Thermal Diffusion Technology

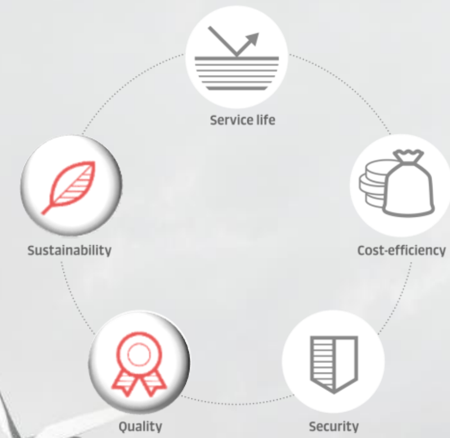
Follow up to the NAS speech in Washington

The National Academies of Science (NAS) Bolt Root Cause Analysis (RCA) Workshop this last April. I stated that it was not one single issue which caused Hydrogen Embrittlement , but the persistence to add variables rather than to eliminate them. Which when we divide the issues and do not look at the variables a s a whole we only get part of the story. To look on the life of a part as a whole we would indeed see many variables not just in our area of expertise, but would see how metallurgy / material science think, environments react to one another, design of parts harden on contact, country of origins see rules and regulations, how coatings are applied, field operations use torque, where cathodic solutions do not work, and supply chains get involved. TDZ, was brought to the oil and gas industry with all of this in mind.

Thermal Diffused Zinc/ ASTM A1059

Quality & Sustainability

Resource-friendly coating
at the highest level



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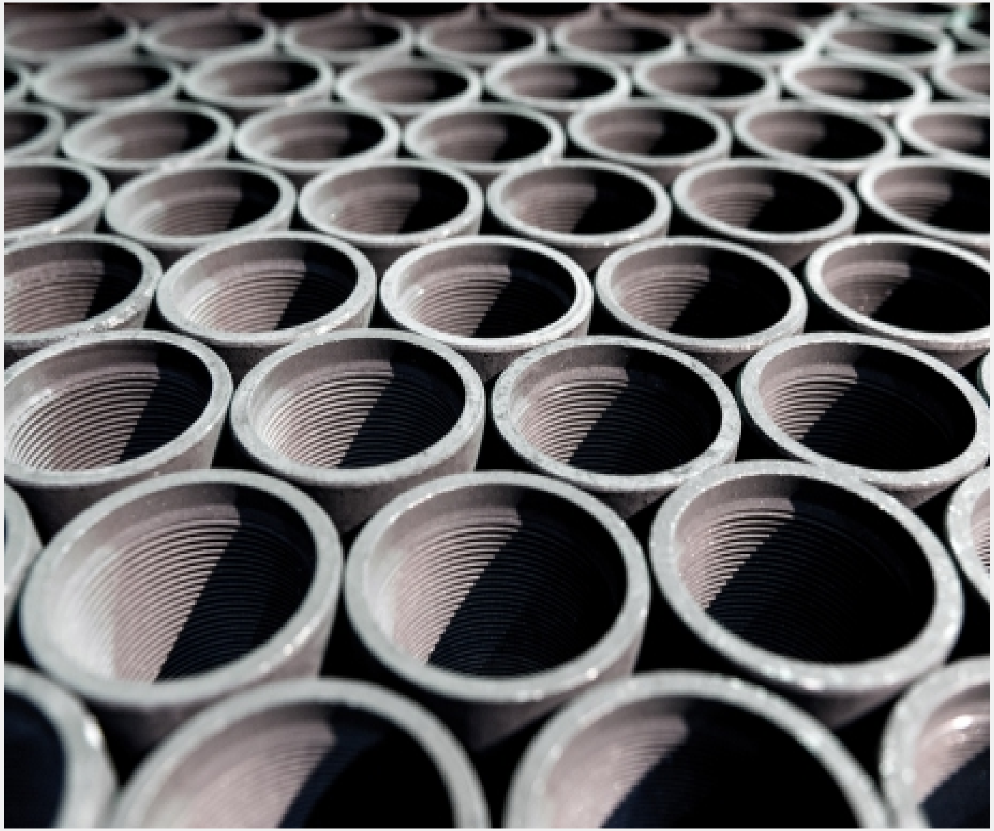
Oil & Gas

