SONATRACH SCIENTIFIC AND TECHNICAL DAYS

''THE ENERGY OF INNOVATION''

Oran, 24-26 June 2025

Embrittlement barrier coatings and thin films for renewable hydrogen transportation applications

Technical Axis: The environment and sustainable development at the heart of the energy transition process
Session title: Green hydrogen, production, storage and transport
Presentation Code: AXE2-T5-0880

Khaled Chemaa

Why do we need wear and corrosion resistant coatings?

Despite the existence of cathodic protection, coatings are necessary because the amount of the injected current is proportional to the exposed area which is too expensive.

Sever wear is due to the transportation of poorly filtrated natural gas at high velocity and pressure especially in pipelines bends and elbows.

Figures: DOI: 10.1016/j.conbuildmat.2023.133014

What is the proposed coating ?

The proposed solution is to apply stainless-steel multilayer coatings deposited by twin wires arc spray process, then annealed and nitrided under specific conditions. At the end, W-Ti-N thin film is deposited using PVD (Physical Vapor Disposition) process. The four steps of optimizations are :

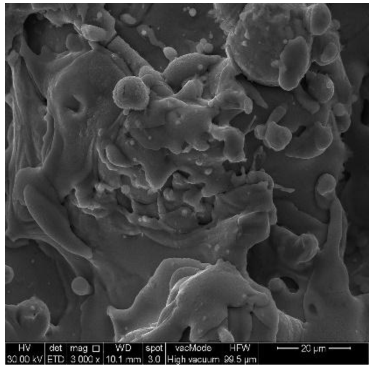
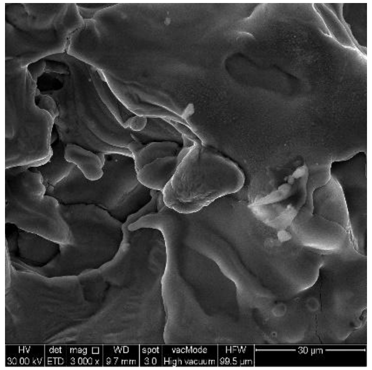
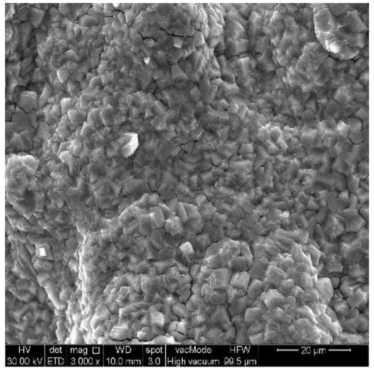
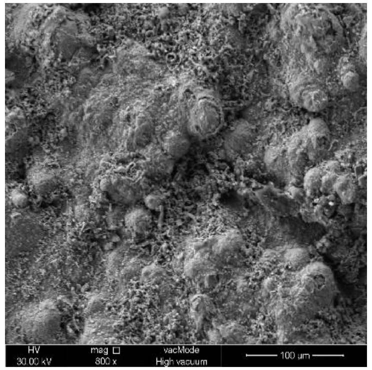
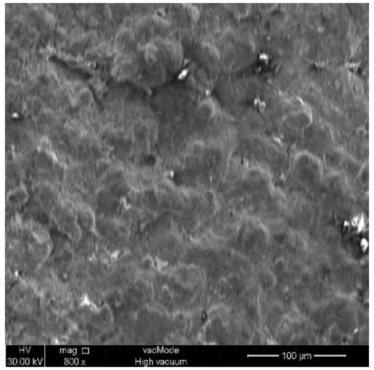
1. The first step: Four layers of 304L stainless steel coating are deposited.

2. The second step: Post spraying vacuum annealing under three different temperatures on the multilayer coatings, the temperature that gives the optimal properties is 800°C.

3. The third step: Nitriding the annealed multilayer coatings by PIII (Plasma Immersion Ion Implantation) process with different injected powers.

4. The fourth step: Deposition of W-Ti-N thin film that is optimized before *(DOI: 10.1080/02670844.2020.1827127* and *DOI: 10.1007/s11665-021-05996-7)* on the nitrided and annealed multilayer coatings.

