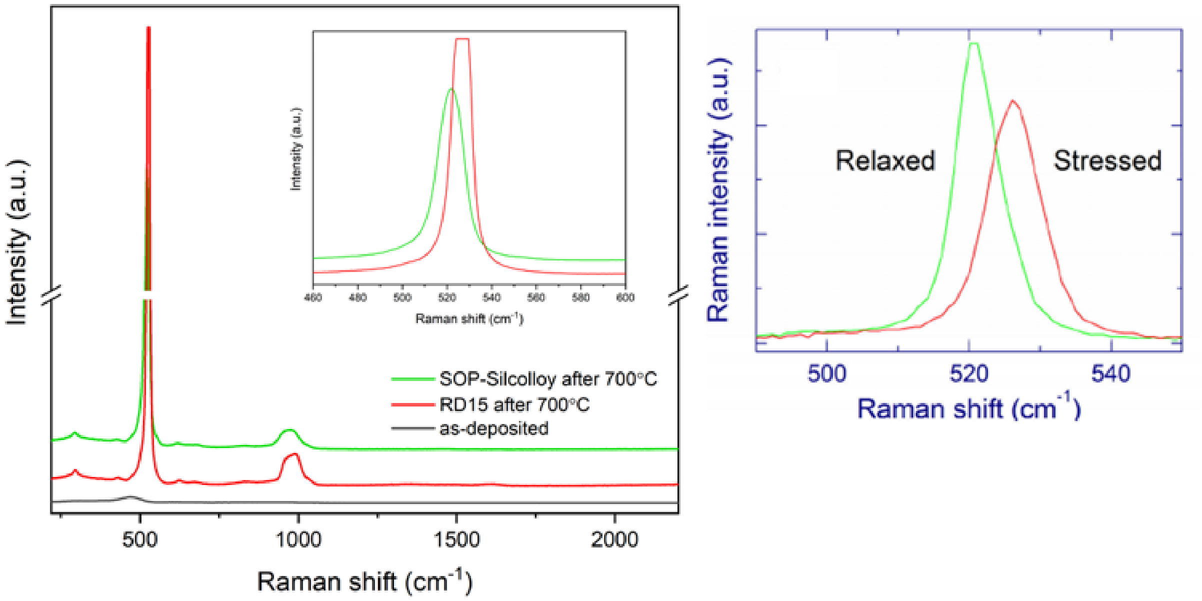


Figure 3: left - Raman spectra comparison of RD15 and SOP after 700°C thermal exposure (for 6 hours in air). Inset is a blowup comparison showing the Raman peak blue shift by about 5 cm-1 in RD15; right – literature report of similar Raman shift in c-Si due to compressive stress experienced by Si nanocrystals1,2

Since both coatings crystallized at 700°C, does it mean that the benefits provided by the primer layer stop at the intrinsic crystallization temperature, and beyond that point the two coatings perform equally? A closer examination revealed a somewhat unexpected but encouraging answer. The primer layer, it appeared, not only prevents premature crystallization of silicon, but also acts as a stabilizing matrix for the silicon coating once crystallization does occur, limiting the degree of structural disruption and damage imposed by the crystallization event. As a result, RD15 retains much of its barrier properties after thermal exposure, demonstrating superior thermal stability compared to SOP-Silcolloy.

Figure 4 records the visual evolution of the two coatings starting at the baseline condition (as-deposited), and going through the different thermal exposures (all held at the peak temperature for six hours in air). The SOP coating showed a more drastic change in color once reaching 700°C, turning dark brown first, then completely black at 800°C, whereas the RD15 coating maintained a rainbow appearance (with some change in color) throughout the whole process.

