VTT-R-04178-13



# Thermally Sprayed Sulphur Trap Coating proof-of-concept study

Authors: Henriikka Brandt, Tomi Suhonen and Peter Andersson

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#### Summary

The goal of the Sulphur Trap project, carried out from July 2011 to April 2013, was to perform a proof-of-concept (POC) study on the thermally sprayed Sulphur Trap coating. The coating has been developed and patented by VTT. The POC study consisted of two parts. In order to prove the technical feasibility a set of laboratory tests was performed for the coating and to prove the commercial feasibility a market study clarifying the potential applications, markets and clients was accomplished. Based on the technical and commercial feasibility studies, the commercialisation route was chosen.

The potential applications included industrial processes in extreme, sulphur-rich conditions such as diesel engines and boilers. The laboratory tests were conducted in laboratory environments corresponding to industrial applications. The tests included corrosion tests at Outotec and VTT and tribological tests at Metso Automation and VTT. The Sulphur Trap coating gave 10 to 25% lower average coefficient of friction in tribological tests and performed significantly better in conducted corrosion tests than the reference coating. The reference coating was catastrophically corroded in 800 °C sulphuric corrosion tests while the Sulphur-Trap coating survived basically intacted. The Sulphur Trap coating also gave better resistance against scuffing than the reference coating in all tested configurations.

During the project the technology readiness level, when measured using the NASA Technology readiness level (TRL), increased from the initial level of 3 (analytical and experimental critical function proof-of-concept) to the level of 5 (component validation in a relevant environment). At the end of the project VTT was negotiating out-licensing of the Suphur Trap coating into three separate application areas with three different companies.

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Written by Reviewed by

Menny Miles I W

Henriikka Brandt Inká Orko Eva Häkkä-Rönnholm
Specialist, Business development Manager, Business development Vice President, Materials and Built Environment

Accepted by

VTT's contact address

VTT, P.O. Box 1000, FI-02044 VTT, Finland

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#### **Preface**

This publication is the final research report of the proof-of-concept project Sulphur Trap (Rikkiträppi). The project ran during the time period from July 2011 to April 2013 and it was funded by Tekes and VTT.

The project had an ambitious goal of analysing the commercial potential of the thermally sprayed Sulphur Trap coating, proving the technical feasibility of the patented concept in an industrial application, and as a result, defining the route for commercialisation for the technology. The goal was reached: an understanding was gained on the maturity and commercial potential of the technology, and the commercialisation route was defined. Further, commercial discussions were initiated with the industry. Due to certain technicalities, the initial plan to perform long-term tests in a true industrial application was replaced with laboratory tests in simulated environment. However, the laboratory tests were performed in close cooperation with the industrial partners providing us feedback about the feasibility of the coating in industrial processes.

We want to thank project's steering group (VTT and Tekes) for guiding the project and VTT's internal advisor group which had an especially active and helpful role in steering the work throughout the project. We also want to thank the industrial partners Outotec Oyj, Metso Automation Oy and Wärtsilä Oyj for cooperation and active participation. In addition, we wish to express our gratitude to all colleagues at VTT who have helped us, especially laboratory personnel and VTT Knowledge Solutions. We also thank all companies who have given us valuable information on markets and technological aspects.

Espoo 6.11.2013

Authors



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# 1. Introduction to Sulphur Trap technology

Sulphur trap is a technology developed and patented by VTT. The first laboratory scale tests were carried out in 2010 before the start of this project. The initial test results showed that the coating provides a shield against high temperature sulphur corrosion and also reduces friction and wear. The results were seen beneficial for the industry. After initial laboratory tests it was considered important to conduct a larger scale proof-of-concept in an industrial environment and increase the understanding of the potential markets of the technology. The Sulphur Trap project was carried out from July 2011 to April 2013 and was funded by Tekes and VTT.

Protective coatings produced with such techniques as thermal spray have found industrial applications in wide field of industries to protect components against e.g. wear and/or corrosion. Today, it is estimated that the thermal spray industry is worth approximately \$6.5 billion with the majority of revenue generated in coating services [1]. Thermal spray coatings have their unique structure compared to bulk material, typically described as a lamellar structure. Especially in demanding corrosive conditions this lamellar structure needs to be taken into account. In such conditions the lamella boundaries (like grain boundaries in bulk materials) will act as a main route for corrosive compounds. If corrosive compounds are able to penetrate even slightly all the way to the coating-substrate interface, a catastrophic delamination of the coating can occur as presented in Figure 1.

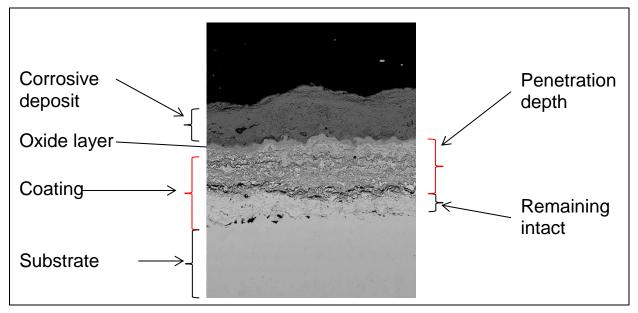


Figure 1. Highly corrosive compound penetration to coating structure through formed oxide layer at high temperature. The corrosion has nearly reached to substrate-coating interface.

The idea of Sulphur Trap technology is to manufacture coatings where the basic structure can provide other functionalities, such as wear resistance and low the friction, by introducing an elemental or compound solid phase to the lamella boundaries. This additional "trap" phase is selected to withstand vaporisation and to form a stable solid compound with the corrosive element or compound. For example, trap material molybdenum will react with sulphur in wide variety of conditions (see section 5.1.1 for thermodynamical evaluation) and form molybdenum disulfide (Mo + S -> MoS<sub>2</sub>). MoS<sub>2</sub> is a highly stable compound which possesses closed packed structure (densest possible way to pack atoms) with easy glide lattices between sulphur and molybdenum layers. The volume grove (Mo to MoS<sub>2</sub>) also benefits the lamella boundary blockage. Schematic representation of the concept is shown in Figure 2.



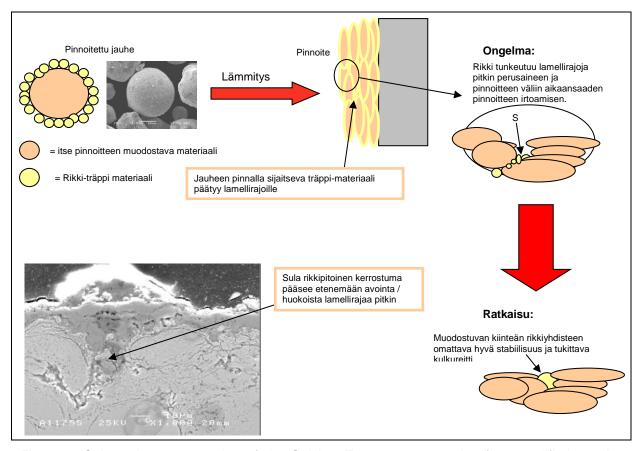


Figure 2. Schematic representation of the Sulphur Trap concept starting from modified powder, desired coating structure and the formation of stable solid lubricant in sulphuric conditions.

MoS<sub>2</sub> is also a well-known solid lubricant which provides a dual function for Sulphur Trap coatings. In sulphuric conditions the coating prevents corrosion and provides lubrication lowering the friction and protecting the coating as well as the counterpart. The solid lubricant will continuously form throughout the coatings lifetime.

Sulphur Trap coatings are manufactured from modified powder with industrial thermal spray equipment. The technical aim of this project was to optimise the powder manufacturing for selected powders, optimise the deposition process and compare the corrosion and wear properties of the coatings against reference coatings in selected, industrially relevant conditions. A more detailed description of technical solutions are presented in sections 5 Methods and 6 Technical results.

Sulphur Trap is a technology developed and patented by VTT (T.Suhonen, T.Varis, PCT/FI2012/050304).

#### 2. Goal

The goal of this proof-of-concept project was to demonstrate the Sulphur Trap coating in selected industrial applications and based on the test results continue towards commercialisation in the most potentials applications. This was planned to be achieved by

- Analysing of the value chain, market potential and business opportunities
- Proving the concept with the aim to launch business within a year after the project has ended.

The project had the following tasks

- 1) Identification of the most potential companies and engaging them in the technical
  - o Recognition of the most potential companies in Finland and internationally
  - Industrial interviews



- inviting 2–4 companies to demonstrate the coating in their own applications and in an advisor role in the project
- Analysis of bottlenecks for commercialisation
- 2) Identification of the most potential value chains and marketing channels
  - Market study
  - Identification of key marketing channels
  - Market benchmark by interviewing potential customers or users of the technology
- 3) Technical demonstration in several applications
  - o Powder manufacturing
  - o Manufacturing of the coating to industrial components provided by partner companies
  - Delivering the coated components to partner companies for a relevant test in real environment (one year) / or optionally testing the coatings in a laboratory corresponding a real environment
  - Analysis of the sulphur exposed coatings
- 4) Choosing the commercialisation strategy
  - Defining the distribution channels
  - Investigating different pricing models (licensing)
  - Decision concerning a spin-off company
- 5) Project management
  - Ensuring the project will follow the schedule, stay within the budget and reach the agreed goals
  - o Reporting to Tekes

The NASA Technology Readiness Level (TRL, see scale on page 4), Figure 3, acted as a guideline for the level of technological development in the project. The goal was to increase the TRL from initial level three (analytical experimental critical function and/or characteristic proof-of-concept) to target level six (coating prototype demonstration in real industrial environment).

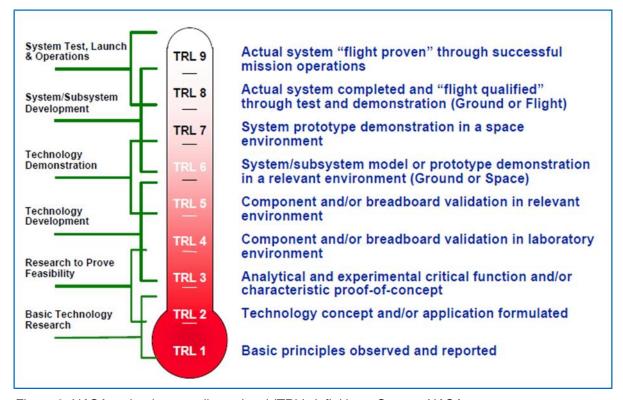


Figure 3. NASA technology readiness level (TRL) definitions. Source: NASA.gov.



