Ammonia and Ammonium Hydroxide

Unalloyed and low-alloy steels/cast steel Unalloyed and low-alloyed cast iron

The unalloyed and low-alloyed steels are practically resistant to dry gaseous ammonia. However, at higher temperatures nitrogen can be taken up in the surface zones. This reaction is exploited for nitride hardening of the steels. Thereby, as reversal of the reaction according to Equation 1, the primary atomic nitrogen produced by thermal dissociation diffuses at temperatures of 773 K to 803 K (500°C to 530°C) into the steel and produces nitrides giving high and uniformly distributed hardness values in the surface zones.

Equation 1:
$$N_2 + 3 H_2 \leftrightarrow 2 NH_3 + 92.44 kJ$$

This procedure achieves hardness values of up to 1,000 HV 0.5. The hardness values decrease continuously with increasing distance from the surface, and at a distance of about 0.4 to 0.5 mm from the surface the initial values for the particular steel are reached again, as shown in Figure 1 for the example of a special constructional steel [1].

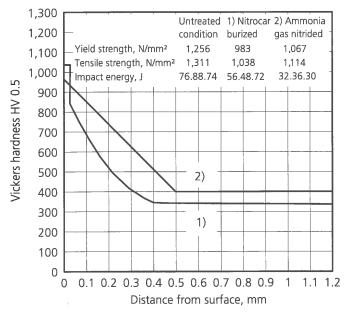


Figure 1: Typical hardness profile for nitriding of a constructional steel [1]

In moist ammonia gas stress corrosion cracking can take place, as experience has shown in the gas space of spherical containers for liquid ammonia (see further below).

Liquid ammonia is a water-similar solvent, in which comparable electrochemical reactions can take place, and an active dissolution of iron is conceivable according to the following equations [2]:

 $Fe \rightarrow Fe^{2+} + 2e^{-}$ Equation 2, anodic part reaction:

Equation 3, cathodic part reaction: $2 \text{ NH}_4^+ + 2 \text{ e}^- \rightarrow 2 \text{ NH}_3 + 2 \text{ H}$

Equation 4, cathodic part reaction: $O_2 + 2 NH_4^+ + 4 e^- \rightarrow 2 NH_3 + 2 OH^-$

However, the uniform surface corrosion of iron and unalloyed steel in gaseous and water-free liquid ammonia is negligibly small at the free corrosion potential (see also Table 17), because due to the very small dissociation of the NH3 according to

 $2 \text{ NH}_3 \rightarrow \text{NH}_4^+ + \text{NH}_2^-$ Equation 5

the NH₄⁺ ions required for the cathodic reaction are not available in sufficient number.

Various low-alloy steel grades are utilized in large quantities for tank vehicles and pipelines for transporting as well as for cylindrical pressurized and large spherical pressurized containers for storing liquid ammonia. Here stress corrosion cracking can take place in the liquid space as well as in the vapor space.

In 1956, the American specialist literature first mentioned cracking damage on containers made of water quenched and tempered fine grain constructional steels. The containers served for storage, transportation and bringing in of liquid ammonia for fertilizing the soil. The damage cause was recognized to be stress corrosion cracking [3]. The cracks appeared predominantly in the region of weld seams.

From the fact that these cases of damage appeared only on transportation or storage containers but not in production plants it was concluded that pure ammonia does not produce stress corrosion cracking, but that contaminations, that come into the ammonia through contact with air when filling and decanting the ammonia, are responsible for the damage.

Numerous investigations were carried out in connection with this damage, with the objective of clarifying the influence of contaminations of the ammonia, essentially by the gases air, oxygen, nitrogen and carbon dioxide as well as by water.

Already in 1962, the results of an extensive test program were reported, that was carried out as joint project by various industrial companies as a consequence of the damages observed in the USA [4]. Various steel grades utilized in the affected plant sections were examined in these investigations. The chemical composition and the chief mechanical key parameter values of these steels are specified in Table 1 and in Table 2.

For the investigations, welded as well as non-welded pre-stressed fork and ring specimens were exposed in containers of an ammonia distribution plant for agricultural utilization. The results of these exposure tests for the various investigated specimens of the steel grades T 1, ASTM A202 and A212, as well as ASME Case 1056 are collected in Table 3.