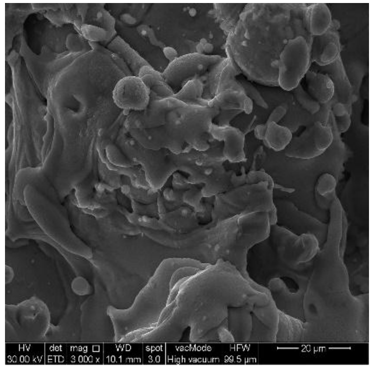
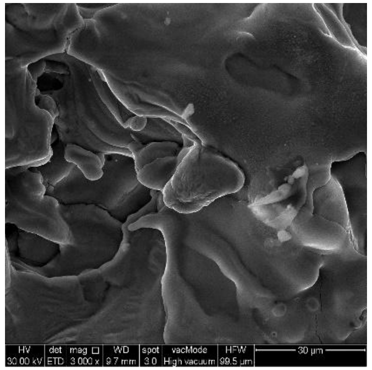
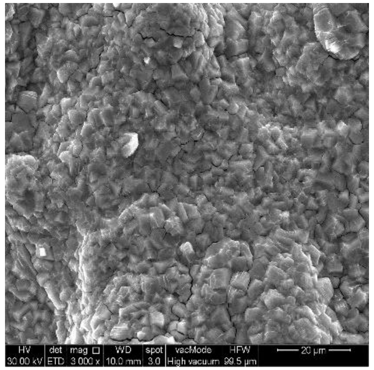
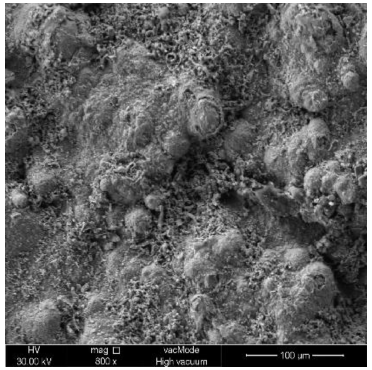
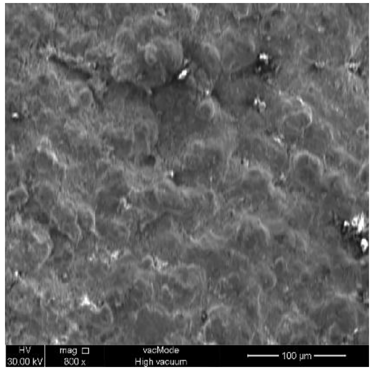
How is the hardness affected ?

Bar	Monolayer	Multilayer	Annealed	Nitrided	Thin film
					
H=9,6	H=8,7	H=13,9	H=11,7	H=16,4	H=22,3
	-9,36%	+59,77%	-15,83%	+40,17%	+35,98%

H: hardness (GPa).
Bar: 304 Stainless steel massif material.
Monolayer: 304L Stainless steel coating with 1 layer.
Multilayer: 304L Stainless steel coating with 4 layers.
Annealed: 304L Stainless steel coating with 4 layers annealed under 800°C.

Nitrided: 304L Stainless steel multilayer coating annealed at 800°C and nitrided by PIII process.
Thin film: W-Ti-N thin film on 304L Stainless steel multilayer coating annealed at 800°C and nitrided by PIII process.

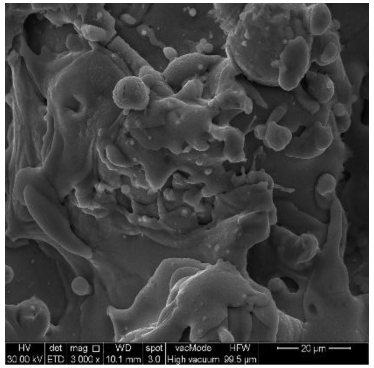
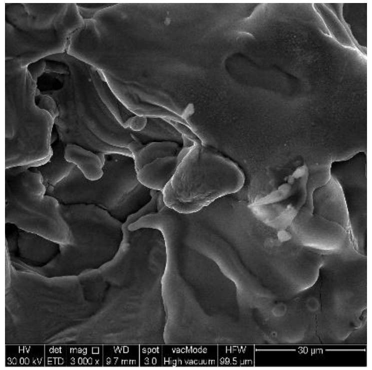
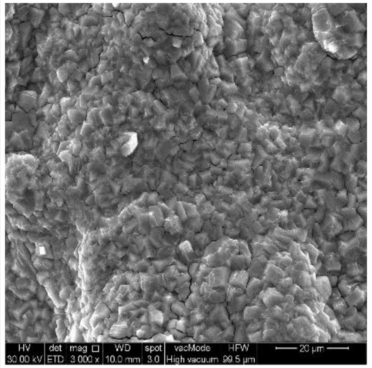
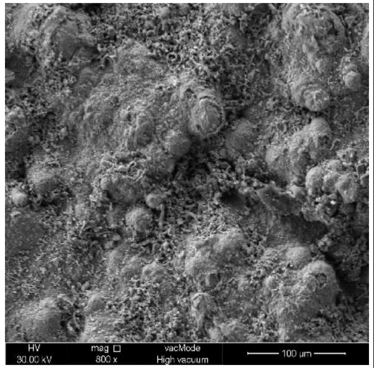
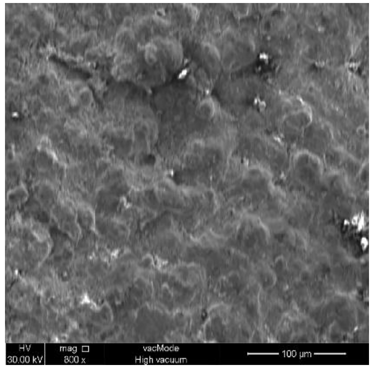
How is the friction coefficient affected ?