# 3. Limitations

The tests could not be performed in actual commercial processes because the project schedule did not allow for a long enough observation period and/or due to schedule synchronization issues with the potential test users. An alternative approach was selected where the test users (Outotec, Metso Automation and Wärtsilä) and VTT defined the test conditions to mimic the actual process conditions as closely as possible.

#### 4. Methods

# 4.1 Technological feasibility

### 4.1.1 Thermodynamic modelling

Thermodynamical modelling was conducted mainly by using HSC Chemistry program modules (Outotec) at VTT. Gibbs free energy, Lpp and Tpp-modules were utilized in order to select a suitable trap material that is also suitable for selected base powder materials, powder and thermal spray processing.

Preferable, the trap materials should 1)form of solid lubricant in sulphuric conditions, 2) form of a stable compound with sulphur that increases in volume compared to trap material and that packs densely in a lattice structure with easy glide atom planes and 3) have fast enough kinetics and good stability of the formed compound in a wide temperature range.

Based on thermodynamical studies pure molybdenum was selected, because it fulfilled all the above requirements. Molybdenum forms molybdenum disulphide  $MoS_2$  in a wide temperature range (~0–1000 °C) and possesses a good stability in the same range in solid state.  $MoS_2$  is known as a solid lubricant and has a closed backed cubic structure (densest possible arrangement to pack atoms) with easy glide lattices between Mo and S atom layers. Mo is also highly suitable for Sulphur Trap powder and coating processing.

Figure 4 shows selected modelling results for molybdenum with and without the base material selections.

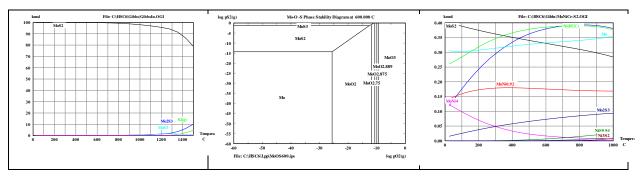


Figure 4. a) HSC-Gibbs diagram on the stability of  $MoS_2$  as a function of temperature, b) HSC-Lpp diagram of Mo-S system as a function of partial pressure of sulphur (log  $pS_2(g)$ ) and partial pressure of oxygen (log  $pO_2(g)$ ) and HSC-Gibbs diagram on the formation and stability of Mo with NiCr-matrix (Cr supersaturated in Ni-lattice) as a function of temperature

# 4.2 Powder manufacturing

Sulphur Trap powders were manufactured experimentally at VTT by combining commercially available thermal spray powders with a specially designed trap material. The trap material was selected based on thermodynamical modelling conducted in this project (see section 5.1.1). A procedure to combine the base material powder and the trap material was developed. Sulphur Trap powders were manufactured by planetary ball milling and after treatments. Milling parameters, like the amount of raw materials and milling balls, the milling speed, and milling time were optimized to achieve good coverage of the trap material on the surface of the base material powder. Commercially available



milling equipment was used. The following base material powders were used in this study: gas atomized Ni49Cr1Fe, and agglomerated and sintered  $Cr_3C_2$ -25%(Ni20Cr). The trap material was nanosized molybdenum.

The cost increase of such Sulphur-Trap powder is relatively small compared to the reference powder (without Trap addition) because of small weight ratio of Trap material to the base material (Mo /  $Cr_3C_2-25\%(Ni20Cr)=1/9$  in wt-%). The cost increase is determined by the price of molybdenum and batch size. The actual process steps are conducted with equipment already in use in powder manufacturing companies and are not labour intensive.

# 4.3 Coating deposition

The coatings were deposited on low carbon steel (S355) samples by using commercially available thermal spray coating system, Sulzer Metco DJ Hybrid, and by using hydrogen as a fuel gas. Deposition parameters were optimized in order to achieve good adhesion, high density and good thermomechanical properties.

Following coatings were deposited:

• Reference Ni49Cr1Fe

Sulphur Trap Ni49Cr1Fe-10p-%n-Mo

• Reference Cr<sub>3</sub>C<sub>2</sub>-25(Ni20Cr)

• Sulphur Trap Cr<sub>3</sub>C<sub>2</sub>-25(Ni20Cr)-10p-%n-Mo

#### 4.4 Structural characterization

Cross sectional samples were prepared from coating samples by using conventional metallographic procedures. The powders and coatings were characterized by scanning electron microscope (SEM) equipped with an energy dispersive spectroscopy (EDS) sensor. Characterization was performed for coatings prior and after the conducted tests.

Coatings were also deposited on sintered, porous buttons (diameter 25.4 mm) in order to study the density of the coatings. Gas permeability of the coatings was tested with nitrogen gas up to 7 bars by commercial equipment. The porous substrates have practically zero resistance to the gas flow. In the test, the specimen is sealed in a test cell. Then gas pressure is increased in steps while volumetric gas flow though the specimen is measured by a flow meter. Viscous gas permeability coefficient  $\Psi_{\nu}$  can then be calculated using Darcy's law

$$\frac{\Delta P}{\delta} = \frac{Q * \eta}{A * \Psi_{v}}$$

$$\frac{\Psi_v}{\delta} = \frac{Q * \eta}{A * \Delta P}$$

$$\Psi_v = \frac{Q * \eta * \delta}{A * \Delta P}$$

Where Q = flow rate,  $\eta$  = absolute dynamic viscosity of the test fluid,  $\delta$  = the thickness of the coating, A = sample test area and  $\Delta P$  = gas cage pressure.

The characterization of the piston ring tribometer test samples is described in Section 5.1.4.

#### 4.4.1 Corrosion tests

Six different corrosion tests were conducted for Sulphur Trap coatings. Four were conducted at Outotec Research Laboratory in a test atmosphere resembling actual process conditions. Two laboratory tests were conducted at VTT.



Following coatings were tested at Outotec: Reference Ni49Cr1Fe and Sulphur Trap Ni49Cr1Fe-10p-%n-Mo as well as Reference  $Cr_3C_2$ -25(Ni20Cr) and Sulphur Trap  $Cr_3C_2$ -25(Ni20Cr)-10p-%n-Mo. The test conditions were:

Test 1: Temperature 275 °C, gas atmosphere 40% SO<sub>2</sub>, 2% O<sub>2</sub>, 5% H<sub>2</sub>O and 53% N<sub>2</sub>

**Test 2**: Same as in test 1 but with 3 cm dust layer containing: 24.1% Fe (29.9% Fe<sub>3</sub>O<sub>4</sub>), 25.9% Cu, 5.9% Zn, 3.8% SiO<sub>2</sub>, 3.5% S (12.5% SO<sub>4</sub><sup>2-</sup>), 3.1% Pb, 2.8% As, 0.9% Bi, 0.84% Cd, 0.47% K, 0.35& Sn, 0.009% Cl, 6 ppm F

Test 3: Same as in test 2 but added 1000 ppm Cl to the dust layer

Test 4: Same as in test 2 but added 1000 ppm F to the dust layer

Test duration was 5 days for all Outotec tests.

Corrosion tests at VTT were conducted in laboratory tube ovens in following conditions:

**Test 5**: Temperature 650 °C, duration 1 week and solid sodium sulphide-potassium sulphide (eutectic composition which will be molten at test temperature)

**Test 6**: Test conditions were determined by Wärtsilä to simulate actual process conditions. Test were conducted at VTT. Temperature 800 °C, gas atmosphere 15%  $O_2$  – 5%  $H_2O$  – 5%  $CO_2$  – 1000 ppm  $SO_2$  – balance  $N_2$  with solid  $Na_2SO_4$  deposition layer, test duration 1000 h.

The edges of all coating samples were protected with a high temperature resistant ceramic paste in order to prevent the corrosion to propagate from the non-coated areas. Cross sections of tested samples were characterised with SEM to detect possible corrosion products in the coating surface.

#### 4.4.2 Adhesive wear tests

Adhesive wear tests were performed according to standard ASTM G99. The Pin-On-Disc machine is a tribometer designed to evaluate the wear and friction characteristics of selected material in sliding contacts in dry or lubricated environments. The sliding friction test occurs between a stationary pin stylus and a rotating disk. Normal load, rotational speed, and wear track diameter can be varied. Electronic sensors monitor wear and the tangential force of friction as a function of load, speed, lubrication, or environmental condition. All of these parameters are recorded during the test. Pin-On-Disk tribometer is shown in Figure 5.



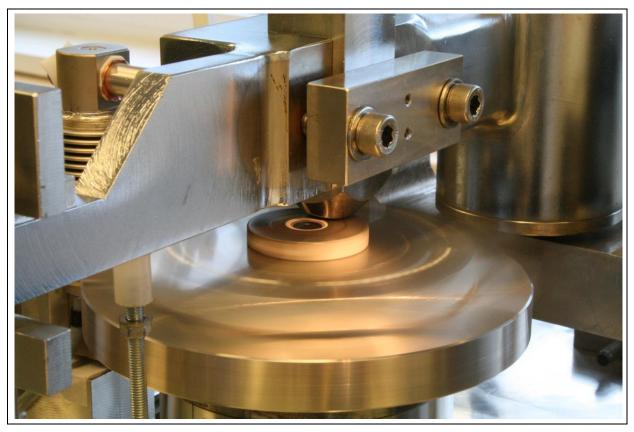


Figure 5. Image of Pin-On-Disk test equipment. The coated sample is the "Disk" and alumina ball is the "Pin" pressed against the sample surface.

#### 4.4.3 Tests using the VTT piston ring tribometer

# 4.4.3.1 Equipment

The profiles and the surface roughness of the piston ring and cylinder liner plate samples for the tests were measured using a Mitutoyo Formtracer SV-C3100 diamond stylus instrument.

The running-in tests and the scuffing tests were performed using a piece of equipment called the VTT Piston Ring Tribometer, see Figure 6.

The features of the sliding surfaces of the samples were investigated and photographed using an Olympus BH2-UMA light optical microscope.



