A Fire in titanium Structured Packing Involving Thermite Reactions

Summary

In a recent incident at a chemical plant, two beds of titanium structured packing in a distillation tower ignited. Ignition occurred while a hand held battery powered grinder was in use as part of an inspection activity. Sparks formed when the grinder touched stainless steel or titanium are believed to have initiated a thermite reaction between the thin sheet titanium structured packing and a dried iron oxide layer that had accumulated on the packing surfaces.

There were no fatalities or serious injuries associated with this incident. The metal fire caused extensive damage to the bottom head of the vessel as well as various internal components located in the lower portion of the tower. Replacement of the lower section of the vessel and all of the beds of structured packing was required.

Samples of the packing had been removed before the fire. Inspection and testing of this material after the incident confirmed both the existence of the iron oxide layer and its ability to sustain a propagating thermite reaction with the underlying thin sheet titanium.

Description of Tower

The tower, which is rated above 20 bar, included multiple beds of structured packing manufactured from grade 2 titanium. Other internal components, such as liquid distribution troughs and rings and support structures, were also constructed from grade 2 titanium. The structured packing is assembled from 0.1 mm thick corrugated titanium sheets fastened together to form bundles. Individual bundles are stacked vertically and horizontally (edge up) to produce a bed of the desired diameter and depth.

The Event

The unit was down for repair/inspection, and had been opened and prepared for entry using established plant procedures. Personnel noted a dark coating (including some rust colored streaking) adhering to the structured packing surfaces. Samples of the coated packing from the beds were taken to assess corrosion and verify materials of construction. The coating did not appear to contain any organic material.

After completing entry and hot work procedures per the site's established policies, inspectors carried a hand held battery powered grinder into the tower between the bottom two beds. They planned to utilize a materials identification screening procedure (see NFPA 481, Appendix B) that involved passing the rotating grinding wheel lightly and quickly across the surface of components being checked and noting the characteristics of the sparks generated.

The inspector started testing individual bundles with the grinder. During this activity he noticed a small localized orange glow originating down inside the packing structure of the bottom bed. The glow occurred in an area towards which sparks had previously traveled. About that same time, a very faint white cloud/fog was observed rising through one of the structured packing channels. The inspector alerted the crew to a possible fire, and he and the attending operator quickly moved towards the manway. Within an estimated 30-45 seconds, the orange glow had turned into a brilliant white area about ½ meter in diameter and was spreading through the bed at a rapid rate. The entire bed had become brilliant white as the inspector exited the tower.

Emergency alarms were activated, and within 12-14 minutes personnel started water flowing into the tower via an overhead reflux line in an attempt to extinguish the metal fire. Data retrieved later indicated that temperatures exceeded 600 deg C (the maximum range of the thermal measurement) at several locations around the two beds within 2 minutes from the start of the fire. The data also suggested that the support structure of the bed located above the work area failed, causing it to collapse onto the lower bed. Temperatures in the bottom section of the tower started falling approximately 4-6 minutes after water was added to the top of the tower. The entire fire event was over within 23-24 minutes from the time the orange glow was detected.

Explosive noises occurred within the opened tower after the water reflux was started. Cause of the noises is not known but they may have resulted from rapid vaporization of water, release and subsequent ignition of hydrogen (which is generated by the reaction of hot titanium and steam), or both. The vessel, which was designed for pressures well above atmospheric, did not appear to suffer additional damage from these occurrences. The initial "steam" or "smoke" exiting all manways on the tower was initially a brownish-red, rust color, but this quickly became a white cloud.

The burning, molten mass of titanium, including its combustion products, melted through additional structures in the tower and migrated to the bottom. A hole melted through the bottom head and allowed portions of the molten metal to fall into tower support skirt where it continued to burn. Brilliant white sparks (consistent with burning titanium) and molten metal slugs were expelled from the bottom manways and the openings in the support skirt. These sparks and slugs traveled 30-50 meters.

In addition to starting water flow through the reflux line, emergency response personnel directed water from various firewater turrets onto the outside of the tower shell, tower skirt, and adjacent equipment for cooling. Also, they attempted to spray water into the lower tower manways. Within 23 minutes the thin sheet titanium packing material in the two beds was consumed and the fire ceased. It is believed that the metal fire self extinguished when the thin sheet material was consumed.

