# Nanotechnology in Steel Tubular Goods: Challenges and Prospects

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## ABSTRACT

For a mature and settled industry like the steel tubular goods manufacturing, nanotechnology offers unique opportunities to provide higher performance products and better services to oil and gas companies and to anticipate future demands by creating new products and processes. In this paper examples of developments, carried out by Tenaris, incorporating nanotechnology concepts to solve specific problems, are presented together with the difficulties and challenges nano-engineered solutions faces in this industry due to robustness and durability in harsh environments.

***Keywords***: nanotechnology, steel, tubes, pipes, oil & gas

## 1 INTRODUCTION

As the safety and environmental regulations tighten and the production and transport of oil and gas conditions get harsher, the requirements for higher performance and reliability in tubular goods increase. Tenaris, a leading supplier of tubes and related services for most of the world's main oil & gas companies as well as engineering companies engaged in constructing oil & gas gathering, transportation and processing facilities, has addressed the need to pursuit enhanced performance tubular products. Casing, tubing, line pipe, and mechanical and structural pipes are Tenaris' principal products. While traditional steel tubular goods manufacturing and finishing technologies are getting closer to their limits, nanotechnology, through the creation of new materials and surfaces with new or enhanced properties and functionalities, offers unique opportunities to achieve these new demands.

Although bulk nanostructured materials having very high strength while retaining good ductility, possessing high values of fatigue resistance and fracture toughness would be very interesting for tubular oil and gas products, there are still both technical difficulties and high production costs for fabricating wares in large dimensions. On the other hand, it is in the field of coatings, nanostructured surfaces and composite materials where nanotechnology can make its greatest contribution to this mature industry not only for products but also for "greener" and enhanced steel pipes manufacturing processes.

## 2 CHALLENGES

In the developing of new oil and gas products or materials, and even more in the case of adopting nano-engineered solutions, it is worth reminding what Schlumberger's Ashok Belani and Steve Orr [1] described as the "Mission Profile" list of challenges to be considered:

- Shocks and vibration
- Cycles
- Absolute temperature and temperature range
- Absolute pressure and differential pressure
- Reliability
- Bandwidth
- Control
- Duration of operations
- Compressive, shear, and tensile strength
- Flow rate

To this list, aggressive chemicals and physico-chemical (pH, ionic force, etc.) conditions should be added. As the authors remarked, "the combination of some or all of these profiles creates myriad parameter linkages that describe the operating range of equipment". In the case of steel tubulars manufacturing processes conditions are far from being soft. Nanotechnology applied to manufacturing processes – tooling, etc.- should address these factors as well.

The challenge for nanotechnology in this industry is huge since the requirements for robustness and durability in harsh environments are serious limitations for nanotechnology solutions that in other areas have found a relatively smooth implementation.

## 3 PERSPECTIVES

Among other applications, nanotechnology research for steel tubular goods lead by Tenaris and associates is focused in coatings or modified surfaces for improved fluids flow (gas, water, oil ), higher wear and corrosion resistance, enhanced tribological properties in threaded connections, better thermal insulation for Line Pipes (LPs), chromium replacement in tooling and accessories, etc. The following are some examples of developments carried out by Tenaris were nanotechnology concepts were used.

### 3.1 Corrosion and wear resistant coatings

In a number of oil and gas wells steel pipes are subject not only to abrasive sand-containing oil, high temperature and pressure, but also to a considerable amount of corrosive substances that can attack it. In addition to formation and injection water with high salt content, which generally leads to corrosion, hydrogen sulfide and carbon dioxide can also be found. Continued exposure to hydrogen sulfide leads to embrittlement (sulfide stress cracking) and/or sour corrosion of the steel while carbon dioxide causes surface corrosion with the formation of iron carbonate, which can be easily rubbed off by the entrained sand in the oil-sea water mixture (sweet corrosion). This can eventually lead to the replacement of the pipe or pipes causing a complete halt of production and thus to heavy financial losses and possible accidents. Although these problems can be prevented by using high-chromium-containing steels and other expensive alloys, the use of such materials is actually economically viable only in specific cases. For this reason, the use of carbon-steel pipes with a coating that, in addition to corrosion protection, meets all other requirements for abrasion resistance, temperature resistance and impact resistance, could lead to a significant cost reductions. A recent patent publication [2] by Tenaris and research associates presented a coating system that can provide these characteristics to "equipment for oil and/or gas drilling, completion, storage and transportation, including pressure vessels, tools, pipes, tubes, connections and any other parts" by using nanostructured materials.