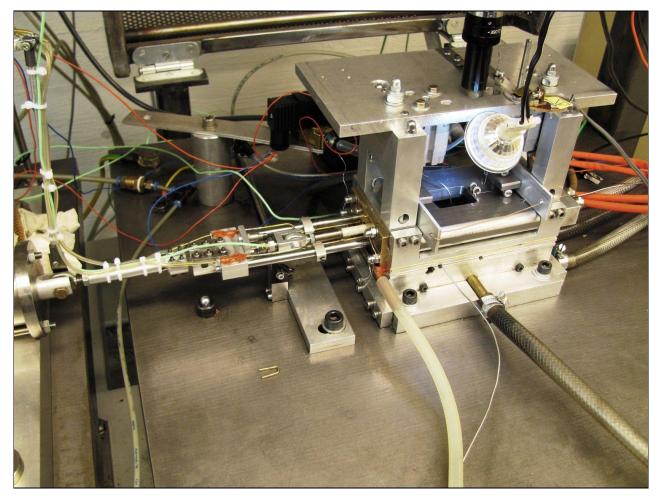


Figure 6. The friction measurement chamber of the VTT piston ring tribometer, as equipped for the present investigation.

#### 4.4.3.2 Samples

The samples for the present investigation consisted of straight piston ring samples, flat cylinder liner samples and marine diesel engine oil in two different conditions.

The piston ring samples were straight, tailor-made piston ring samples with thermally sprayed VTT 661-3 reference coatings and VTT 661-4 "Sulphur Trap" coatings, ground to a radius of curvature of 125 mm in the direction of sliding. Four of the piston ring samples were strongly exposed to sulphur in prior to the tests. The flat cylinder liner samples had been cut from a cylinder liner made of lamellar cast iron, milled into 70×24×10.5 mm size, and longitudinally ground on the sliding surfaces. The piston ring and cylinder liner plate samples are presented in Table 1.

Shell Argina XL 40 marine diesel engine oil in two different conditions was used for the lubrication of the piston ring and cylinder liner samples in the tests:

- New, clean Shell Argina XL 40 oil with a kinematic viscosity of 135 cSt @ 40 °C and 14 cSt @ 100 °C [1]. The same type of oil was used for the lubrication of the moving tribometer parts in the vicinity of the test samples.
- Used, contaminated Shell Argina XL 40 oil from engine tests at VTT, filtered by a filter with 12
   µm nominal retention rate. A ferrography image of a sample of the contaminated oil after the
   filtering is shown in Figure 7.



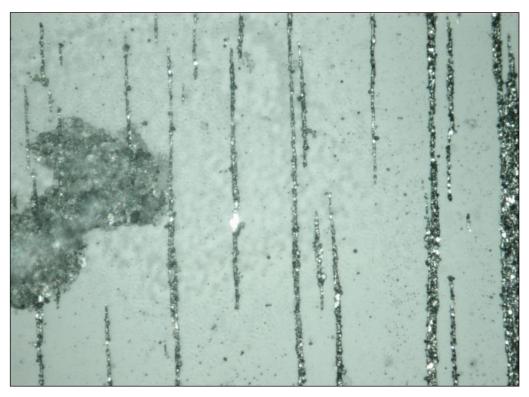


Figure 7. A ferrography image of a sample of the contaminated oil after filtering. The shiny particle close to the centre of the image has a width of about 10  $\mu$ m.

Table 1. The tests and the samples used in the tests (details are given in the Appendices 2 and 3). The tests with numbers in brackets were pre-tests or discarded tests, hence not reported in the present work.

Test N:o	Ring sample	Liner sample	Oil
Running-in test #1	661-41	ST1	Clean
Running-in test #2	661-31	ST2	Clean
Running-in test #3	661-32	ST3	Contaminated
Running-in test #4	661-42	ST4	Contaminated
Running-in test #5	S-ALT1	ST5	Contaminated
Running-in test #6	S-ALT2	ST6	Contaminated
Running-in test #7	S-ALT3	ST1B	Contaminated
Running-in test #8	661-35	ST2B	Contaminated
Running-in test #9	S-ALT4	ST3B	Contaminated
Running-in test #10	661-38	ST7	Contaminated
Running-in test #11	661-44	ST4B	Contaminated
Running-in test #12	661-43	ST6B	Clean
Scuffing test #13	661-35	ST2B	Clean
Scuffing test #14	661-44	ST4B	Contaminated
Scuffing test #15	S-ALT1	ST5	Contaminated
Scuffing test #16	661-38	ST7	Contaminated
Scuffing test #17	S-ALT2	ST6	Contaminated
Scuffing test #18	661-42	ST4	Contaminated
Scuffing test #19	S-ALT4	ST3B	Contaminated
Scuffing test #20	661-41	ST1	Contaminated
Scuffing test #21	661-31	ST2	Contaminated
Scuffing test #22	661-43	ST6B	Contaminated



#### 4.4.4 Procedure

The investigation consisted of long running-in tests, and of subsequent shorter scuffing tests with the run-in sample pairs after intermediate surface roughness and profile measurements.

The long running-in tests were carried out with an amplitude or stroke of 40 mm, a frequency of reciprocation of 10 Hz and a static normal force of 500 N. The cylinder liner samples were electrically heated to a temperature of 180 °C (heating and slow, intermittent motion of the piston ring sample under lubrication for 30 minutes before the start of the test). The lubrication of the piston ring and cylinder liner sample pairs was arranged by drip feed directly onto the test specimens. The duration of each running-in test was 24 hours, during which the friction force was measured at certain intervals (intervals of 3 minutes between the recording of the average friction force during two full strokes, and intervals of 15 minutes between detailed measurements of two full strokes with 500 measurements per stroke), and images of the top dead centre region of the cylinder liner were captured by video recording. The relevant diversions from the procedure are presented in Table 2.

Table 2. Relevant diversions from the procedure for the long running-in tests.

Test	Comments
Running-in test #1	The test was automatically interrupted after the first 1.5 hours due to breaking of the Fn-wire. The test was continued after replacing the Fn-wire, cleaning of the samples by wiping off oil with a tissue soaked with petroleum ether, and applying a new pre-lubrication and heating procedure. Due to too many data recordings for the data acquisition program, the friction force during the hours 10-22.5 was not recorded. The recording was re-started for the hours 22.5 to 24.
Running-in test #2	Stopped by a fatigue fracture in the hinge-blade of the force transmission rod from the actuator of the tribometer, which shortened the duration to only 21.5 hours.
Running-in test #3	The test was automatically interrupted after the first 1.5 hours and after the first 3 hours due to breaking of the Fn-wire. The test was continued after replacing the Fn-wire, cleaning of the samples by wiping off oil with a tissue soaked with petroleum ether, and applying a new prelubrication and heating procedure. After the second replacing of the Fn-wire, or starting from 3 hours after the start of the test, no re-lubricating oil was supplied to the test samples, and for this reason the sample combination eventually was subjected to scuffing and the test was automatically terminated at 4.1 hours from the start.
Running-in test #4	According to the procedure.
Running-in test #5	The test was automatically interrupted after the first 1.5 hours due to breaking of the Fn-wire. The test was continued after replacing the Fn-wire, cleaning of the samples by wiping off oil with a tissue soaked with petroleum ether, and applying a new pre-lubrication and heating procedure.
Running-in test #6	According to the procedure.
Running-in test #7	The sample combination was subjected to scuffing and the test was automatically terminated at 0.3 hours from the start.
Running-in test #8	Due to a human error, the first 24.2 hours of the test were performed under a frequency of 5.9 Hz. Due to the low number of cycles cumulated during the first 24 hours, the test was continued with 9.8 hours at 10 Hz frequency. However, due to timer malfunction, the test continued for another 24 hours at 10 Hz frequency. The total length of the test was therefore about 58 hours. The data acquisition program stopped recording data after about 50 hours from the start of the test.
Running-in test #9	The test was automatically interrupted after the first 2 hours due to breaking of the Fn-wire. The test was continued after replacing the Fn-wire, cleaning of the samples by wiping off oil with a tissue soaked with petroleum ether, and applying a new pre-lubrication and heating procedure.
Running-in test #10	According to the procedure.
Running-in test #11	According to the procedure plus 1 hour of additional testing time.
Running-in test #12	According to the procedure.



The scuffing tests were carried out on the samples from the running-in tests, after surface roughness and profile measurements, visual inspection and microscopy of the sliding surfaces. The long runningin tests were carried out with an amplitude or stroke of 40 mm and a frequency of reciprocation of 10 Hz. For the first 5 minutes of each scuffing test, the normal force was 500 N, and after that the normal force was increased in steps of 100 N every 5 minutes until the onset of scuffing or until 5 minutes of testing at the 1000 N level (Normal force  $500 \rightarrow 600 \rightarrow 700 \rightarrow 800 \rightarrow 900 \rightarrow 1000$  N, increased in intervals of 5 minutes). The cylinder liner samples were electrically heated to a temperature of 180 °C (heating under slow, intermittent motion of the piston ring sample for 30 minutes before starting the test). The lubrication of the piston ring and cylinder liner sample pairs was performed by using an adjustable syringe, with which 15 µl of old, contaminated oil was spread out on the sliding surface area of the cylinder liner sample before the test, in portions of 5 µl at intervals of 15 minutes during the heating period before the test. The test sequence is shown in Table 3. The duration of each scuffing test depended on its resistance against scuffing; the test was terminated when the scuffing caused a significant increase (µ>0.25) in the coefficient of friction. During the scuffing tests, the friction force was measured at certain intervals (intervals of 10 s between the recording of the average friction force during two full strokes, and intervals of 60 s between detailed measurements of two full strokes with 500 measurements per stroke), and images of the top dead centre region of the cylinder liner were captured by video recording.

Table 3. Test sequence for the scuffing tests.