Internal inspection of the tower revealed significant damage to the lower section of the tower. The two titanium beds were consumed and there was extensive damage to internal structures such as support grids, liquid distribution troughs, support rings, etc. In addition, a 150mm diameter hole through the bottom of the tower was found. The evidence indicated that titanium metal combustion was largely limited to the thin packing sheets. Thicker, more massive components such as bed support structures and distributor troughs appeared to experience little or no direct combustion, though these components suffered significant damage from the heat.

Background on Titanium Fires

Prior to this incident, a considerable amount of literature existed on titanium burning in oxygen enriched atmospheres using test specimens that were thicker than the thin sheets used to construct the structured packing. This earlier work, by itself, suggested that clean titanium would not propagate sustained burning in air at atmospheric pressure. Previously reported fires with titanium structured packing tended to involve supplementary fuels such as combustible organic deposits and/or pyrophoric materials (e.g., iron sulfide). However, the reported testing was not designed to address the effects of very thin components or thermite reactions with iron oxide.

A "thermite" reaction can occur between a metal oxide and another metal that has a greater affinity for oxygen. When iron oxide and titanium metal are involved, the products of the reaction are titanium oxide, elemental iron, and a large exothermic heat of reaction. If the reaction occurs in an oxidizing environment, the iron may "burn" to iron oxide, a process that releases additional heat as well as regenerates the iron oxide to perpetuate the thermite reaction.

Little systematic work has been reported on thermite reactions involving titanium and iron oxide. Prior to this incident, there had been a small number of reported cases in which titanium combustion occurred in air in the presence of significant quantities of iron oxide. However, these incidents generally involved welding, torch cutting, or other situations where very high temperatures or high energy densities were applied to titanium/iron oxide

Post-Fire Analysis of Recovered Samples

Tests and examinations of the iron oxide coated packing samples recovered before the fire indicated the coating was mainly iron oxide. No organic materials were detected. The thickness of the coating ranged from 2.5 to 25 microns with significant portions of the samples averaging 15-25 microns. The coating could best be described as adhering loosely rather than tenaciously.

After the tower was repaired and placed back in service, investigations confirmed that soluble iron would precipitate as Fe_2O_3 in the tower and adhere to the packing surface. Significant accumulation was observed to occur within a few months with an average soluble iron concentration of less than 1 ppm in the tower liquid.

Ignition Studies on Thin Sheets

After the incident, studies were conducted on (1) new "clean" samples of 0.1 mm thick titanium packing; (2) samples with very thin iron oxide coatings; and (3) samples from the tower with 15 – 25 micron thick coatings of iron oxide. (Note: Testing was done at a facility in New Mexico, where the local atmospheric pressure averages 12.4 psia.) Some observations include:

- Clean samples of 0.1 mm thick titanium would not sustain combustion at local atmospheric pressure unless the air was significantly enriched with oxygen.
- Samples with thin iron oxide coatings (1 – 2 microns) behaved in a manner indistinguishable from clean titanium.
- Under test conditions, samples with a 15 – 25 micron iron oxide layer required a slight amount of oxygen enrichment to undergo self-sustained combustion at the local atmospheric pressure at the test facility.
- At elevated test pressures, self-sustaining "combustion" of the 15 – 25 micron coated material occurred in pure nitrogen.

Conclusions

As a matter of general practice, extreme caution should be observed in work on equipment constructed from titanium and vessels with titanium internal components. Specific conclusions and measures identified or suggested as a result of this incident and follow up activities are:

- Accumulations of iron oxide (or other materials such as organic residues, pyrophoric substances, etc.) on titanium structured packing can promote or accelerate combustion of titanium. It may be appropriate to periodically remove accumulations of such materials through chemical or other means. However, if removal is accompanied by loss of titanium, it can create thinner metal, which may be even more sensitive to ignition.
- Use of water to mitigate an active titanium metal fire can produce negative as well as positive effects.
- Measures that may be used to prevent ignition during maintenance of towers containing structured packing made from thin sheet titanium include the following:
    - Keeping the packing wet with water
    - Flooding the tower with water to a level just below the work area
    - Isolating the packing from the work area using physical barriers such as non combustible blankets
    - Strictly controlling hot work

- Entry procedures for towers containing structured packing made from thin sheet titanium should account for situations where the packing is coated with combustible materials, pyrophoric substances, or materials that can react with the packing (e.g., iron oxide).