TDZ is currently being used in Oil and Gas for:

- Tooljoint connections (as seen here) (4130)
- Actuation springs (A229, 6150 and 5160)
- Tension bolting in subsea drilling risers (L43)
- In splash environments on ships and in cable and pipe retreival (none listed)
- Topside pressure control and sub-sea pressure control valves. (none)



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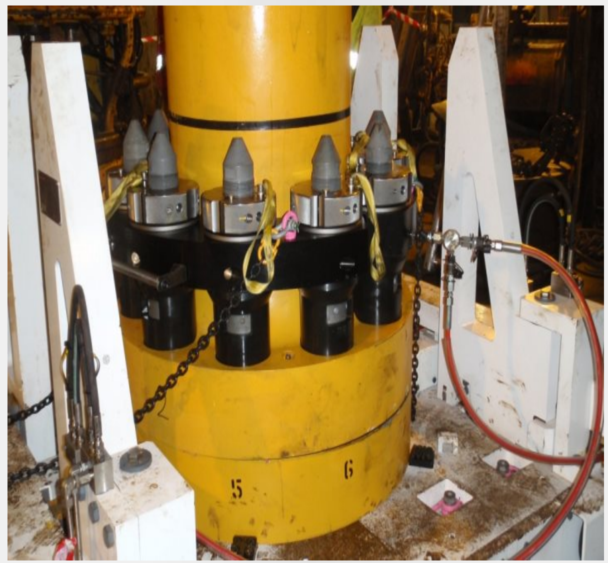
Zinc thermal diffusion guarantees a wide range of materials and parts

Wide range of materials

- Low- and high-alloy steels
- Non-ferrous metals,
  - Aluminum
  - Titanium
  - Magnesium
  - Copper
  - Stainless
- Gray cast
- Casting alloy
- Sinter metals



High variety of parts

- Uniform coating of complex components with difficult to access areas and cavities
- Retention of threaded engagement on connecting parts
- Parts with weld seams
- Technology is suitable for sub-sea tension
- Adhesion to rubber
- Formation of a natural solid lubricant in zinc oxide




The coating and system concepts can be customized for a variety of applications.

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Patented technology according to API Q1 standards

High quality


- Certified Technical Authority is easily obtained with a semi and fully automated applications making repeatability programmable to a data base.
- Time, Temperature and Substrate are the variables in which the process uses to obtain the correct thickness, hardness and corrosion level for the substrate. All by which can be programmed.

Patented Technology

- The specific know-how in the area of thermal diffusion is protected by already granted and pending patents
- Licensing models ensure a technological assurance of the process
- A data base of the three variables can be shared at other licensed locations all over the world and repeated.

Sustainable

- Without harmful substances
  - Chrome VI-free
  - CMR-free (carcinogenic, mutagenic, reprotoxic substances)
  - Acid free
- Wastewater- and emissions-free production process in a closed system
- All process-related substances are recyclable

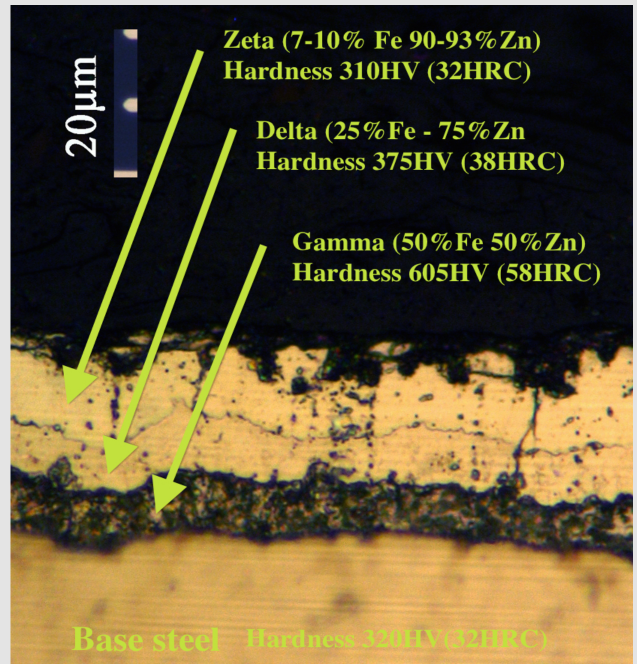
"Poisons create Hydrogen Embrittlement, cyanided, arsnic, acids all of these are poisons and all of them create internal hydrogen embrittlement" - Mehrooz Zamanzadeh Ph.D of Material Science