Time [minutes]	Air pressure to normal	Normal force [N]	
	force cylinders [bar]		Action
			Oiled; 2 X 2.5 µl
0	0,4	50	Heating begins
			(180C)
5	0,4	50	1Hz X 5 strokes
10	0,4	50	1Hz X 5 strokes
15	0,4	50	Oiled; 2 X 2.5 µl
13	0,4	50	1Hz X 5 strokes
20	0,4	50	1Hz X 5 strokes
25	0,4	50	1Hz X 5 strokes
30	0,4	50	Oiled; 2 X 2.5 µl
			Increase of
30	4,1	505	pressure, Start;
			f=10Hz
			Increase
35	4,9	604	pressure (f=10Hz
			continues)
			Increase of
40	5,7	702	pressure (f=10Hz
			continues)
			Increase of
45	6,5	801	pressure (f=10Hz
			continues)
			Increase of
50	7,3	899	pressure (f=10Hz
			continues)
			Increase of
55	8,1	998	pressure (f=10Hz
			continues)
End time			,

# 4.5 Commercial feasibility

A major goal in the project was to investigate the commercial potential of the sulphur trap coating in industrial applications. The analysis of commercial feasibility was performed using two main methods, business intelligence analysis and patent landscape study.



#### 4.5.1 Business intelligence

New potential application areas were investigated in cooperation with the project group (company interviews and business intelligence) and VTT's Knowledge Solutions team. The analysis covered a wide range of applications, e.g., diesel engine manufacturers and solid lubricants producers, and determined the possible legislative drivers in Europe.

VTT's thermal spraying research team has a wide network of national and global companies providing coating services. Coating providers and potential end users were interviewed in order to find out their needs, capabilities and interest to utilize the Sulphur Trap coating.

#### 4.5.2 Patent landscape

Patent landscape is a tool which allows analysing a wide selection of patents by grouping them according to specific factors. Similar patent documents are gathered into clusters. The similarity is decided on how many similar terms are used in the documents. The two words next to each cluster show the two most frequent words in the documents. The closer two clusters or documents are the more similar the contents of them are. Colors indicate the size of the cluster, the redder the color the bigger the cluster is (and the more documents are included in the cluster). As an end result of the analysis, a visual image of patent landscape (Figure 8) was produced.

The Thermal Spray Sulphur Trap patent landscape vas visualised in November 2011 by VTT Knowledge solutions and analysed by the project group. It included 333 patent applications filed before May 2010. The landscape gave a general view on the main players, geographic locations, contents of publications, and trends.

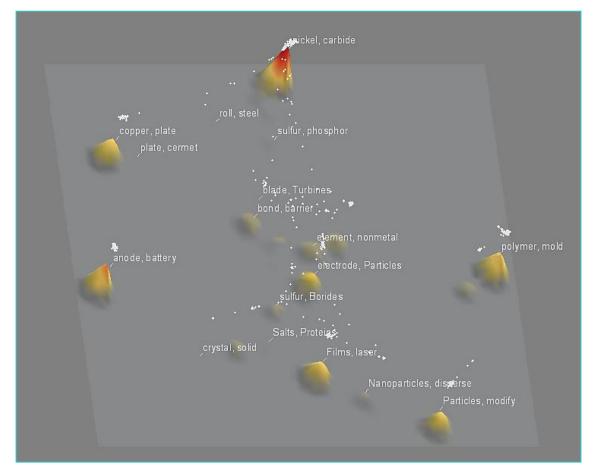


Figure 8. En example of STN AnaVist visualization of the 333 documents retrieved from the WPINDEX and HCAplus databases. Red and yellow peaks indicate the most active patenting areas.



#### 4.5.3 NABC analysis

Based on the business intelligence and patent landscape studies conducted in the project, the NABC analysis (Need, Approach, Benefit, Competition) was performed to identify the status of the Sulphur Trap technology. The method is described in the Figure 9.

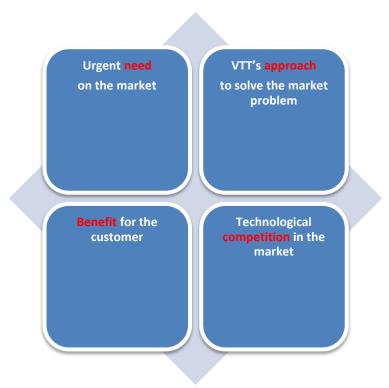


Figure 9. NABC method modified for the Sulphur Trap technology.

# 5. Technical results and discussion

# 5.1 Powder manufacturing

Experimental Ni49Cr1Fe-10 wt-% nano-Mo and  $Cr_3C_2$ -25(Ni20Cr)-10 wt-% nano-Mo powders were manufactured from commercials raw materials with planetary ball milling. Optimized milling process pot contained 300g NiCr or  $Cr_3C_2$ -NiCr powder (base material), 30 g nanosized molybdenum (Trap material), 3,3 g heksane and 300 g milling balls. Optimal milling time was 90 min and milling speed 150 rmp. Powders were sieved with 125  $\mu$ m sieve to remove large agglomerates and with 25  $\mu$ m sieve to remove separate nano particles. With these milling parameters both base materials (Ni49Cr1Fe or  $Cr_3C_2$ -25(Ni20Cr)) were coated with nanosized Mo without any harmful deformation. Example of uncoated Ni49Cr1Fe and coated Ni49Cr1Fe-10wt%n-Mo powders are presented in Figure 10.



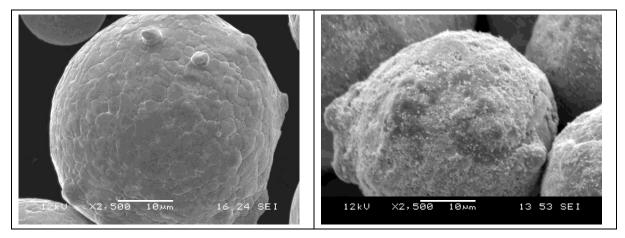


Figure 10. a) SEM image of uncoated atomized Ni49Cr1Fe powder (used to produce reference coatings) and b) coated Ni49Cr1Fe-10wt%n-Mo powder (used to produce Sulphur Trap coating)

# 5.2 Coating deposition

Reference coatings (Ni49Cr1Fe and  $Cr_3C_2$ -25(Ni20Cr)) and Sulphur Trap coatings (Ni49Cr1Fe-10wt%n-Mo and  $Cr_3C_2$ -25(Ni20Cr)-10wt%n-Mo) were manufactured using commercial Sulzer Metco DJ Hybrid HVOF-system using hydrogen as a fuel gas. Deposition parameters were optimized in order to reach dense coating structure, good adhesion to the base material and good mechanical properties. Examples of coating cross sections are shown in Figure 11. The trap material shows in bright contrast located in lamella boundaries throughout the coating structure as desired.

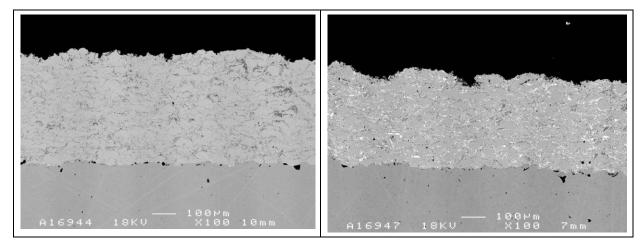


Figure 11. a) Cross section of reference Ni49Cr1Fe coating and b) Sulphur Trap Ni49Cr1Fe-10wt%n-Mo.

The densities of the deposited coatings were measured by gas penetration test. Coatings were deposited on top of sintered, porous buttons (diameter 25.4mm). Gas permeability of the coatings was tested with nitrogen gas up to 7 bars by commercial equipment. The porous substrates have practically zero resistance to the gas flow. In the test, the specimen is sealed in a test cell. Then gas pressure is increased in steps while volumetric gas flow though the specimen is measured by a flow meter. Viscous gas permeability coefficient  $\Psi_{\nu}$  can then be calculated using Darcy's law. The results show that all of the deposited coatings have high density and the Trap treatment slightly increases the density (e.g. reference  $\text{Cr}_3\text{C}_2\text{-}25(\text{Ni}20\text{Cr})$  permeability coefficient was 6.0 and 5.3 for Sulphur Trap  $\text{Cr}_3\text{C}_2\text{-}25(\text{Ni}20\text{Cr})\text{-}10\text{wt}\%\text{n-Mo coating})$ .

#### 5.3 Corrosion tests

Six different corrosion tests were conducted for Sulphur Trap coatings. Four were conducted at Outotec Research Laboratory with test atmosphere resembling real process conditions. Two laboratory tests were conducted at VTT.



The edges of all coating samples were protected with high temperature resistant ceramic paste in order to prevent the corrosion to propagate from the non-coated areas. Cross sections of tested samples were characterised with SEM to detect possible corrosion products in the coating surface.

Following coatings were tested at Outotec: Reference Ni49Cr1Fe and Sulphur Trap Ni49Cr1Fe-10p-%n-Mo as well as Reference  $Cr_3C_2$ -25(Ni20Cr) and Sulphur Trap  $Cr_3C_2$ -25(Ni20Cr)-10p-%n-Mo. The test conditions were:

Test 1: Teperature 275°C, gas atmosphere 40% SO<sub>2</sub>, 2% O<sub>2</sub>, 5% H<sub>2</sub>O and 53% N<sub>2</sub>

**Test 2**: Same as in test 1 but with 3 cm dust layer containing: 24.1% Fe (29.9% Fe<sub>3</sub>O<sub>4</sub>), 25.9% Cu, 5.9% Zn, 3.8% SiO<sub>2</sub>, 3.5% S (12.5%  $SO_4^{2-}$ ), 3.1% Pb, 2.8% As, 0.9% Bi, 0.84% Cd, 0.47% K, 0.35& Sn, 0.009% Cl, 6 ppm F

Test 3: Same as in test 2 but added 1000 ppm Cl to the dust layer

Test 4: Same as in test 2 but added 1000 ppm F to the dust layer

Test duration was 5 days for all Outotec tests. The test conditions were selected to match real life process conditions and to provide a comparison against several previously tested bulk materials. Weight loss/increase was measured and cross sectional SEM-EDS analysis was performed for all coatings. Example of mass losses/increase is shown in Figure 12.