Bar	Monolayer	Multilayer	Annealed	Nitrided	Thin film
					
μ=0,56	μ=0,52	μ=0,49	μ=0,52	μ=0,16	μ=0,14
	-7,14%	-5,77%	+6,12%	-69,23%	-12,50%

μ: friction coefficient.
Bar: 304 Stainless steel massif material.
Monolayer: 304L Stainless steel coating with 1 layer.
Multilayer: 304L Stainless steel coating with 4 layers.
Annealed: 304L Stainless steel coating with 4 layers annealed under 800°C.

Nitrided: 304L Stainless steel multilayer coating annealed at 800°C and nitrided by PIII process.
Thin film: W-Ti-N thin film on 304L Stainless steel multilayer coating annealed at 800°C and nitrided by PIII process.

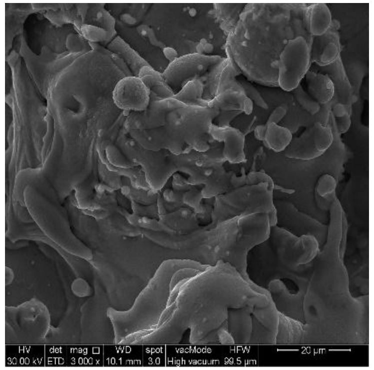
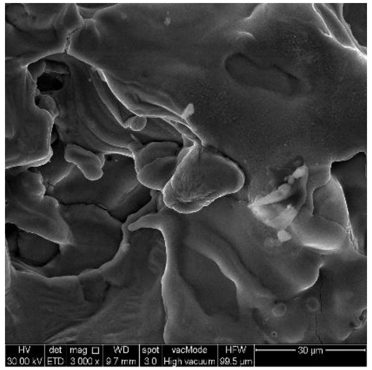
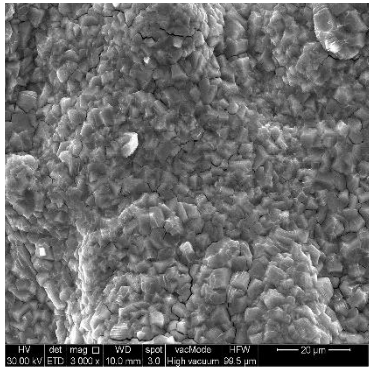
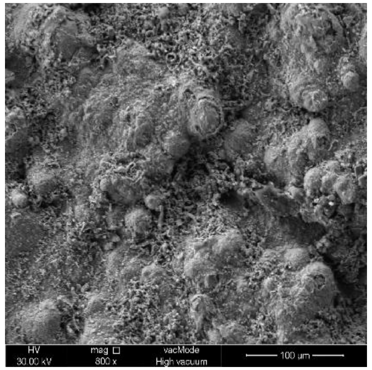
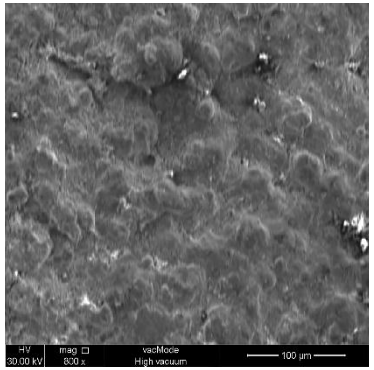
How is the wear rate affected ?