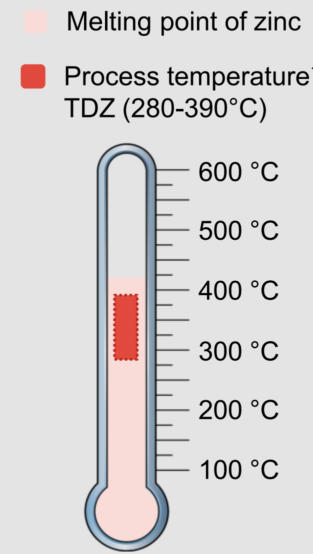
Unique technology for innovative solutions

The characteristics of the TDZ technology

While a conventional zinc process is merely applied as a layer on the base material, zinc thermal diffusion bonds to **the base material** where it forms a **resilient, zinc-alloy metallurgical bond**.

This micro alloy provides extensive protection against corrosion and wear **without a significant application layer**. At the same time, the **structure and properties of the materials** are protected and **improved** from the inside.





[1] Process temperature dependent on base material and desired result

Zinc thermal diffusion is an extremely effective and material-friendly process for the coating and refining of metals and metal products.

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Thermal diffused zinc in comparison to other methods

Method	Process temperature
Hot dip galvanizing	~450–600°C ~842–1112°F
Sheradising	~380–450°C ~716–842°F
Zinc thermal diffusion	**~280–390°C ~536–734°F**
Zinc flake coating	~200°C ~392°F
Plating	~30°C ~86°F

Deterioration of mechanical properties during the coating sequence

Ideal temperature range

Inadequate adhesion, hydrogen embrittlement, resulting in poor corrosion protection, of coating and substrate

Thermal diffused zinc provides high corrosion protection as well as good joining properties while maintaining or improving the physical properties of the base material.

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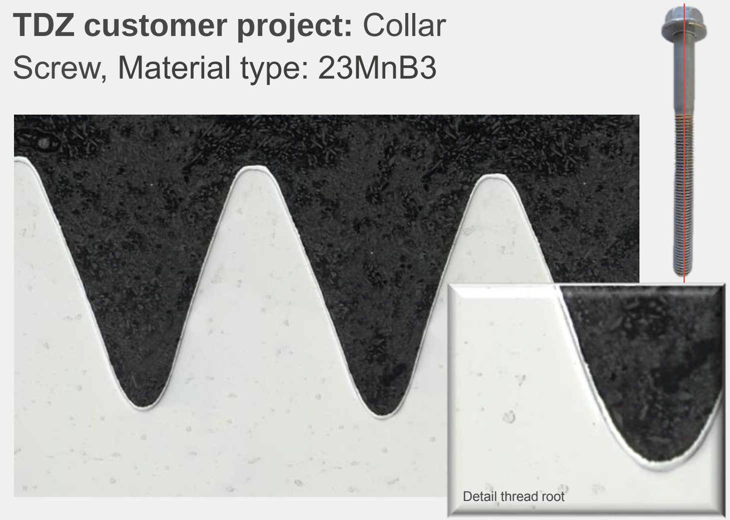
Homogenous coating even in cavities and threads

In comparison:
Electroplating vs.Thermal Diffusion Zinc

Console rear axle, separated for layer thickness measurement µm

Test and validation performed externally by OEM.