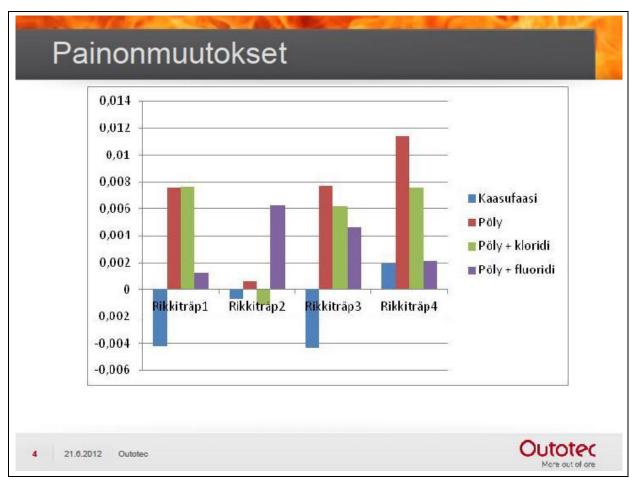


Figure 12. Mass loss/increase in all four test conditions (Test 1 = kaasufaasi, blue, Test 2 = pöly, red, Test 3 = pöly+kloridi, green, Test 4 = pöly+fluoride, purple). Sample Rikkiträp1 = Reference Ni49Cr1Fe, Rikkiträp2 = Sulphur Trap Ni49Cr1Fe-10wt%n-Mo, Rikkiträp3 = Reference  $Cr_3C_2$ -25(Ni20Cr) and Rikkiträp4 = Sulphur Trap  $Cr_3C_2$ -25(Ni20Cr)-10wt%n-Mo

The weight loss/increase was observed to be so small that no clear conclusions could be made from these results. This was verified in cross sectional SEM-EDS studies (example of coating surface in Figure 13). Basically no corrosion layer could be observed for any of the tested coatings.



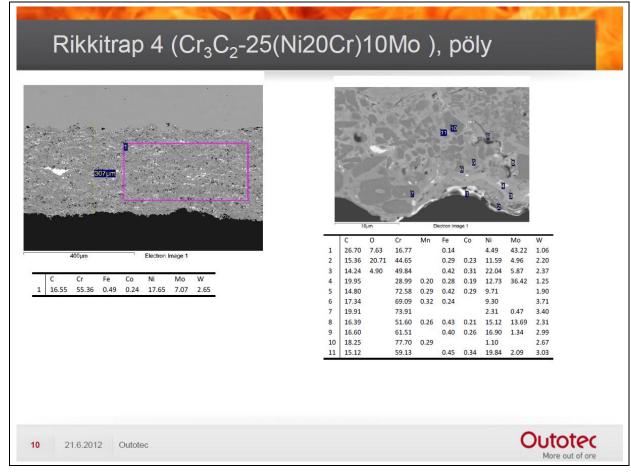


Figure 13. SEM-EDS analysis of tested Sulphur Trap Cr<sub>3</sub>C<sub>2</sub>-25(Ni20Cr)-10wt%n-Mo coating.

The main conclusion of these corrosion tests was that this type of thermal spray coatings withstand such process like conditions extremely well compared to several previously tested bulk materials.

Corrosion tests conducted at VTT were conducted in laboratory tube ovens in following conditions:

**Test 5**: Temperature 650 °C, duration 1 week and solid natriumsulphide-kaliumsulphide (eutectic composition which will be molten at test temperature)

SEM-EDS study was conducted for the coatings before and after the test. All of the coating survived the test well. No corrosion products could be clearly detected from the surfaces of the coatings. Slight interdiffusion between coating and substrate was observed. This typically increases the adhesion of the coating to the substrate. These high temperature sulphur exposed coatings were also subjected to adhesive wear tests. The results are shown in following section 5.4. Cross sectional images of the coating are shown in figure 14.



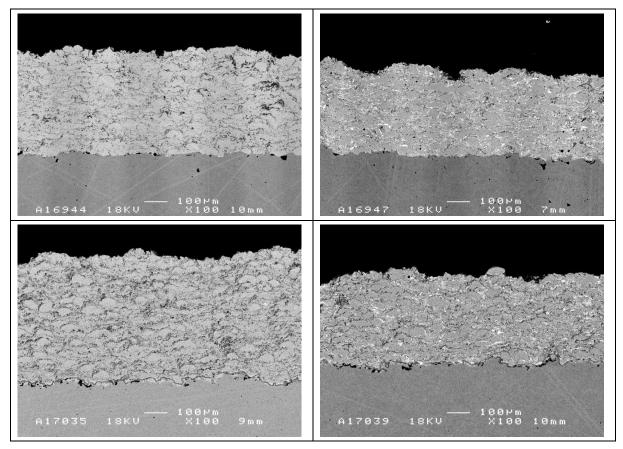


Figure 14. a) SEM (BSE) image of N49iCr1Fe-coating cross-section before the test, b) Ni49Cr1Fe-10wt%n-Mo-coating before the test, c) Ni49Cr1Fe-coating after the test and d) Ni49Cr1Fe-10wt%n-Mo-coating after the test. Figures from a to d clockwise starting from up-left.

In order to observe differences between reference and Sulphur Trap coatings a test with higher temperature and longer test duration was conducted in following conditions:

**Test 6**: Test conditions were determined by Wärtsilä to simulate real process conditions. Test was conducted at VTT. Temperature 800 °C, gas atmosphere 15%  $O_2$  – 5%  $H_2O$  – 5%  $CO_2$  – 1000 ppm  $SO_2$  – balance  $N_2$  with solid  $Na_2SO_4$  deposition layer, test duration 1000h.

SEM-EDS study was conducted for the tested reference  $Cr_3C_2$ -25(Ni20Cr) and Sulphur Trap  $Cr_3C_2$ -25(Ni20Cr)-10wt%n-Mo coatings. Cross section of reference coating after the test is shown in Figure 15. It can be observed that the coating did not suffer from catastrophic corrosion from the top surface, but major cracking can be observed. Such cracks will result in catastrophic delamination failure when they reach the substrate. In this test the major cracks propagated almost to the substrate (vertical crack length 4/5 of the coating thickness). Such coatings cannot be used in tested process conditions.



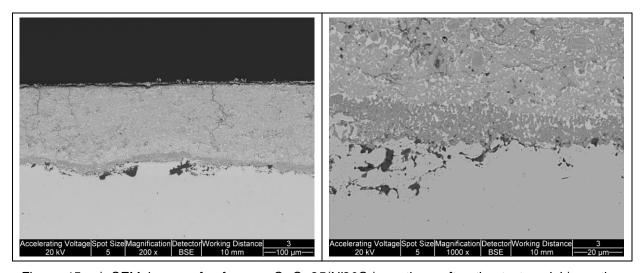


Figure 15. a) SEM image of reference  $Cr_3C_2$ -25(Ni20Cr) coatings after the test and b) coating-substrate interface.

EDS study of the reference coatings confirmed cracking and crack oxidation as shown in Figure 16.

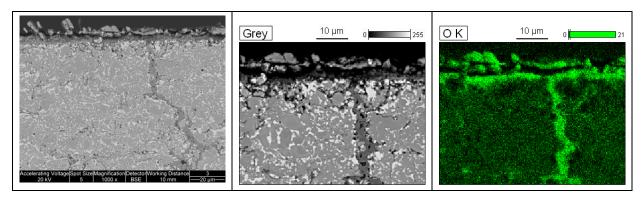


Figure 16. a) Higher magnification SEM-image of reference coating after the test, b) studied EDS area and c) oxide map revealing heavy crack oxidation.

No crack formation or significant corrosion was observed for Sulphur Trap  $Cr_3C_2$ -25(Ni20Cr)-10wt%n-Mo coating. The coating survived the test conditions extremely well compared to the reference coating. Cross sectional image of the Sulphur Trap coating after the test is shown in Figure 17.

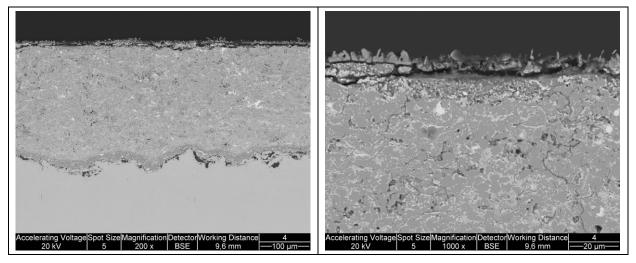


Figure 17. a) SEM image of Sulphur Trap coating after the test and b) higher magnification from the cross section surface



EDS study showed only slight oxidation layer at the top most surface of the Sulphur Trap coating as shown if Figure 18.

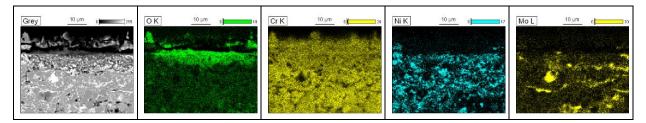


Figure 18. a) SEM-EDS image of coating surface after the test, b) oxygen map, c) chromium map, d) nickel map and e) molybdenum map

Evidence of extremely corrosive condition of test 6 was observed when the substrate material (low carbon steel S355) was studied. The substrate steel suffered extreme corrosion even though it was protected with ceramic paste specially designed to protect from the surface. Figure y shown an example of the formed corrosion layer.

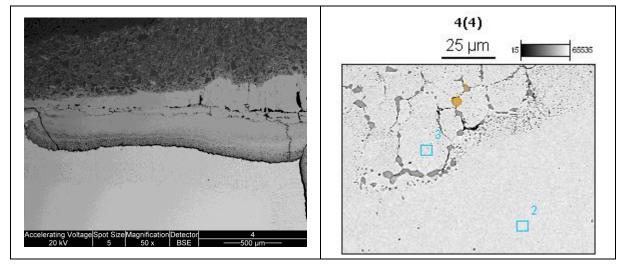


Figure 19. a) Cross sectional SEM image of the substrate material after the test and b) more detailed image of the area beneath the fully oxidized layer

In Figure 19 a) a thick fully oxidized layer (approximately 500  $\mu$ m thick) can be observed but also evidence of grain boundary corrosion beneath it. More detailed image is shown in Figure 19 b). The EDS analysis revealed the presence of high concentrations of sulphur from the grain boundaries (e.g. 35at% of sulphur in location 1).

# 5.4 Pin-On-Disk tests

Pin-On-Disk tests were conducted to reference  $Cr_3C_2$ -25(Ni20Cr) and Sulphur Trap  $Cr_3C_2$ -25(Ni20Cr)-10wt%n-Mo coatings according to standard ASTM G99. Samples were exposed to high temperature sulphuric conditions prior to the test in order to study the formation and frictional benefits of formed solid lubricant,  $MoS_2$ .