The highly structured composition of the coating presented in the patent is an effective barrier to protect carbon steel not only against the corrosive attack of substances such as hydrogen sulfide, carbon dioxide and sea water, even under hydrothermal conditions (elevated pressure and temperature, e.g. > 5 bar and < 200 °C) but also provides abrasion protection against sand, impact of tools, etc. This is achieved by a coating comprising a resin binder with excellent adhesion to carbon steel and nanostructured additives. One of the possible additives used in the formulation are highly oriented inorganic hydrophilic flakes with thickness from 100 nm to 1 micron coated by a metallic oxide layer with a typically thickness between 10 nm and 1000 nm. The interaction of this nano-coating with functional groups present in the binder and other additives allows platelet to align parallel to the substrate surface. The platelets arrangement, similar to roof tiles, makes a highly structured barrier with high tortuosity for the diffusion of aggressive substances. For abrasion resistance surface modified nano-scale solid hard particles (such as boron carbide) with a mean particle diameter below 100 nm can be used although micro-sized particles can also be employed.

Coatings based on the described system were subjected to a severe test program including: NACE Method A -for Sulfide Stress Cracking (SSC) susceptibility-, autoclave tests ($H_2S$, $CO_2$, 5 wt.-% sodium chloride liquid phase, T: 85 °C, P: 1.4 bars), Cross Cut-Tape Test (DIN ISO 2409), Vibrational Tensile Testing (Fatigue test), Taber Abrader ( DIN 53754), neutral salt spray test (SST), Impact test and cyclic slow strain rate tests (in autoclave: $CH_4$, $CO_2$ and $H_2S$ with condensation of water vapor). The obtained results demonstrated the ability of the coating to provide corrosion and abrasion resistance to carbon steel against attack by corrosive substances such as hydrogen sulfide, carbon dioxide and sea water, if necessary under hydrothermal conditions.

## 3.2 Lotus leaf effect

Reducing the wettability of a surface to a minimum, thus reducing the area in contact with a liquid phase, can result in very interesting and useful characteristics such as corrosion resistance, self-cleaning, elimination of fouling, reduction drag of fluids, anti-icing, etc. Evidently, some of these characteristics are also of interest for oil and gas tubular goods and thus the so-called lotus leaf effect has being study for this applications for many years.

The clue to the "lotus effect" is that air or gas pockets retained by the micro and nano-structured surface minimize the contact area of water with the surface. It can be said that a water droplet rolling on a superhydrophobic surface is almost running on air or gas. Once the mechanism behind the lotus effect was described in 1997 by Barthlott and Neinhuis [3] a plethora of methods for producing superhydrophobic surface were published. Only a few superhydrophobic surfaces production methods resulted in industrialized products. The reason behind this is the lack of robustness of the surfaces since most of them utilize fragile textures that would not survive the rigors of industrial applications not to mention oil and gas conditions.

One of these superhydrophobic surfaces preparation methods was developed by Tenaris in recent years [4 and 5]. The method is based on the direct covalent attachment of silica nanoparticles and microparticles to steel surfaces. Diazonium-functionalized nanoparticles were covalently bonded to steel surfaces via reduction of the diazonium group with no previous metal modification. This spontaneous deposition of diazo-functionalized microparticles followed by phenol-functionalized nanoparticles, thus creating a double surface roughness over steel, when made hydrophobic results in a superhydrophobic steel surface having a water contact angle of 155° to 163° (Figure 1)

Superhydrophobic surfaces obtained with different methods based on silica particles hierarchical structured surface, either obtained in our laboratories or from commercially available paint based products, were subjected to diverse tests in our research facilities: corrosion resistance (neutral salt spray test (SST), Scab test, long-term electrochemical impedance spectrometry (EIS)), handling and friction tests, autoclave tests (50% brine, 25% toluene and 25% kerosene at 80°C during 10 days), pressure resistance test, chemical stability/compatibility, etc.