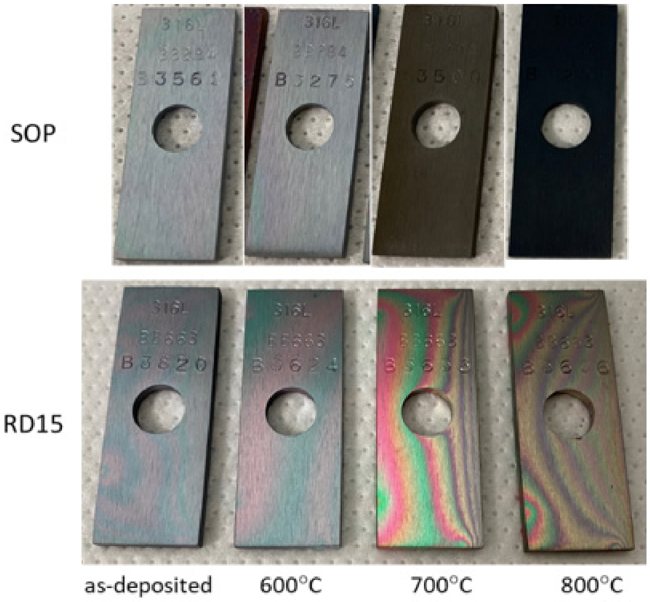


Figure 4: Visual evolution of the two coatings going through thermal exposure (all carried out for 6 hours in air)

SEM (Scanning Electron Microscope) images were taken on individual coupons through the thermal exposure stages, to correlate the macroscopic visual evolution with microscopic structural changes in the coating, as shown in Figure 5. In addition, EDS (Energy Dispersive Spectroscopy) maps of silicon Kα1 line are displayed in Figure 6, which can be used as an indicator of coating coverage on the substrate surface. Elemental silicon is represented in blue; the continuity and relative intensity of the blue color reflect the continuity and relative thickness of the coating. A lack of blue signifies a discontinuity in the coating.

Figures 5 and 6 together deliver a consistent and clear message: the SOP coating suffers significant structural damage and coverage degradation as the temperature rises, while the RD15 coating displays respectable structural integrity and coverage continuity under the same conditions. At 600°C, both coatings appeared smooth and unaltered under SEM, but small coating gaps started to show in the EDS map of SOP, likely due to the onset of crystallization confirmed by Raman (Figure 2); at 700°C, the crystal grains broke out in islands, the silicon intensity became much weaker and the film coverage appeared mostly discontinuous for SOP; finally at 800°C, the surface of SOP was dominated by a mixture of metal (from the 316L stainless-steel substrate) and crystalline silicon grains, and the silicon signal detected by EDS weakened even more. The RD15 coating, on the other hand, remained smooth and continuous under the same exposure conditions and only began to show some void spots in the film at 800°C according to the EDS map. These void spots contain high Mn and O, indicating that the coating was replaced by manganese oxide at these spots. The SEM images of RD15 after thermal exposure provided support to our earlier speculation that the primer layer acts as a stabilizing matrix in the event of crystallization, a barrier to slow down and reduce the associated damage from crystallization and metal diffusion, as we can see that even though it did not completely stop localized disruptions (especially at 800°C), it did help the coating stay in place and survive the thermal exposures considerably better.