The exposure conditions were: Temperature 650 °C, duration 1 week and solid natriumsulphide-kaliumsulphide (eutectic composition which will be molten at test temperature). The edges of all coating samples were protected with high temperature resistant ceramic paste in order to prevent the corrosion to propagate from the non-coated areas. Prior to the Pin-On-Disk test the ceramic paste was removed and the surfaces of the coatings were lightly grinded with SiC paper in order to remove the excess sulphide deposits.

The counted material (pin) was bearing steel, normal load 5 N, speed 0.1 m/s and temperature 25 °C. An example of friction coefficient curves is presented in Figure 20.



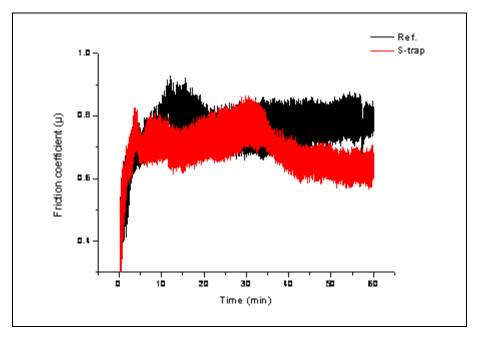


Figure 20. Recorder friction coefficients for reference (black) and Sulphur Trap (red) coatings.

Sulphur Trap coating had approximately 25% lower friction coefficient at the end of the test compared to the reference coating. Other interesting observation was the decreasing trend in friction coefficient for Sulphur Trap coating, starting from 30 minutes test time. These phenomena are assumed to be caused by the transfer of MoS<sub>2</sub> also to the pin material. The increasing trend as a function of time (like for reference coating) is highly typical for thermal spray coatings.

# 5.5 Piston ring tribometer tests

# 5.5.1 Long running-in tests

An example of the development of the average value for the coefficient of friction in a running-in test (Test #4, Sulphur Trap coating) is shown in Figure 21, with detailed graphs from the beginning and the end of the test in the Figures 22 and 23.



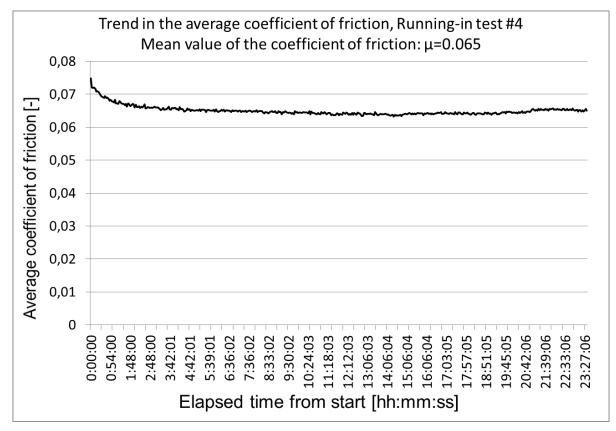


Figure 21. Example of the trend in the average coefficient of friction in a running-in test.

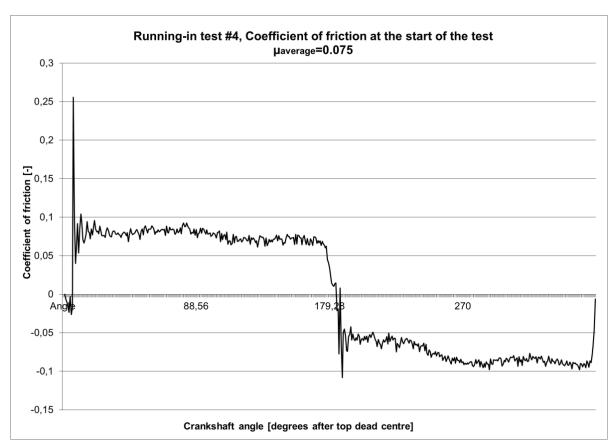


Figure 22. Example of a detailed friction graph, for a full crankshaft revolution, at the start of a running-in test.



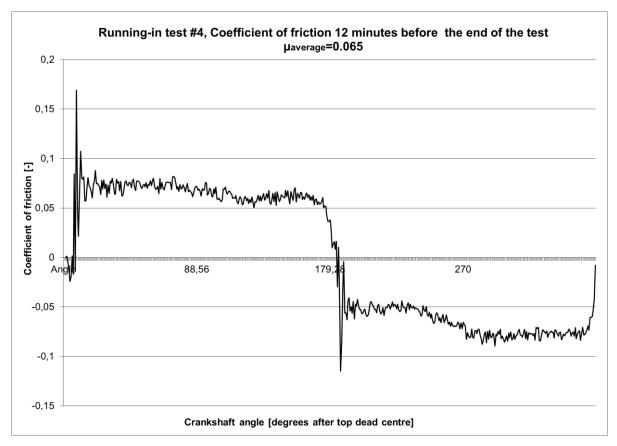


Figure 23. Example of a detailed friction graph, for a full crankshaft revolution, 12 minutes before the end of a running-in test.

A summary of the results of the friction measurements, or the calculated coefficients of friction, during the running-in tests, is given in Table 4 and Figure 24. A comparison of the calculated coefficients of friction in the running-in tests, for the three groups of coatings studied, is shown in Figure 25. The mean values for the average coefficient of friction were  $\mu$ =0.072 for the 661-3 reference coating,  $\mu$ =0.065 for the 661-4 Sulphur Trap coating and  $\mu$ =0.076 for the SALT coatings.

A conclusion of the friction measurements during the running-in tests is that among the coatings studied in the present work, the 661-4 Sulphur Trap coating gave the lowest average coefficients of friction. On an average, the 661-4 Sulphur Trap surfaces had a slightly lower initial surface roughness than did the 661-3 reference coatings and the SALT coatings, but the exact influence of this on the coefficients of friction would require further studies. Sulphur Trap coatings provided lower coefficient of friction and clearly more stable frictional behaviour in all tests conducted in this study.



Running-in test #10

Running-in test #11

Running-in test #12

Test	μaverage start	μaverage test	$\mu$ average end
Running-in test #1	0,073	0,064	0,066
Running-in test #2	0,084	0,07	0,071
Running-in test #3	0,078	0,064	0,072
Running-in test #4	0,075	0,065	0,065
Running-in test #5	0,079	0,066	0,065
Running-in test #6	0,071	0,069	0,067
Running-in test #7	0,096	0,093	0,086
Running-in test #8	μaverage=	0.078 for the las	t 24 hours
Running-in test #9	0,086	0,076	0,076

0,076

0,065

0,066

0,075

0,064

0,067

0,102

0,074

0,072

Table 4. Summary of the calculated coefficients of friction in the running-in tests.

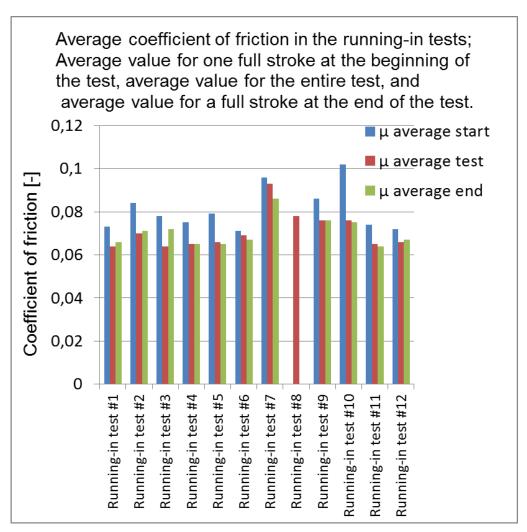


Figure 24. Summary of the calculated coefficients of friction in the running-in tests.



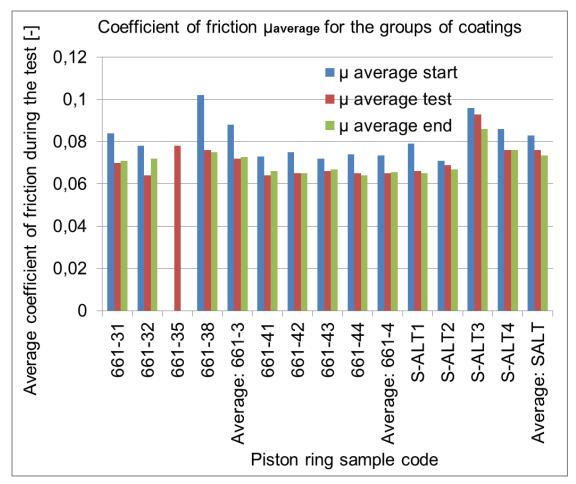


Figure 25. Comparison of the calculated coefficients of friction in the running-in tests, for the three groups of coatings studied.

# 5.5.2 Results of surface roughness and profile measurements

Before the running-in tests, the mean arithmetic average surface roughness of the 12 piston ring samples had a mean value of Ra=0.43  $\mu$ m  $\pm$  0.17  $\mu$ m ( $\pm$ 38.9%). After the running-in tests, the mean value on the worn proportions of those of the piston-ring surfaces that had not been subjected to scuffing was Ra=0.28  $\mu$ m  $\pm$  0.10  $\mu$ m ( $\pm$ 35.0%), which indicates a smoothening of the sliding surfaces of those of the piston ring samples that had not been subjected to scuffing, see the overview of the Ravalues before and after the running-in tests in Figure 26. The initial Ra-values were particularly high for the piston ring samples 661-35, 661-38, SALT-1 and SALT-2.



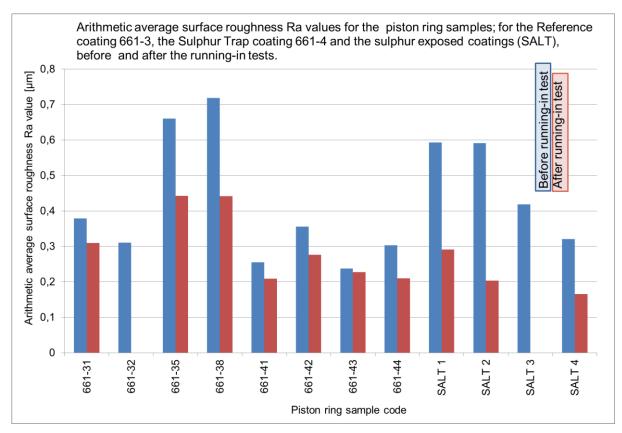


Figure 26. Overview of the surface roughness Ra-values for the piston ring samples before and after the running-in tests.

