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 as 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.
Quality & Sustainability

Resource-friendly coating at the highest level
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 retrieval (none listed)
- Topside pressure control and sub-sea pressure control valves. (none)
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.
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, arsenic, 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.
Thermal diffused zinc in comparison to other methods

<table>
<thead>
<tr>
<th>Method</th>
<th>Process Temperature</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hot dip galvanizing</td>
<td>~450–600°C</td>
</tr>
<tr>
<td></td>
<td>~842–1112°F</td>
</tr>
<tr>
<td>Sheradising</td>
<td>~380–450°C</td>
</tr>
<tr>
<td></td>
<td>~716–842°F</td>
</tr>
<tr>
<td>Zinc thermal diffusion</td>
<td>~280–390°C</td>
</tr>
<tr>
<td></td>
<td>~536–734°F</td>
</tr>
<tr>
<td>Zinc flake coating</td>
<td>~200°C</td>
</tr>
<tr>
<td></td>
<td>~392°F</td>
</tr>
<tr>
<td>Plating</td>
<td>~30°C</td>
</tr>
<tr>
<td></td>
<td>~86°F</td>
</tr>
</tbody>
</table>

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

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 manager
- ✓ Company management according to ISO standards

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

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

1 carcinogenic, mutagenic, reprotoxic substances
Service Life

Long-lasting corrosion protection
Best Price-Performance Ratio in relation to alternative corrosion protection

 depending on the requirements, TDZ can adjust the corrosion protection according to the customer's requirements by means of process control, and can be applied to Stainless Steel to double its life as well.
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

<table>
<thead>
<tr>
<th>Material</th>
<th>High-strength, low-alloy steel (340 XF 3.0 mm), screwed on an aluminum plate (Al 5000) screwed</th>
</tr>
</thead>
<tbody>
<tr>
<td>Test</td>
<td>10 years field test (50 cycles) Test and validation carried out by BASF (US)</td>
</tr>
</tbody>
</table>

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...
Reliable protection at edges and connection points

**Alternative Technology** (HSS & KTL)

Customer test represents 4 years field test

**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.
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)

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.
Security

Reliable operation for demanding components
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 than the steel, and that the bulk coating has a hardness comparable with a high tensile steel.

Table 1: Microhardness Results

<table>
<thead>
<tr>
<th>Location</th>
<th>Hardness Results</th>
<th>Average (HV)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>1</td>
<td>2</td>
</tr>
<tr>
<td>Steel</td>
<td>343</td>
<td>329</td>
</tr>
<tr>
<td>Gamma Layer</td>
<td>679</td>
<td>568</td>
</tr>
<tr>
<td>Adjacent Gamma Layer</td>
<td>482</td>
<td>329</td>
</tr>
<tr>
<td>Bulk Coating</td>
<td>376</td>
<td>262</td>
</tr>
</tbody>
</table>
The elasticity and ductility are increased through thermal diffusion

**Spring Force Measurement**

<table>
<thead>
<tr>
<th>travel [mm]</th>
<th>load [N] part no. before TD</th>
<th>load [N] part no. after TD</th>
</tr>
</thead>
<tbody>
<tr>
<td>18.3</td>
<td>214</td>
<td>216</td>
</tr>
<tr>
<td>19.3</td>
<td>414</td>
<td>418</td>
</tr>
<tr>
<td>20.3</td>
<td>615</td>
<td>619</td>
</tr>
</tbody>
</table>

No significant change of spring force after thermodiffusion

**Salt spray test:**

Customer Specification:
Applied standards:

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

<table>
<thead>
<tr>
<th>Hours</th>
<th>Degree of rusting (Ri)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>part 1</td>
</tr>
<tr>
<td></td>
<td>WR</td>
</tr>
<tr>
<td>458h</td>
<td>0</td>
</tr>
<tr>
<td>973h</td>
<td>0</td>
</tr>
</tbody>
</table>

Material: oil tempered ASTM A229, Carbon steel
Thickness of TDZ: 7.6 microns

Currently no abnormalities, test ongoing

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
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.
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.
Individual change and optimization of the material properties

Material:
Hot-rolled steel

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

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

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

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

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

Test and validation accompanied by the independent material institute MatExpert.
Hydrogen Embrittlement Testing

Stopping Hydrogen Embrittlement!
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.

Internal Hydrogen Embrittlement
Non-acidic, non-toxic, non-stress inducing. Simplification and removal of variables to account for tension, stress hardening, resistivity in other metals and dimension.

External Hydrogen Embrittlement
Establishes an alloy barrier which eliminates hydrogen blistering, work hardening, dissimilar metals and strengthens metal from micro cracking.

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.
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 |

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