TDZ customer project: Collar Screw, Material type: 23MnB3



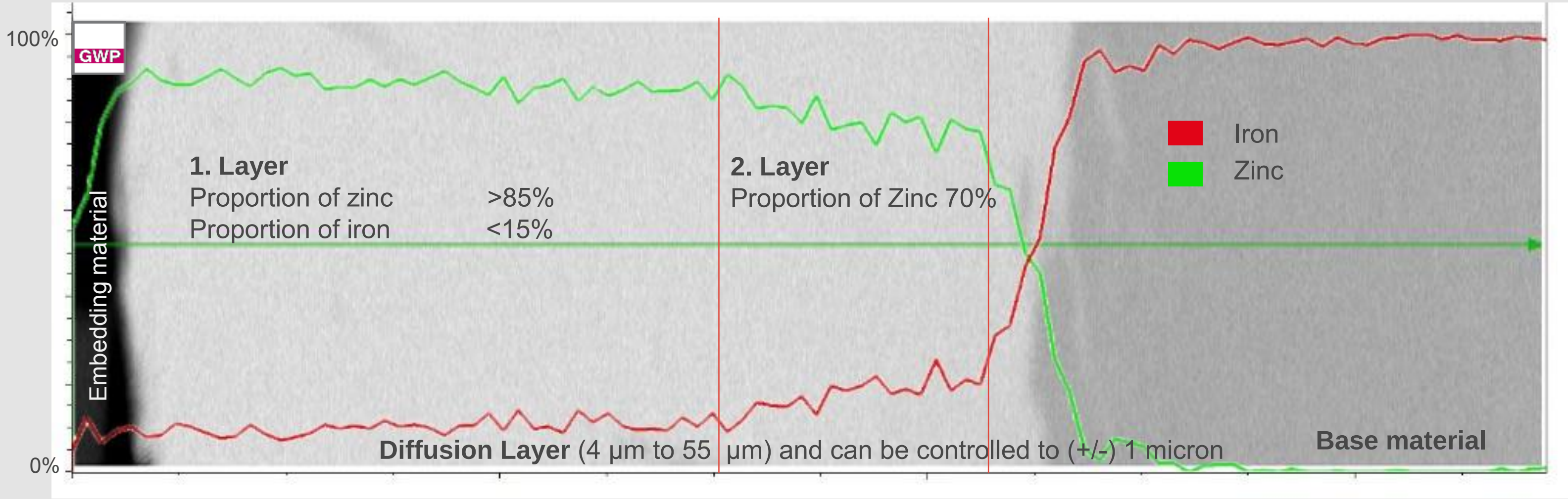
Cross section over longitudinal axis, uniform layer

Internal validation according to DIN EN ISO 1463 - 2004.

With Zinc thermal diffusion, a uniform layer thickness can be achieved even in difficult to access parts or geometrically complex components (for example cavities, threads, threaded heads).

Thermal diffusion forms a metallic compound as a micro alloy

Line scan[1] through a layer of the zinc thermal diffusion



Test and validation accompanied by the independent institute for material testing (GWP)

[1] Line scan (concentration profile): representation of the site-dependent chemical composition in the micro range. Measurement is carried out by means of an energy-dispersive X-ray spectroscopy (EDS) in the scanning electron microscope.

The various phases of the micro alloy are the basis for the outstanding properties of thermal diffusion.

The benefits of the TDZ technology

Service Life

- ✓ No contact corrosion
- ✓ High wear resistance
- ✓ Suitable for cavities and inner threads
- ✓ Protects even on damaged surfaces

Process

- ✓ Extended part's life time
- ✓ Broad diversity of materials
- ✓ No blasting required for adhesion
- ✓ Reduction of variables in IHE/ EHE
- ✓ Supports dissimilar metal construction and material mix

Safety

- ✓ Increased elasticity and ductility
- ✓ No hydrogen embrittlement
- ✓ Increased robustness
- ✓ OCP = -.82
- ✓ Optimized and safe further processing

Quality

- ✓ Practicing and further develop quality guidelines
- ✓ Professional control by quality manger
- ✓ Company management according to ISO standards

Sustainability

- ✓ Free of Chrome VI and harmful CMR-substances[1]
- ✓ Process carried out wastewater- and emission-free
- ✓ No special disposal requirements

[1] carcinogenic, mutagenic, reprotoxic substances

Thermal diffusion guarantees that the treated parts have a longer service life and therefore improve the profitability of the enterprises.