Bar	Monolayer	Multilayer	Annealed	Nitrided	Thin film
					
$k=3,08 \cdot 10^{-3}$	$k=2,63 \cdot 10^{-4}$	$k=5,43 \cdot 10^{-5}$	$k=7,07 \cdot 10^{-5}$	$k=2,17 \cdot 10^{-7}$	$k=7,55 \cdot 10^{-8}$
	One-fold reduction	**One-fold reduction**	**+30,2%**	**Twofold reduction**	**One-fold reduction**

k: wear rate ($mm^3/N \cdot m$).
Bar: 304 Stainless steel massif material.
Monolayer: 304L Stainless steel coating with 1 layer.
Multilayer: 304L Stainless steel coating with 4 layers.
Annealed: 304L Stainless steel coating with 4 layers annealed under 800°C.

Nitrided: 304L Stainless steel multilayer coating annealed at 800°C and nitrided by PIII process.
Thin film: W-Ti-N thin film on 304L Stainless steel multilayer coating annealed at 800°C and nitrided by PIII process.

How is the corrosion rate affected ?

Bar	Monolayer	Multilayer	Annealed	Nitrided	Thin film
					
Cr=0,77	Cr=13,03	Cr=0,19	Cr=0,07	N/A	N/A
	Twofold increasing	**Twofold reduction**	**One-fold reduction**	N/A	N/A

Cr: Corrosion rate (mpy).
Bar: 304 Stainless steel bar as reference.
Monolayer: 304L Stainless steel coating with 1 layer.
Multilayer: 304L Stainless steel coating with 4 layers
Annealed: 304L Stainless steel coating with 4 layers annealed under 800°C.

Nitrided: 304L Stainless steel multilayer coating annealed at 800°C and nitrided by PIII process.
Thin film: W-Ti-N thin film on 304L Stainless steel multilayer coating annealed at 800°C and nitrided by PIII process.

Detailed results ?

Applied Physics A (2022) 128:137
https://doi.org/10.1007/s00339-022-05272-y
Applied Physics A
Materials Science & Processing

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Investigation of the effect of vacuum annealing on the tribological properties of the austenite stainless steel multilayer coatings

Khaled Chemaa[1] · Salim Hassani[2] · Mohamed Kezrane[1] · Yazid Khereddine[2] · Brahim Idir[3]

Received: 5 October 2021 / Accepted: 7 January 2022

Abstract
The present work was dedicated to study the microstructural, mechanical, tribological and electrochemical properties of the 304L stainless steel multilayer coating formed from four successive layers obtained by twin-wire arc spraying and post-annealed with different temperatures. Microstructural results showed that the transformations of the surface aspects from a coating formed of the typical splats features into dot-like shapes morphologies after annealing at 800 °C and to dense flakes and needle-like shapes morphologies at 1000 °C and 1100 °C were taking place. Roughness analysis revealed that the coating annealed at 1100 °C exhibits a very smooth surface. Mechanical analysis showed that with increasing the annealing temperature, the hardness decreases. Tribological analysis results revealed that the coating annealed at 1100 °C possess a low friction coefficient for a stainless steel coating, while for the wear resistance, it decreases with increasing the annealing temperatures which correlated well with the hardness results. The electrochemical results showed that all the four coating has a very interesting corrosion rate, while the coating annealed at 800 °C presents the lowest thermal sprayed coatings corrosion rate. The application of the present work is devoted to replace the mechanical components manufactured by the expensive massive stainless steels that suffer from the sever wear, friction and corrosion with reduced cost and better surface properties.

Keywords Stainless steel coatings · Multilayers · Twin-wire arc spraying · Annealing · Tribology · Corrosion

DOI: 10.1007/s11665-022-06830-4

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TECHNICAL ARTICLE

Tribological and Corrosion Behaviors of 304L and 317L Stainless Steel Coatings for Mechanical Parts Subjected to Friction and Wear