# 5.5.3 Visual inspection and microscopy

The visual inspection of the piston ring samples and the cylinder liner plate samples after the runningin tests showed that the sliding surfaces had been smoothened or slightly polished, with the exception of the samples from the tests #3 and #7, which had been prematurely terminated because of scuffing. An example of a sample combination after a running-in test (Test #2) is shown in Figure 27, and detailed views from the run-in surfaces of a piston ring sample and a cylinder liner plate sample (from Test #4) are shown in Figure 28.





Figure 27. Example of a piston ring sample and cylinder liner plate sample combination after a running-in test (Test #2).



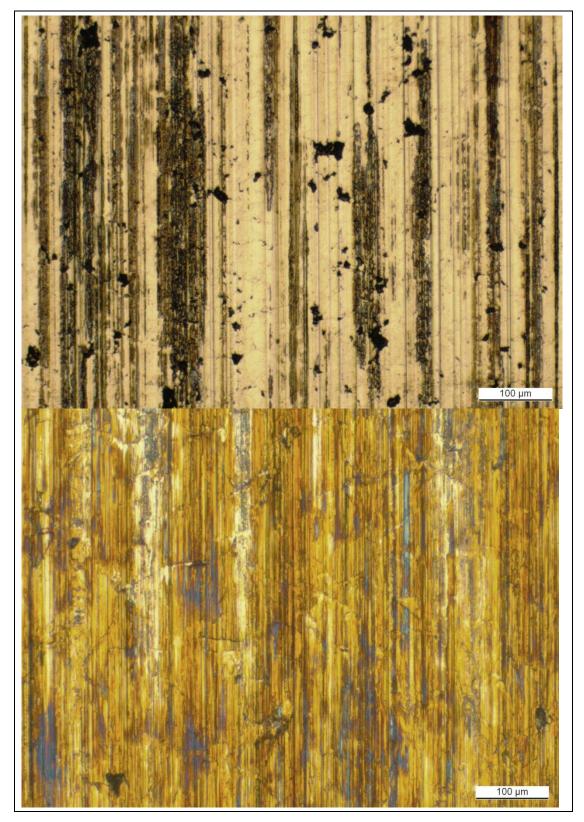


Figure 28. Example of detailed views showing the run-in surfaces of a (upper image) piston ring sample and the bottom dead centre zone of a (lower image) cylinder liner plate sample (from Test #4)

# 5.6 Scuffing tests

# 5.6.1 Time-to-scuffing

An example of the development of the average value for the coefficient of friction in a scuffing (Test #17) is shown in Figure 29.



A summary of the Time-to-scuffing results of the scuffing tests is given in Table 5. In Figure 30 the Time-to-scuffing values and the mean values for the 661-3 Reference coating (mean value: 11 minutes and 6 seconds), the 661-4 Sulphur Trap coating (mean value: 19 minutes and 18 seconds) and the SALT sulphur exposed coatings (mean value: 15 minutes and 20 seconds) are presented.

A conclusion of the present scuffing tests is that the 661-4 Sulphur Trap coating gave the best resistance against scuffing among the materials of the present study, with a mean values of 19 minutes and 18 seconds, to be compared with only 11 minutes and 6 seconds for the 661-3 Reference coating, and 15 minutes and 20 seconds for the SALT sulphur exposed coatings. The mean values for the maximum normal force were correspondingly higher for the Sulphur Trap coating than for the other coatings of the present study.

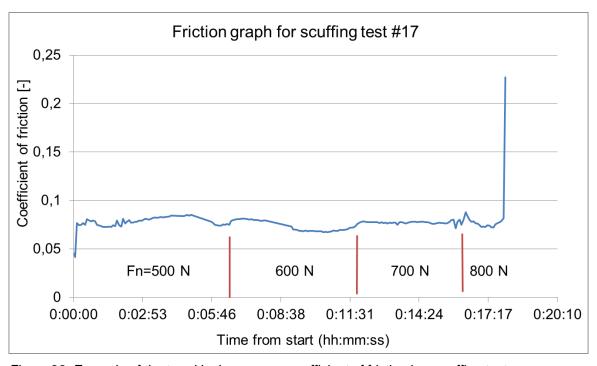


Figure 29. Example of the trend in the average coefficient of friction in a scuffing test.

Table 5. Summary of the Time-to-scuffing and maximum normal force results of the scuffing tests.

			Time-to-scuffing	Maximum normal
Test N:o	Ring sample	Liner sample	(h:mm:ss)	force [N]
#13	661-35	ST2B	0:02:50	500
#14 C	661-44	ST4B	0:33:52	1000
#15	S-ALT1	ST5	0:18:25	800
#16	661-38	ST7	0:05:50	600
#17	S-ALT2	ST6	0:18:00	800
#18 B	661-42	ST4	0:05:50	600
#19	S-ALT4	ST3B	0:09:35	600
#20	661-41	ST1	0:06:52	600
#21 B	661-31	ST2	0:24:37	900
#22	661-43	ST6B	0:30:38	1000

A letter B or C at the end of the test code indicates that the test reported was carried out subsequently to 1-2 trials with excessive oil due to apparent leakage from the oil feed circuit for the Fn-roller shafts.



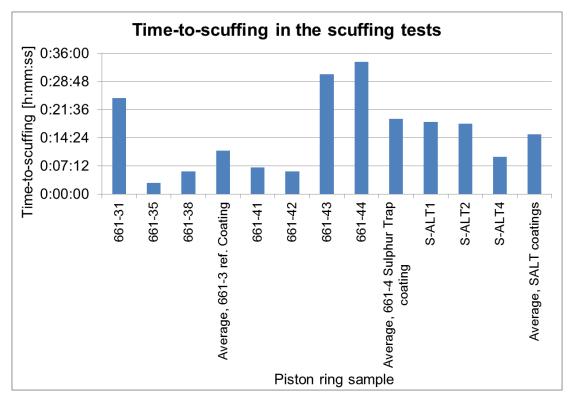


Figure 30. Summary of the Time-to-scuffing results of the scuffing tests.

#### 5.6.2 Surface roughness and profile measurements

The initial surface roughness of the piston ring samples and the cylinder liner sample plates before the scuffing tests was identical with that of the samples after the running-in tests, see paragraph 5.5.1.

#### 5.6.3 Visual inspection and microscopy

The visual inspection of the piston ring samples and the cylinder liner plate samples after the scuffing tests showed that the sliding surfaces had been roughened by strong adhesion and the subsequent tearing-off of adhesively formed joints. An example of a sample combination after a scuffing test (Test #17) is shown in Figure 31.



Figure 31. Example of a sample combination after a scuffing test (Test #17).



In the long running-in tests of the present work, the 661-4 Sulphur Trap coating gave the lowest average coefficients of friction. On an average, the 661-4 Sulphur Trap surfaces had a slightly lower initial surface roughness than did the 661-3 reference coatings and the SALT coatings, but the exact influence of this on the coefficients of friction would require further studies. The visual inspection of the piston ring samples and the cylinder liner plate samples after the running-in tests showed that the sliding surfaces had been smoothened or slightly polished, with the exception of the samples from the tests #3 and #7, which had been prematurely terminated because of scuffing. Surface roughness measurements before and after the tests supported this consclusion.

In the present scuffing tests, the 661-4 Sulphur Trap coating gave the best resistance against scuffing among the materials of the present study, with a mean length of the tests of 19 minutes and 18 seconds, to be compared with only 11 minutes and 6 seconds for the 661-3 Reference coating, and 15 minutes and 20 seconds for the SALT sulphur exposed coatings. The mean values for the maximum normal force were correspondingly higher for the Sulphur Trap coating than for the other coatings of the present study.

#### 6. Commercial results and discussion

Potential markets were identified by analysing data gathered by business intelligence, patent analysis and industry interviews. The results are presented below.

# 6.1 Business intelligence

Based on the information generated in the project, the most potential customer segment is considered to be low and medium speed diesel engines. These engines operate in conditions where sulphur corrosion causes severe problems and overcoming this problem with a thermal spray coating is considered an optimal solution. In diesel engines, the Sulphur Trap coating brings most added value in pistons and cylinders, the parts which are exposed to severe sulphur corrosion and abrasion. Due to legislative actions such as the EU Directive restricting the use of sulphur in industrial processes and marine transport may restrict the commercial potential for the coating in the long run. However this would require transition to completely sulphur free fuels and oils.

In the project, the diesel engine manufacturing value chain was analysed. The ultimate decision makers in the chain are the engine manufacturers whose subcontractors act according to their needs. Companies who manufacture engine parts such as piston rings, valves or cylinders show interest in the coating technology. However, they consider product development to be done in cooperation with the engine manufacturer and not the subcontractor.

In other transport sectors such as high speed diesel engines, road vehicles and heavy vehicles the need for Sulphur Trap coating was not as obviously recognised. This is mainly due to the fact that in these sectors sulphur concentration of fuels is low. However in components where oil is used for lubrication the potential to utilise Sulphur Trap technology exists.

Another industry analysed in the project was industrial boilers. The boiler manufacturers were initially considered a potential customer segment with an urgent need for the Sulphur Trap coating. In the project it was however concluded that the chlorine corrosion is typically the most critical problem to be solved and therefore the effort to overcome the sulphur corrosion is given minor importance.

Solid lubricant producers were identified a potential customer segment in the beginning of the project. In co-operation with VTT Knowledge Solutions, European solid lubricants producers were listed and analysed. The analysis did not bring any specific new information.

#### 6.2 Patent landscape

The Thermal Spray Sulphur Trap patent landscape visualised in November 2011 by VTT Knowledge solutions includes 333 patent applications filed during the period 1973 - May 2010 in the thermal spray field with the keyword *sulphur* (Figure 32). The peaks show the most patented areas.



The most active country patenting has been Japan (Figure 33). The key patenting organisations are presented in the Figure 34. In both figures the coloured part of the bar denotes to the proportion of the company's documents in relation to all documents in the landscape (the grey part of the bar).