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Service Life

Long-lasting corrosion protection

Service Life

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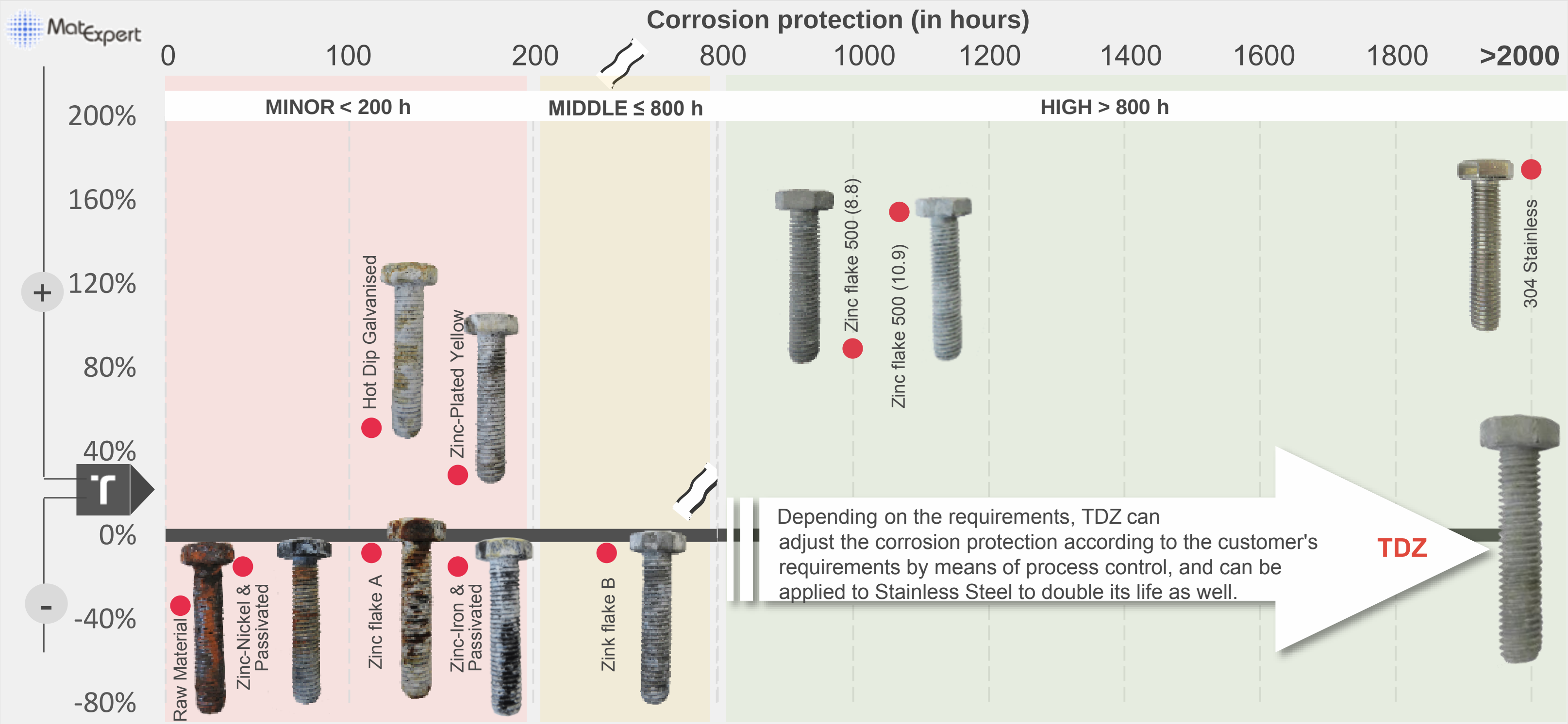
Best Price-Perfomance Ratio in relation to alternative corrosion protection



Test and validation accompanied by the independent material institute MatExpert. Salt spray test according to DIN EN ISO 9227.

In standard tests, results were obtained that are far above the coating technologies currently in use.