Khaled Chemaa, Mohamed Kezrane, Salim Hassani, Said Abdi, and Sofiane Haireche

Submitted: 14 April 2021 / Revised: 11 December 2021 / Accepted: 29 January 2022

Ball valves were subjected to severe working conditions that shortened the service life of their components and required additional costs for their maintenance and renovation. The ball valves were mainly made from 304 stainless steels (304 SSs). However, its low hardness and corrosion resistance had limited its use. In this study, 317L and 304L stainless steel coatings (317L SSC and 304L SSC, respectively) with thicknesses of 432 and 434 μm respectively were deposited on carbon steel substrates using the twin-wire arc spray system and were comparatively investigated. The mechanical, tribological, and electrochemical properties of the bulk 304 SS were also investigated. Microstructural analysis was carried out using x-ray diffraction, Raman Spectroscopy, Scanning Electron Microscopy and energy-dispersive x-ray spectroscopy. The surface roughness was characterized using Atomic Force Microscope. Lower porosity and oxides content were obtained for 304L SSC, while smooth surface with lower roughness were observed for 317L SSC. Hardness measurement revealed that 317L SSC had higher hardness than 304L SSC. The tribological characterization results showed that both coatings had excellent friction coefficient and wear resistance. The electrochemical tests were carried out in a 3.5wt.% NaCl solution and their results revealed that 304L SSC had a high corrosion resistance.

DOI: 10.1007/s00339-022-05770-z

Detailed results ?

Applied Physics A (2022) 128:616
https://doi.org/10.1007/s00339-022-05770-z
Applied Physics A
Materials Science & Processing

Austenite stainless steel multilayers coatings on ball valves for tribological behavior improvement

Khaled Chemaa[1] · Mohamed Kezrane[1] · Salim Hassani[2] · Khereddine Abd-El-Yazid[2] · Zoubir Benmaamar[3]

Received: 14 March 2022 / Accepted: 6 June 2022

Abstract
Austenite stainless steel coatings were deposited on the surface of carbon steel alloy by the twin-wire arc spray (TWAS) process for future application on ball valves surfaces to improve their tribological behavior and corrosion performance. Microstructural analysis showed that the sprayed splats size increases with the coatings layers. The coating hardness followed the same trend and reached a value approaching 14 GPa for the four layer coating. The measured Young's modulus decreased considerably leading to high value of hardness to modulus ratio H/E, thus indicating a superior wear resistance with increasing the number of layers. Tribological test results revealed that the coatings with three and four layers had the lowest friction coefficient of $\mu \sim 0.49$. The lowest wear rate of $0.54 \cdot 10^{-4}$ $mm^3/N \cdot m$ and a four times higher H/E ratio compared to the individual coating layer, were obtained for the coating with four layers. Electrochemical tests results showed that the coatings with two and four layers presented a high capability of protecting the substrate with low corrosion rates that are lower by 8 and 6 times respectively than that of the original ball valve material.

Keywords Stainless steel · Coatings · Multilayers · Twin-wire arc spray · Tribology

DOI: 10.1007/s00339-022-05272-y

Applied Physics A (2023) 129:149
https://doi.org/10.1007/s00339-023-06435-1
Applied Physics A
Materials Science & Processing

Effect of Plasma Immersion Ion Implantation (PIII) nitriding on austenitic stainless steel multilayer coatings

Khaled Chemaa[1] · Salim Hassani[2] · Mohamed Kezrane[3] · Mohamed Mounes Alim[2] · Amar Manseri[4]

Received: 24 June 2022 / Accepted: 17 January 2023 / Published online: 28 January 2023

Abstract
Stainless steel coatings are widely used in abrasive and corrosive environments due to their surface properties, and also to their techno-economic impact. Stainless steel coating deposited by Twin-Wire Arc Spray (TWAS) and post-annealed at the vacuum conditions presented very interesting mechanical and corrosion properties, while their tribological behavior, i.e. friction and wear resistance needs further improvement. To enhance those properties, Plasma Immersion Ion Implantation (PIII) technique was used to nitride the coating, afterward, the coatings microstructures were surveyed using Scanning Electron Microscope (SEM), Energy Dispersive Spectroscopy (EDS), X-Ray Diffraction (XRD) and Atomic Force Microscopy (AFM). Mechanical properties of the coatings were investigated through nanoindentation tests. The tribological properties were also evaluated. A comparison of the obtained results revealed that the hardness of the nitrided coatings could reach 16 GPa, representing a 50% increase compared to the non-nitrided stainless steel coatings. The friction coefficient showed to be 3 times lower after PIII nitriding. Moreover, the wear rate was reduced by 2 orders of magnitude.

Keywords Stainless steel · Coatings · Plasma immersion ion implantation · Nitriding · Twin-wire arc spray · Tribology

DOI: 10.1007/s00339-023-06435-1

Detailed results ?