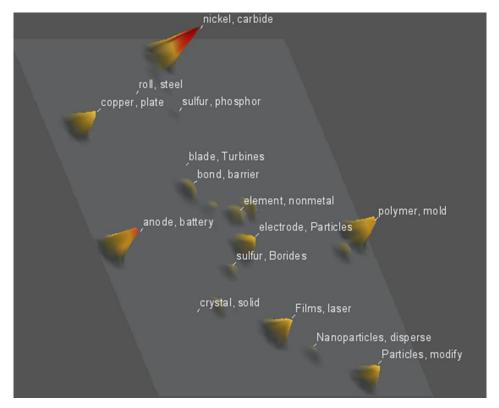


Figure 32. STN AnaVist visualization of the 333 documents, the "Thermal Spray Sulphur Trap patent landscape" retrieved from the WPINDEX and HCAplus databases. Red and yellow peaks indicate the most active patenting areas.

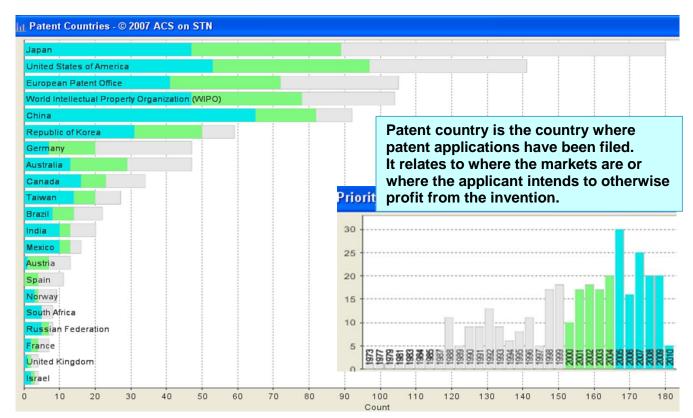


Figure 33. STN AnaVist visualization of the 333 documents retrieved from the WPINDEX and HCAplus databases. Key patenting countries.



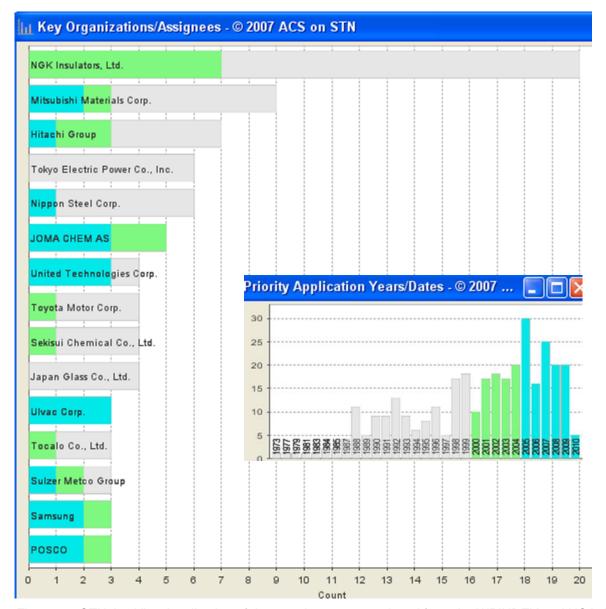


Figure 34. STN AnaVist visualization of the 333 documents retrieved from the WPINDEX and HCAplus databases. Key patenting organisations.

Based on further analysis it was concluded that patents in the landscape did not bring significant new information about potential application areas for the Sulphur Trap technology. Six patents were selected for further investigation. These patents also addressed the sulphuric corrosion protection but did not resemble the Sulphur Trap technology otherwise.

# 6.3 Discussions with industry

The idea of this innovation originated from the needs of heavy duty diesel engines and was a baseline for industrial discussion.

The key benefits of the innovation are:

- 1. improved corrosion resistance in high temperature applications
- 2. lower friction in sliding conditions

Several companies were contacted in order to find applications where both of the key benefits could be exploited. Finding this kind of a "perfect match" proved to be more difficult than anticipated when starting this project. An evident application was sulphur containing fuel used in diesel engines, especially marine engines. Discussions with companies related to this field were halted due to on-



going licensing negotiations with one partner. Applications where only the extra lubrication was the key offering did not lead anywhere; there are competing methods that are proven and readily in use.

Good feedback was received from industrial applications where corrosion conditions are extreme: high temperature and aggressive chemical load.

The outcome of discussions is:

- with <u>low and medium speed diesel engine</u> application licensing negotiations are going on/finalised and a project to verify results is set up
- with thermal energy sector a project has started and negotiations to grant a licence reservation for the project time are on-going.
- with <u>cement manufacturing</u> industry the negotiations to grant a licence reservation for the project time are on-going. A POC trial is offered.

In commercial terms the future looks promising. One application specific licence is granted/ready to be finalised and other industrial enterprises have shown strong interest to verify the potential of the Sulphur Trap technology. All partners promote the idea of industry specific licensing: the more this technology is utilised, the cheaper and more usable it becomes.

This project has clearly increased the technology readiness level of the Sulphur Trap technology making discussions easier with potential licence-holders.

# 6.4 NABC analysis

As a last step, the results of technological tests and market analysis were drawn together in NABC analysis for the Sulphur Trap technology. The analysis presents market needs, VTT's approach to solve the problem, customer benefits and competition as a short introduction to the technology. The analysis is presented below in Figure 35.



Sulphur Trap coating may be the solution if your urgent need in extreme sulphur conditions is to

Find a durable material operating in the temperature range 200 – 900°C

Reduce friction to save materials from wearing and make the process more efficient

Improve coating adhesion

Hard chromium replacement

#### VTT's approach to solve the problem

Powder modification makes thermally sprayed coating resistant against high temperature sulphur corrosion

Innovative coating can be made using standard thermal spray equipment

Technology is proven by a range of laboratory tests

Powder can be modified against cloride corrosion

#### **Benefit** for the customer

Cost savings by decreased occurrence of maintenance breaks

No risk in the coating technology: Coatings can be deposited by industrially proven thermal spray systems

No risk in powder manufacturing technology

# Technological competition in the market

Competing methods other corrosion prevention technologies.

In cases where wear both corrosion prevention and resistance is needed, competing technologies do not exist.

Figure 35. NABC analysis for the Sulphur Trap technology.

# 7. Conclusions

Manufacturing of Sulphur Trap powders and thermal spray coatings were successfully demonstrated by using commercial systems already widely utilized industrially.

Basically no corrosion was detected for the Sulphur Trap coatings in lower temperature tests (275 °C and 650 °C) but neither of the reference coatings suffered from corrosion. A clear difference was detected in the higher temperature test (800 °C). The Sulphur Trap coating withstood these conditions significantly better than the reference coating. Severe cracking and corrosion was detected for reference coating while basically no corrosion (or cracking) was observed for the Sulphur Trap coating. Reference coating could not be recommended for use in such conditions while the Sulphur Trap coating withstood the conditions basically intact.

The Sulphur Trap coating demonstrated better tribological performance in all tests conducted during the study. Lower friction coefficient and longer times to scuff were observed in all test conditions during the piston ring tribometer studies and approximately 25% lower friction coefficient was



observed in the pin-on-disk tests. During the pin-on-disk tests a decreasing trend of friction coefficient as a function of time was also observed. This is rarely observed for thermal spray coatings. Pin-on-disk samples were preconditioned at high temperature (600 °C) sulphuric conditions but even without preconditioning the Sulphur Trap coating showed constantly lower friction coefficients during the lubricated piston ring tribometer tests thus indicating that even the low amount of sulphur in the lubricating oil is sufficient for the Sulphur Trap coating technology.

According to market analysis carried out in the project, three potential application areas have been identified:

- low and medium speed diesel engines
- high temperature processes in process industry
- · combustion energy industry

In these conditions sulphur corrosion causes severe problems and overcoming this problem with a thermal spray coating is considered an optimal solution. In diesel engines, the Sulphur Trap coating brings most added value in pistons and cylinders, the parts which are exposed to severe sulphur corrosion and abrasion.

During the project, the technology readiness level, when measured using the NASA Technology readiness level (TRL), increased from the initial level of 3, analytical and experimental critical function proof-of-concept, to the level of 5 level of component validation in a relevant environment. The initial target was 6, coating prototype demonstration in a real industrial environment. The initial target was not reached due to unexpected changes in the test environment.

VTT has a patent for the sulphur and chlorine trap technologies. VTT is willing to develop the technology jointly with the industry and licence out the technology. At the end of the project, negotiations of out-licensing the Sulphur Trap technology are active with three companies.

# 8. Summary

The goal of the Sulphur Trap project, carried out from July 2011 to April 2013, was to perform a proof-of-concept (POC) study on the thermally sprayed Sulphur Trap coating. The coating has been developed and patented by VTT. The POC study consisted of two parts. In order to prove the technical feasibility a set of laboratory tests was performed for the coating and to prove the commercial feasibility a market study clarifying the potential applications, markets and clients was accomplished. Based on the technical and commercial feasibility studies, the commercialisation route was chosen.

The potential applications included industrial processes in extreme, sulphur-rich conditions such as diesel engines and boilers. The laboratory tests were conducted in laboratory environments corresponding to industrial applications. The tests included corrosion tests at Outotec and VTT and tribological tests at Metso Automation and VTT. The Sulphur Trap coating gave 10 to 25% lower average coefficient of friction in tribological tests and performed significantly better in conducted corrosion tests than the reference coating. The reference coating was catastrophically corroded in 800 °C sulphuric corrosion tests while the Sulphur-Trap coating survived basically intacted. The Sulphur Trap coating also gave better resistance against scuffing than the reference coating in all tested configurations.

During the project the technology readiness level, when measured using the NASA Technology readiness level (TRL), increased from the initial level of 3 (analytical and experimental critical function proof-of-concept) to the level of 5 (component validation in a relevant environment). At the end of the project VTT was negotiating out-licensing of the Suphur Trap coating into three separate application areas with three different companies.



# **References**

[1] Dorfman, M.R. & Sharma, A.Challenges and Strategies for Growth of Thermal Spray Markets: The Six-Pillar Plan. Journal of Thermal Spray Technology, 2013, 22(5), pp. 559–563.