Service Life

Thermal Diffused Zinc/ ASTM A1059

Zinc thermal diffusion avoids contact corrosion between different metals

Competitive advantage by Zinc thermal diffusion

In many industries, a smart material mix decides on the lead. TDZ provides a decisive competitive advantage:

- The technology **prevents contact corrosion** between different metals
- The process allows **new, lighter material combinations** such as steel and aluminum or the use of high-strength steels.
- Additional **separating elements** for avoiding contact corrosion can thus be **omitted**.

Performance test for contact corrosion

Material:	High-strength, low-alloy steel (340 XF 3.0 mm), screwed on an aluminum plate (Al 5000) screwed
Test:	**10** years field test (50 cycles) Test and validation carried out by BASF (US)

No corrosion at the contact points:

Test requirements: FLTM BI 123-01, Ford World Specification (WSS-M64J40).

The Zinc thermal diffusion prevents contact corrosion at contact points and thus opens up possibilities for the direct connection of different metals. Aluminum, Stainless, Magnesium, Titanium, chromium,etc...

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Reliable protection at edges and connection points

Alternative Technology (HSS & KTL)

Customer test represents 4 years field test

TDZ Technology (HSS & TDZ & KTL)

Alternative Technology (HSS & Zinc flake)

Customer test represents 1 year field test

TDZ Technology (HSS & TDZ & KTL)

Static **Meko** test (salt spray test in climate change chamber with additives) and validation externally carried out by German Auto manufacture

New and lighter designs benefit from the TDZ technology through the possibility of a direct connection.

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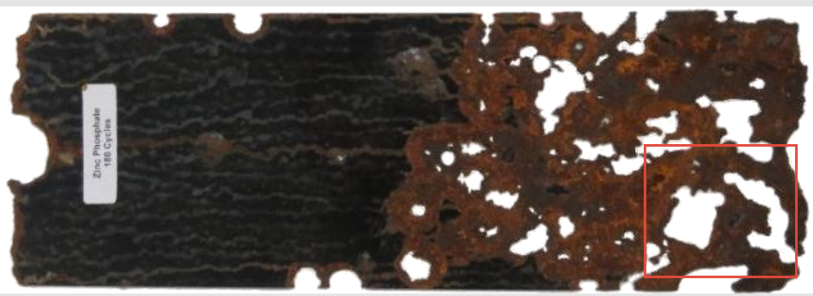
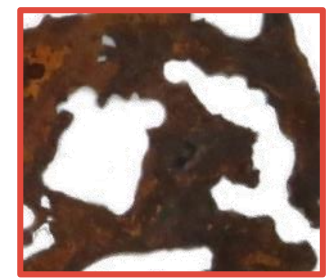
No rust penetration even on damaged surfaces

Independent stone chipping Test, BASF Automotive Solutions Results
after 180 cycles = 15 years (SAE J 2334, completed after 180 Cycles)

Zinc thermal diffsuon + Standard ZnPhos + E-coating

Standard ZnPhos + E-Coating





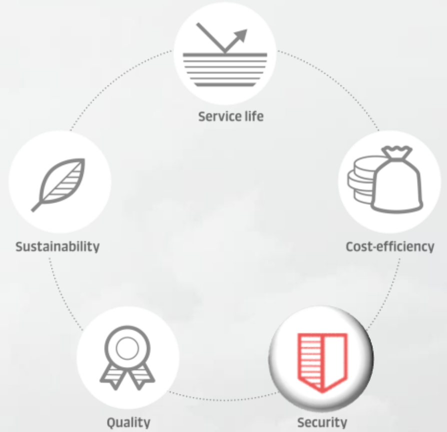
External test and validation by BASF Automotive Solutions, material: cold-rolled steel, material thickness of the test plates approx. 2mm.

There is no corrosion with Thermal Diffused Zinc even on damaged surfaces. This fulfills the new requirements of 15 years corrosion protection of the US automotive industry.

Thermal Diffused Zinc/ ASTM A1059

Security

Reliable operation for demanding components



Thermal Diffused Zinc/ ASTM A1059

INVESTIGATION

Coating Micrographs

A cross section was mounted in resin and polished to a 1 micron finish, and etched in 0.5% Nital. Micrographs were taken at various magnifications both in the etched and unetched conditions. Some micrographs have already been provided and further micrographs with the coating thicknesses are given in appendix 1.