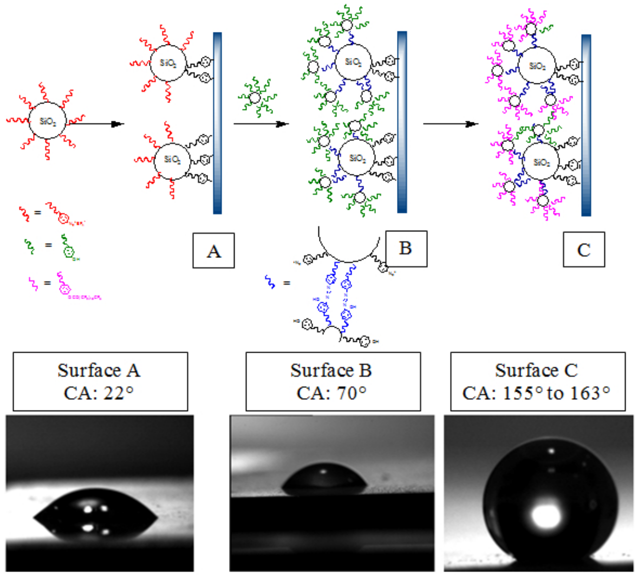

Figure 1: Steps followed to create a superhydrophobic steel surface. A Surface: diazo-functionalized silica microparticles are covalently bond to steel; B Surface: phenol functionalized nanoparticles attached to the microparticles; C Surface: reaction with a fluorinated molecule to create a superhydrophobic surface.

Although differences were observed between the different superhydrophobic systems analyzed, general conclusions could be drawn that applied to even the most robust industrial superhydrophobic paint studied.

In terms of corrosion resistance lotus effect based coatings presented an outstanding behavior in all the long term electrochemical and accelerated corrosion tests, outranking conventional paint based systems. Some of the systems presented the ability to retain air under water during prolonged time indicating that can be used as an underwater corrosion protection system at least moderate pressure and flow conditions. Nevertheless, there are serious limitations to the stability of superhydrophobic properties based on the “lotus leaf effect”:

- Air can be reversibly displaced by low hydrostatic pressure (~1 bar) and flow as well by tensioactives while contact with simple solvents such as alcohols, toluene, acetone, etc. irreversibly affects superhydrophobicity. Figure 2 shows a simple pressure test: a transparent cylindrical vessel was sealed on top of a flat coupon painted with a lotus leaf coating system and one inch height water column then $N_2$ injection gradually increased the pressure inside the vessel until total internal reflection of light ( produced at the water/air interface when superhydrophobicity is present) is suddenly lost due to air displacement and/or dissolution. These are serious limitations to the use these systems as internal coatings intended for drag reduction, anti-fouling and other flow assurance-related applications.

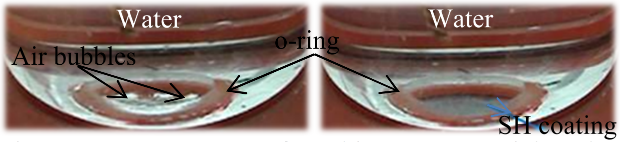

Figure 2: Pressure test. Left: ambient pressure, right: 1 bar applied.

- Contamination also reduces the superhydrophobic effect on these coatings. In fact, simple rubbing, long term handling, wear, dust, etc. proved to be deleterious to the superhydrophobic properties of all the studied coatings.

These results shows that, at least for coatings based on silica particles hierarchical structured surface, lotus effect systems have limited applications in oil and gas tubular products. In principle, these system could be used for environmental corrosion protection in areas protected from abrasion, handling or contact with solvents and tensioactives.

## 3.3 Hard metallic nanostructured coatings

Electrodeposition of nanostructured metallic coatings are one of the most cost effective and simple ways of producing functional nano-materials which are not only extremely strong, they also exhibit appreciable ductility and thus will not readily crack or peel under abrasive loading. In particular, electrodeposited nanocrystalline alloys present very interesting mechanical and chemical properties and are more thermally stable than nanostructured pure metal since the alloying elements provide grain size control.

Electrolytic nanostructured coatings composition can be tuned by changing pulse plating parameters thus, multilayered nanostructured alloys can be deposited from a single solution or bath.