JOM
https://doi.org/10.1007/s11837-023-05854-y

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TECHNICAL ARTICLE

Tribological Investigation of W-Ti-N Thin Film on Plasma Nitrided Stainless-Steel Multilayer Coating

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1.—Laboratory of Petroleum Equipements Reliability and Materials (LFEPM), M'Hamed Bougara University, Boumerdes, Algeria. 2.—MIL Division, Center for Development of Advanced Technologies CDTA, 16081 Baba Hassen, Algiers, Algeria. 3.—Yahia Fares University, 26000 Medea, Algeria. 4.—Laboratory of Materials Science and Engineering (LSGM), USTHB, B.P 32, El Alia, Bab Ezzouar, Alger, Algeria. 5.—e-mail: khaledchemaa@yahoo.com

Duplex treatment consisting of plasma nitriding and tungsten titanium nitride thin film (W-Ti-N) was applied to 304L stainless steel multilayer coatings to enhance their mechanical and tribological properties compared to nitrided and the non-nitrided multilayer coatings. The 304L stainless-steel coating was formed by four layers deposited by twin-wire arc spraying (TWAS) and then post-annealed in vacuum conditions. The coating was nitrided using plasma immersion ion implantation (PIII). W-Ti-N thin film was deposited by physical vapour deposition (PVD) magnetron sputtering using a W + 30 wt.% Ti target. Characterization results showed important mechanical and tribological properties for the duplex-treated stainless-steel multilayer coating, reaching a hardness of 22.3 GPa and a low friction coefficient that was about four times lower than that of the stainless-steel multilayer. Furthermore, the wear rate was three orders of magnitude lower than that of the multilayer. Nitrided stainless-steel multilayers also combined good performance in terms of hardness, friction coefficient, and wear rate.

DOI: 10.1007/s11837-023-05854-y

Why should we think about NG pipelines repurposing ?

In the energy transition strategies, the approach of transporting hydrogen via pipelines requires that this hydrogen must be mixed with natural gas (blending).

- Repurposing and reusing the existing natural gas infrastructures represents a cost-effective energy transition *(EU hydrogen strategy)*.

- Reusing the existing gas pipelines has the benefit of being quicker and cheaper than building new hydrogen pipelines *(Agency for the Cooperation of Energy Regulators ACER)*.

- Using gas pipelines that are not needed anymore for hydrogen transportation, represents a saving in decommissioning costs on the gas sector *(Agency for the Cooperation of Energy Regulators ACER)*.

Why should we think about NG pipelines repurposing ?

Up to about 7 000 km of distance, transporting hydrogen via repurposed pipelines remains the best option.