The coating thickness averaged 40 microns with a 10 micron thick layer adjacent the steel which was identified as the gamma layer.

Hardness Testing

A Shimadzu micro Vickers hardness tester with a 15g load was used to give the smallest indentation possible. The indentations were then measured at x100 magnification on an Olympus PMEG 3 microscope.

The small indentations required have resulted in a loss of accuracy, and are indicative only. However they do demonstrate that the gamma layer is much harder that the steel, and that the bulk coating has a hardness comparable with a high tensile steel.

Table 1: Microhardness Results

Location	Hardness Results			Average (HV)
	1	2	3	
Steel	343	329	308	327
Gamma Layer	679	568	568	605
Adjacent Gamma Layer	482	329	315	375
Bulk Coating	376	262	290	309

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The elasticity and ductility are increased through thermal diffusion

Spring Force Measurement

Material: oil tempered ASTM A229, Carbon steel

Thickness of TDZ: 7.6 microns

Spring Force Measurement				
travel [mm]	load [N] part no. before TD		load [N] part no. after TD	
	1	2	1	2
18.3	214	216	216	217
19.3	414	418	416	416
20.3	615	619	618	620

No significant change of spring force after thermodiffusion

Currently no abnormalities, test ongoing

Salt spray test :

Customer Specification:
Applied standards:

Hours	Degree of rusting (Ri)		
	part 1		remark
	WR	RR	
458h	0	0	
973h	0	0	ongoing

3000h
EN ISO 9227 (NSS) - Salt spray tests
ISO 4628-3 - Assessment of degree of rusting

With a combination of high elastic and plastic deformation, TDZ technology can absorb significantly more deformation energy, working well with spring materials like A229, or 6150 and 5160

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Thermal diffusion increases the resistance of the parts

Alternative Technology
22MnB5/
1500 P (AL/Si)

TDZ Technology
22MnB5/1500
(nur TDZ)

Crash tests and validation externally carried out by OEM.

Tests carried out with an OEM show the increased security of crash profiles with zinc thermal diffusion by improving the material properties.

Thermal Diffused Zinc/ ASTM A1059

Decisive Tests for Industry Bench Mark

Internal qualification test require 100 make and breaks on Too oints

Fragment of the pin and box of ZL-90 tool joint with TDZ after make-up/break-out testing at the VNIIBT Institute. 300 make-ups/break-outs were performed.

The Threaded Connections Laboratory of the National Research Institute of Drilling Equipment (VNIIBT) provided the methodological and engineering support, while the process operations were performed by the technical personnel at the Experimental Production Department of the OAO RPA Burovaya Tekhnika.
To assess the durability of thread coatings, multiple test make-ups of tool joints were made under conditions as close as possible to those of rigsite tripping operations.
The survey was carried out on a well drilling test bench equipped with a Uralmash-4E rig with a VM-53 derrick at the OAO RPA Burovaya Tekhnika facility in Povarovka settlement, Moscow Region.

The achieved result of make-ups/break-outs with intact protective coating on the threaded and thrust surfaces of drill pipe tool joints exceeded all expectations .

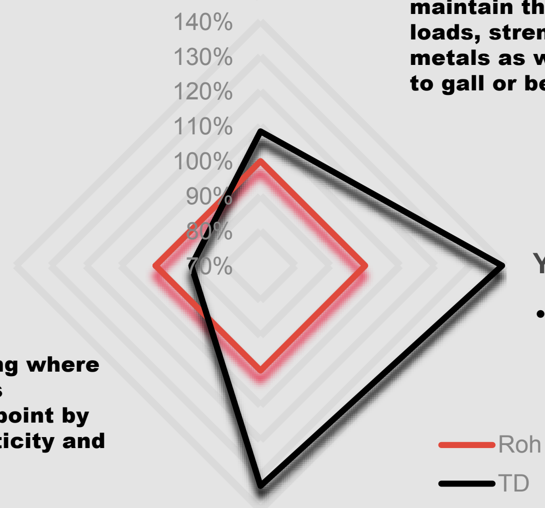
TDZ coating technology offers solutions like metal to metal sealing to meet the highest requirements of effectiveness, safety and environmental protection down hole, or sub sea.