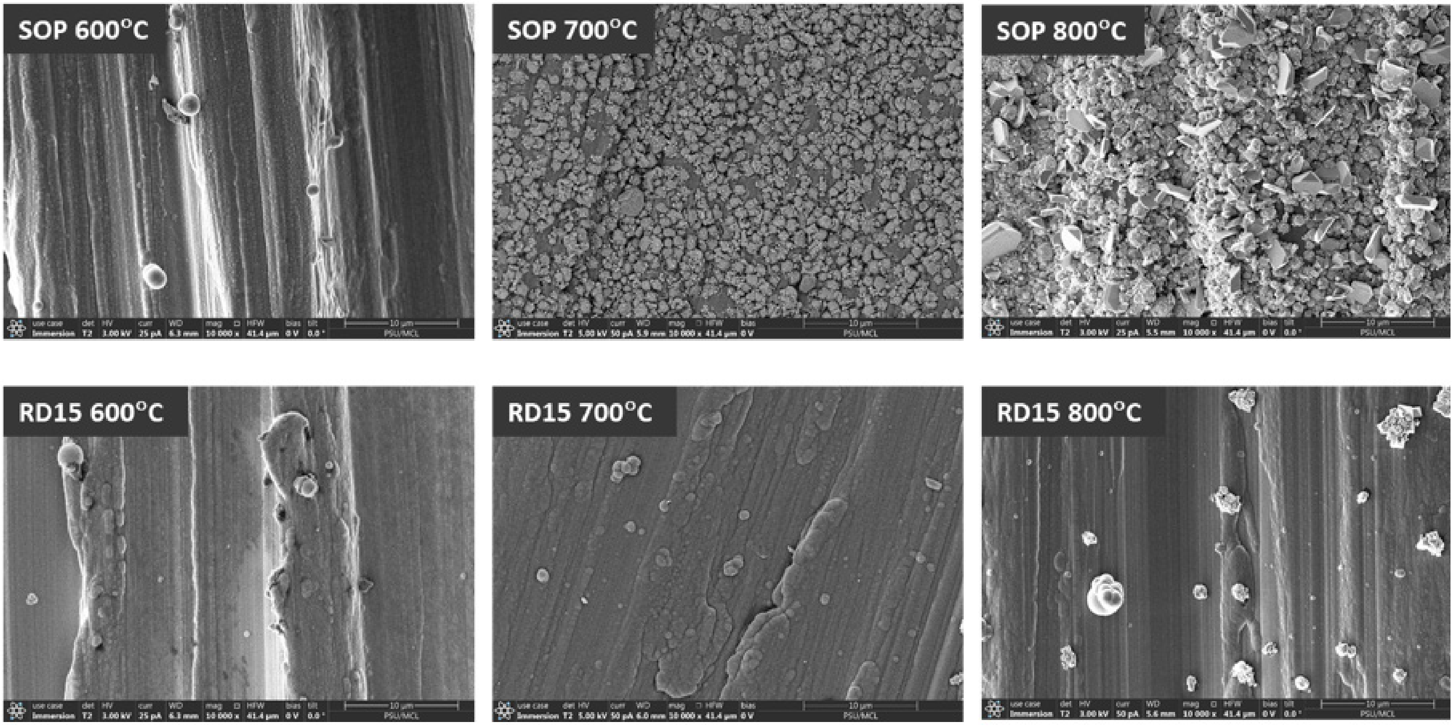


Figure 5: SEM images of the two coatings (all taken at 10K magnification) after thermal exposures to 600, 700 and 800°C for 6 hours in air