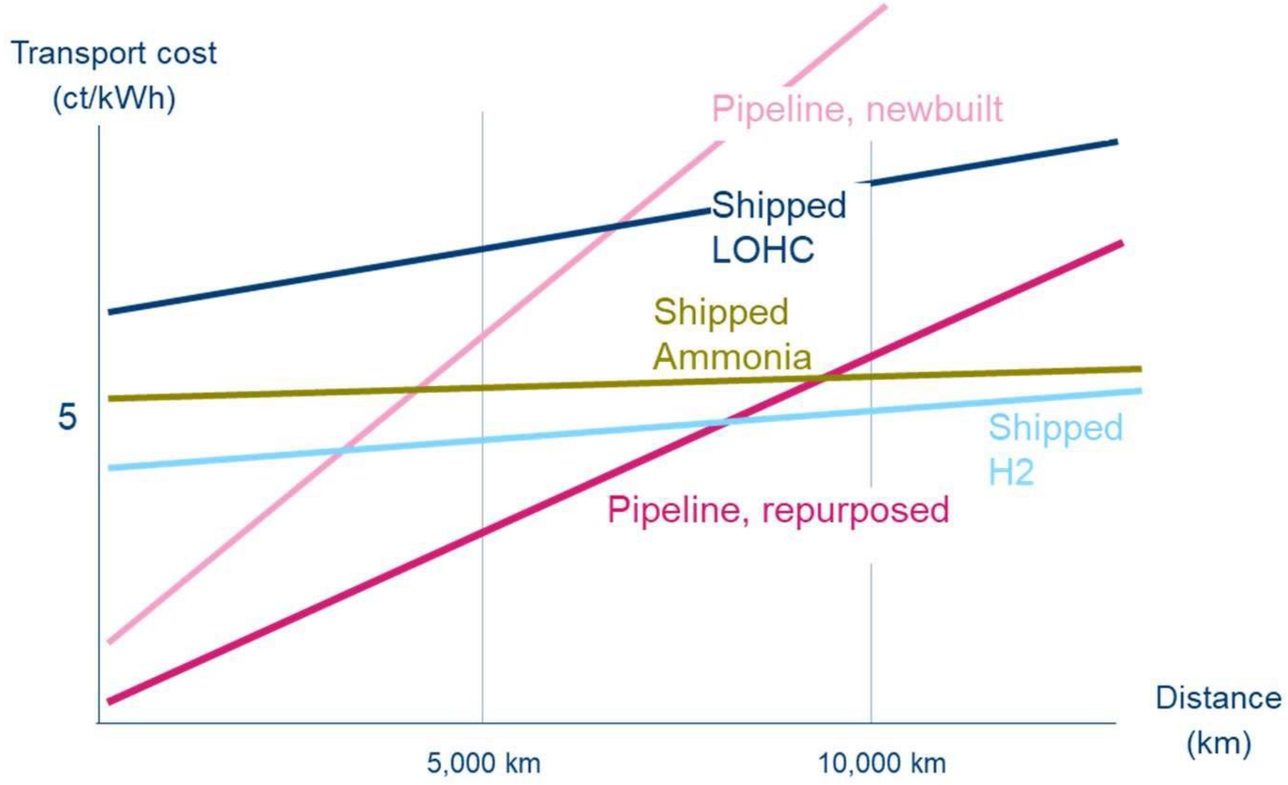


Figure: C. Höft, "Hydrogen transportation via Pipeline"

Why should we think about NG pipelines repurposing ?

- If TRANSMED pipeline (pipeline between Algeria and Italy through Tunisia) is fully repurposed, it could transport around 4 Mt/a, which represents 40% of the EU import target *(SoutH2 Corridor Initiative)*.

- The national strategy for developing hydrogen in Algeria proposes the two options to export blended hydrogen to EU through pipelines: repurposing the existing pipelines: MEDGAZ and TRANSMED, and building new pipelines (possibly the GALSI pipeline). The strategy talks also about the possibility of injecting hydrogen in local natural gas transportation and distribution grid.

3. Motivations pour le développement d'une filière hydrogène en Algérie

3.3. Un réseau important de gazoducs, nationaux et transnationaux, reliant l'Algérie à l'Europe

Un vaste réseau de gazoducs nationaux et transnationaux reliant l'Algérie à l'Europe, offre des perspectives intéressantes pour l'exportation de l'hydrogène, sous forme de mélange avec le gaz naturel, vers le marché européen (MEDGAZ, Gazoduc Enrico MATTEI). Ce réseau pourrait connaitre une extension avec la mise en place de nouveaux gazoducs.

Figure: Stratégie national de développement de l'hydrogène en Algérie p. 7

Where is the problem ?

Repurposing the existing gas pipelines cannot be applied directly for hydrogen transportation, because it is associated to many technical issues, the most relevant issue is the brittleness of the pipelines steel and the associated equipment materials.

In pipelines for green hydrogen transportation, after being diffused inside the steel due to their size, hydrogen weaken the bonding forces, leading to the fracture and the degradation of the toughness and the ductility, this phenomenon is the hydrogen embrittlement.

Figure: https://www.haihaopiping.com/what-is-hydrogen-induced-cracking-hic.html

Why can our coatings be a solution ?

In order to deal with hydrogen embrittlement, many solutions are proposed. Coatings that improve corrosion and wear resistance can have the potential to prevent hydrogen embrittlement in steels.

Nitrided and annealed stainless steel multilayer coatings and W-Ti-N thin films can be used to coat pipelines as hydrogen embrittlement barriers due to the following points:

- Stainless steels and due to their composition of Ni and Mo has high hydrogen compatibility, which leads to the interaction with hydrogen without embrittlement *(DOI: 10.1016/j.surfcoat.2014.09.041)*.

- It was reported before that a monolayer stainless steel coating deposited by thermal spray process and without any optimization has the ability to reduce the hydrogen diffusion *(DOI: 10.1016/j.surfcoat.2020.125940)*.

- In multilayers, the interface between the layers can act as a good hydrogen diffusion barrier *(DOI: 10.4028/www.scientific.net/AMR.1152.9)*.

Why our coatings can be the solution ?

- Heat treatment is an effective method to improve the resistance to hydrogen embrittlement due to the reduction in the grain size and the improvement of the coating bonding strength *(DOI: 10.1116/1.4919736)*.