Hexavalent chromium in plating baths is currently being heavily regulated due to its deleterious health and environment impact. Tenaris uses hard chromium plated tools for producing some of its tubular goods. In particular, plating hot rolling mandrels, having a typical length of 14 m and a diameter from 160 to 400 mm, requires extremely large volumes of hexavalent chromium acid solution. Tenaris is currently in the search of effective nanotechnology solutions in order to find a suitable replacement for hard chromium. In recent years a significant number of nanostructured alloys were tested in our labs and even in full scale tests using full size mandrels in our rolling facilities. Mandrels for cold drawn of steel tubes having a nanocrystalline alloy coating were also tested in real production conditions.

In the particular case of hot rolling mandrels, once again, nano-engineered solutions have to resist severe conditions. During hot rolling of steel pipes the coated mandrels have to endure the following conditions and survive to produce hundreds of additional pipes: contact pressures 10-53 $Kg/mm^2$; high temperatures (~750 °C); wear due to sliding; chemical degradation due to hot lubricants and fluids (borax, graphite, etc.); and last but not least thermal stress (water cooling down from ~750° to 90° C between pipes) which is probably the most severe condition the coating has to face.

Several nanocrystalline alternatives are being evaluated in order to find not only a replacement for hard chromium but also to improve the life of coated mandrels thus impacting in productivity of the rolling facilities:

- Single and multilayer Ni alloys (Ni-P; Ni-W, etc.)
- Co alloys
- Hard chromium from $Cr^{+3}$, Cr-C and Cr-C-P alloys [6]

Very promising results were obtained with these systems. For example, nanocrystalline Ni-W coatings are significantly harder than chrome at temperatures above 300° C while the addition of P to form a Ni-W-P alloy showed that, after annealing, an even harder material than Ni-W can be obtained due to the precipitation of $NiP_3$ within the grain boundaries in the Ni-W matrix [7]. Multilayered Ni-P alloys (Figure 3) showed very good wear resistance compared to hard chromium[8]. In the case of Cr-C obtained from $Cr^{+3}$, and increase in hardness was observed at 600° C due to the evolution of the nanostructure, adding P to form nanocrystalline Cr-C-P pushes the maximum hardness up to 850° C. This means that these alloys can be used at service temperatures were conventional hard chrome get softer [9].

Composite coatings based on nanocrystalline alloys was also explored. Ni–W–$MoS_2$ composite self-lubricated coatings were obtained by pulse plating from a Ni–W electrolyte containing suspended $MoS_2$ particles [10]. Using this simple yet effective deposition technique allows to impart a vast range of mechanical, chemical and tribological properties to coatings on steel.

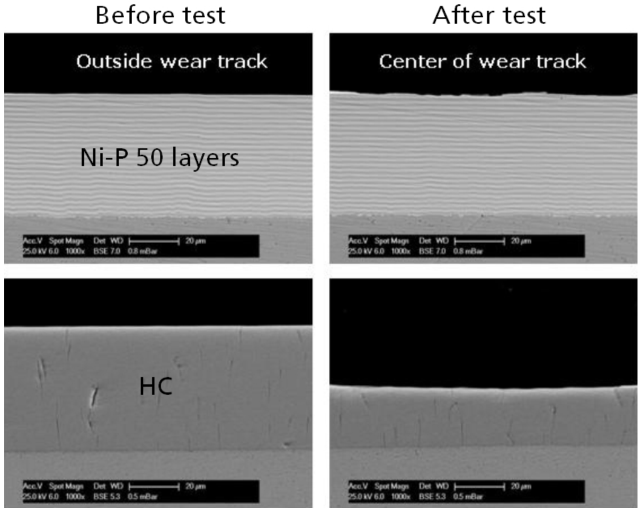

Figure 3: SEM images. Cross-section of multilayer Ni-P nanocrystalline alloys coating and hard chromium coating, before (left) and after (right) a ball-on-cylinder wear test.

Nanostructured alloys are not only useful for tooling applications. For example, a marking system for steel tubes based on electroplated nano-structured metals using a brush plating technique was developed. Main characteristics of the system are: high wear and thermal resistance, high contrast for better reading and can even be deposited directly on the high temperature oxides formed during rolling.

## 4 FINAL REMARKS

Nanotechnology offers new opportunities to a mature industry such as the steel tube manufacture for oil & gas. Due to the requirements for robustness and durability in harsh environments such as those usually found in the oilfields and steel manufacturing facilities the implementation of nanotechnology solutions presents serious challenges. Through extensive research, lab and field trials those limitations can be eventually overcome.

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