Security

Thermal Diffused Zinc/ ASTM A1059

Individual change and optimization of the material properties

Material:
Hot-rolled steel

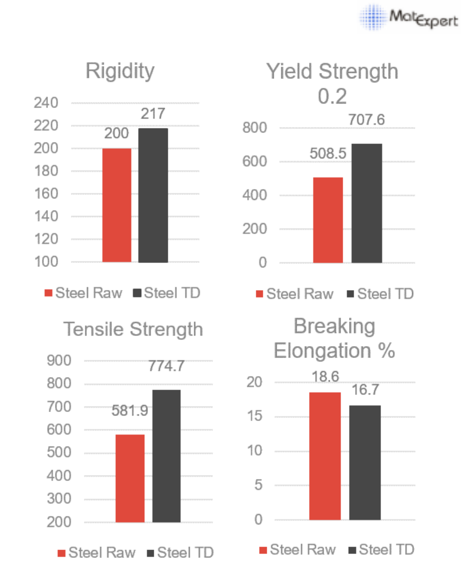


- **Allows tension threads to maintain their form under heavy loads, strengthens non-ferrous metals as well. Allowing them not to gall or become soft.**

- **Springs are able to return to their prestressed form**

- **Reductions in micro-cracking where seen in the metal substrates**
- **Provides a repeatable yield point by which we can measure elasticity and plasticity.**

- **Resistance to tension force, Tension bolts, tool joints, threaded materials**



Test and validation accompanied by the independent material institute MatExpert.

The thermal diffusion process increases the elasticity and / or ductility of the base material and thus significantly minimizes the risk of micro-cracking.

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Hydrogen Embrittlement Testing

Stopping Hydrogen Embrittlement!

EHE/ IHE Elimination

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Prior Service There is a long list of processes and environments which add up to HE in parts, rather than just one thing. Being able to erase those prior processes and events is where TDZ goes further.	✓ Pre-Existing use in the field, EHE ✓ Stress caused by impurities in steel, electroplating, cleaning, IHE, no history at all.
Internal Hydrogen Embrittlement Non-acidic, non-toxic, non-stress inducing. Simplification and removal of variables to account for tension, stress hardening, resitivity in other metals and dimension .	✓ Time, Temperature and Substrate are its only variables. ✓ It is an Alloy w/ metal bond not a coating. ✓ Can be applied to(+/-) 1 micron, 2A/2B (threads)
External Hydrogen Embrittlement Establishes an alloy barrier which eliminates hydrogen blistering, work hardening, dissimilar metals and strengthens metal from micro cracking.	✓ OCP= -.82 in ocean ✓ Allows dissimilar metals to connect to one another ✓ Surface hardening of the zinc alloy only in wear hardening.

Thanks to the dry oven process used in zinc thermal diffusion, there is no risk of hydrogen embrittlement. Aqueous systems are often used in galvanic coatings, in which hydrogen can diffuse into the base material. This can lead to embrittlement in the components. As material strength increases, the risk of hydrogen embrittlement also increases.
Therefore, aqueous electroplating coatings cannot be used without heating for steels over 1,000 Mpa. This additional process step is eliminated when using the dry zinc thermal diffusion process.

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Hydrogen Embrittlement Tested Variables

ASTM A320 (L43) material at 52-55 HRC, 42-45 HRC, 32-35 HRC & at 1.75", 3.25" dia. TDZ and Plain

Open Circuit Potential of ASTM E1290 sample in D1141 Salt water

Tested to find the (HSR) Hydrogen Susceptibility Ratio ASTM F2078

ASTM F1624 RISING STEP LOAD TESTING FOR HYDROGEN EMBRITTLEMENT THRESHOLD

ASTM F606 Standard Test Methods for Determining the Mechanical Properties of Externally and Internally Threaded Fasteners, Washers, Direct Tension Indicators, and Rivets

TDZ has been designated as a non-hydrogen embrittlement service by all DIN, BS, ISO, ASTM standards.