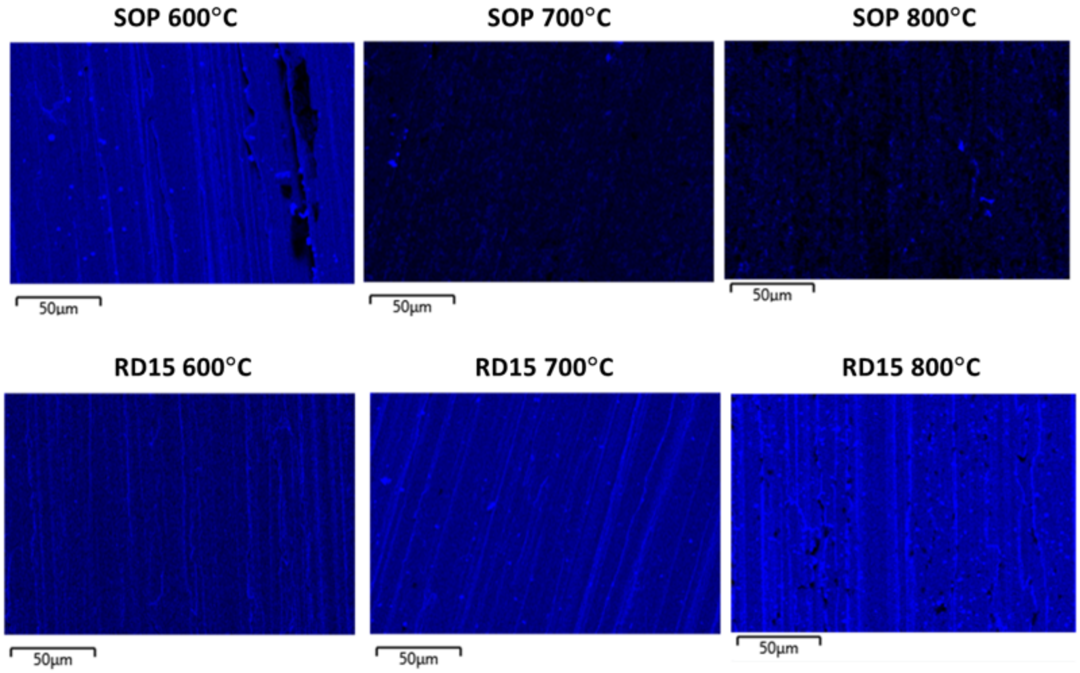


Figure 6: EDS maps of silicon Kα1 line (represented in blue), used as an indication for coating coverage, for the two coatings after thermal exposures to 600, 700 and 800°C for 6 hours in air

To verify that RD15 does indeed retain good barrier properties after thermal exposure, we designed two experiments to investigate 1) how much the coating protects the metal substrate from oxidation during the thermal exposure, and 2) corrosion-resistance of the coating after thermal exposure.

The first experiment was carried out by chemical stripping of the coating in an alkaline bath after thermal exposure and examine the underlying stainless-steel substrate for oxidation. The samples included a baseline uncoated 316L stainless-steel coupon, an SOP-Silcolloy coated coupon and a RD15-coated coupon for each temperature group (600, 700 and 800°C, respectively). Each group of coupons were first exposed to the said temperature for six hours in air, followed by chemical removal of the coating via an alkaline etch (except for the uncoated baseline samples), and finally for visual inspection and EDS analysis. Figure 7 shows that the uncoated coupons were all discolored (from purple to blue to brown as the oxide layer gets thicker), and the measured oxygen concentration rises with increasing temperature. For the coated, RD15 clearly outperformed SOP in protecting the substrate from oxidation. The substrate metal under RD15 experienced little change in color from the original silver, and the measured oxygen contents were significantly lower than both the uncoated and SOP. It is interesting to see higher oxygen content in SOP than uncoated at 800°C, which may be caused by part of the oxidized silicon coating fused with the metal surface and could not be completely removed.

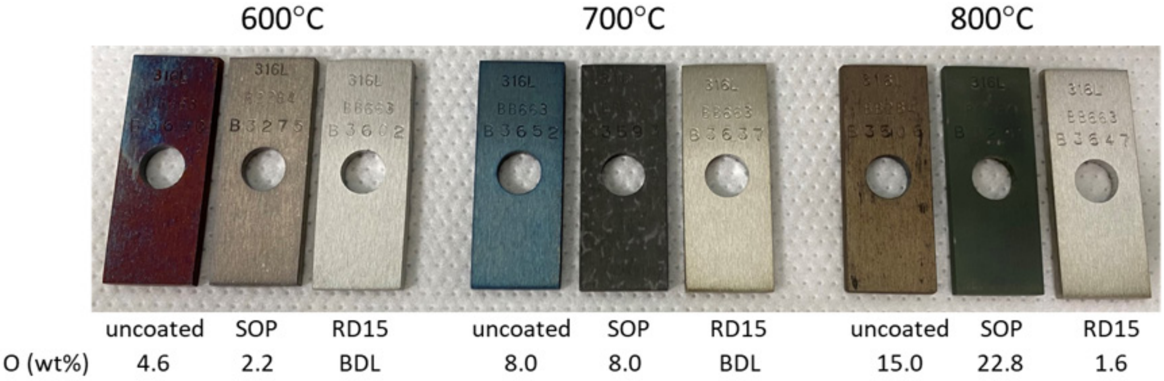


Figure 7: Visual appearances of three groups of coupons that were thermally exposed to 600, 700 and 800°C for 6 hours in air first, followed by coating strip to reveal the SS substrate (except for the uncoated samples). The oxygen content listed under each sample was obtained via EDS analysis using 15kV acceleration voltage; BDL stands for "below detection limit" which is 0.1% for the EDS analysis