- Nitrides can be considered as effective hydrogen barriers due to the formation of the strong H-N bonds *(DOI: 10.1116/6.0002178)*.

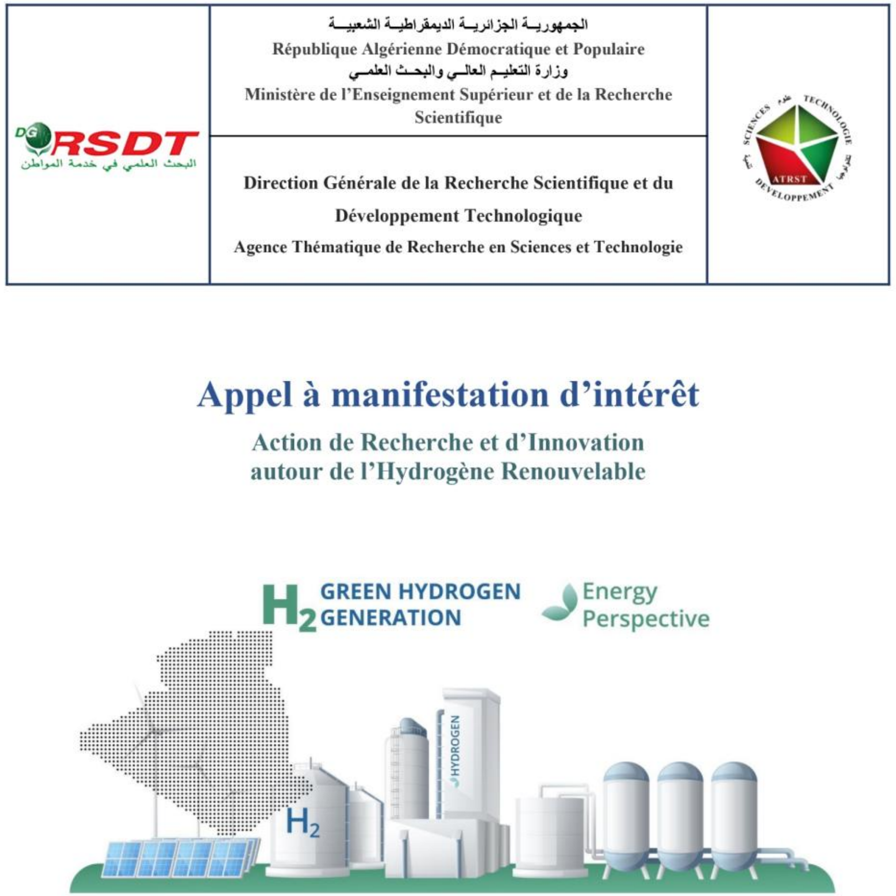
- Ceramic nitrides coatings have good performance as hydrogen barriers especially those composed of Ti associated with N or C *(DOI: 10.17265/2161-6213/2015.5-6.002)*.

- It was reported that the hydrogen permeability resistance is improved with increasing the W content in the coatings *(DOI: 10.1116/6.0002178)*.

Conclusion

Renewable hydrogen in Algeria represents a rewarding field that become a subject of interest nowadays, but until reaching its technological maturity, lots of technical challenges need to overcome; hydrogen embrittlement is one of them.

This work aims to propose a probable solution to that constraint by applying a barrier coatings and thin films that highlighted before their protective capacity against wear and corrosion.



Author Biography : **Dr. Khaled Chemaa**

Dr. Khaled Chemaa is hydrocarbons and mechanical engineer, researcher and author specializing in oil and gas industry equipment, maintenance, tribology, advanced materials and energy regulation. He holds PhD in Mechanical Engineering, Master's degree in Hydrocarbons. Former SLB surface well testing maintenance engineer, currently, he serves as a university lecturer in the Faculty of Hydrocarbons and Chemistry of Boumerdes, research associate in the Laboratory for Hydrocarbons Equipment Reliability and Materials, and gas engineer at the Electricity & Gas Regulatory Commission CREG. He is also member nominated by the Minister of energy in the Permanent Sectorial Committee of Research and Development of the of the Ministry of Energy, Mines and Renewable Energies, member of PNR project with Sonatrach about corrosion, member in a national research project funded by the Ministry of Higher Education and Scientific Research about hydrogen, a frequent contributor to international conferences, and an active member of national energy committees and associations. Dr. Khaled Chemaa has authored numerous scientific articles and three books on materials performance, and corrosion and wear protection.

Thank you for your attention