The second experiment took 316 stainless-steel square coupons that were coated and thermally exposed, subjecting them to 5% NaCl solution for seven days at room temperature. At the end of day seven, linear polarization resistance scan was performed on each sample in the same solution (5% NaCl) to obtain their corrosion rates. Figure 8 compares the visual appearances and corresponding corrosion rates of the two coatings. RD15 again outperformed the SOP coating by exhibiting better visual integrity as well as lower corrosion rates by two orders of magnitude.

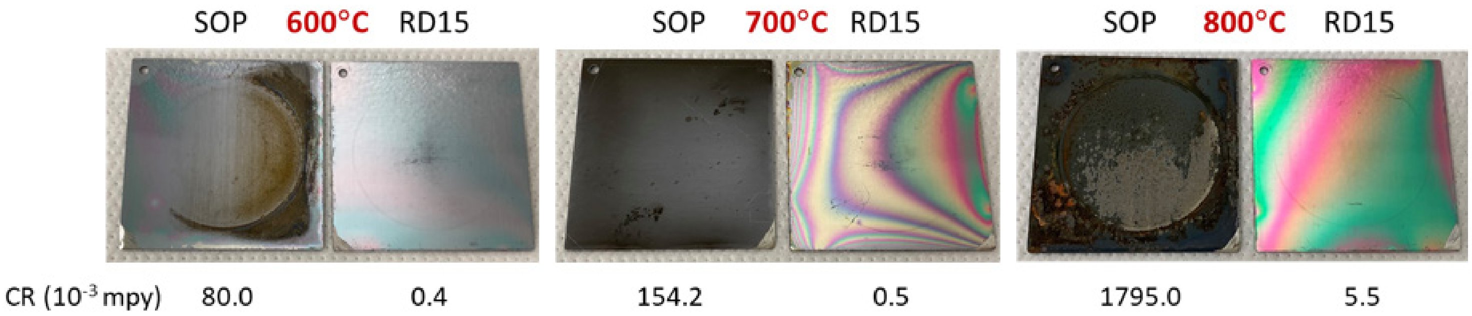


Figure 8: Visual appearances of three pairs of coupons that were thermally exposed to 600, 700 and 800°C for 6 hours in air first, followed by immersion in 5% NaCl solution for seven days. Corrosion rates (CR) were measured via linear polarization resistance scan and reported in 10-3 mpy.

Summary:

This TI focuses on a recent thermal stability property improvement of SilcoTek's Silcolloy coating. The new coating, known as RD15, contains a primer layer that segregates the amorphous silicon coating from the metal substrate, while maintaining the same surface chemistry as Silcolloy. The new coating has effectively eliminated metal-induced silicon crystallization below the intrinsic silicon crystallization temperature, as proven by Raman spectroscopy.

In addition, the primer layer also acts as a stabilizing matrix for the silicon coating once crystallization does occur, limiting the degree of structural disruption and damage imposed by the crystallization transition. As a result, the RD15 coating maintains much better structural integrity and oxygen barrier properties through thermal exposures up to 800°C, as demonstrated by comparative SEM, EDS, metal oxidation analysis and corrosion resistance experiments. The combined data led to the conclusion that RD15 provides superior thermal stability than the current Silcolloy coating.

References:

1. Nikitin, T. et al. "Optical and structural properties of Si nanocrystals in SiO2 films" Nanomaterials **2015**, 5, 614.
2. Nikitin, T. et al. "Optical memory of silicon nanocrystals with submicron spatial resolution and very high thermal stability" Applied Physics Letters **2009**, 94, 173116.