Project 3.3E

Thermally Sprayed Protection Coatings With Highest Resistance Against Wear and Corrosion, Made by Nanostructured Powders

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1. Executive summary

The aim of this project was the development of a new type of coating with a high resistance against wear and corrosion. The new material consists of a high corrosion resistant matrix of type stainless steel (austenitic, martensitic; even without Ni) combined with hard nitrides of partly nanocrystalline dimensions (Fig. 1a, 1b).

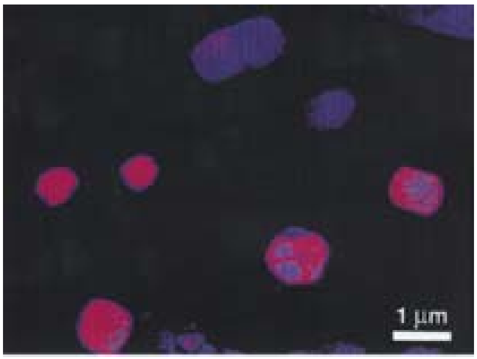

Fig. 1a: TEM-Image showing primary nitrides of µm size.

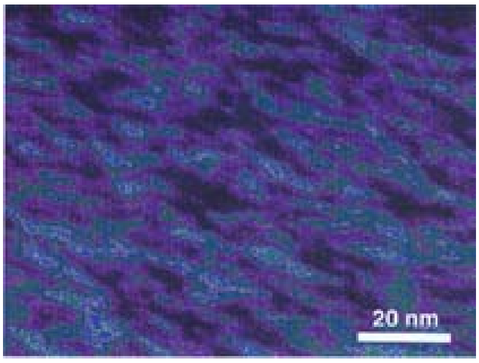

Fig. 1b: TEM-Image showing secondary nitrides of nm size.

To form those nitrides in the final coating three routes have been investigated:

1. Heat treating of the starting powder material under nitrogen atmosphere to form the nitrides and to keep this structure during thermal spraying,
2. Forming of the nitrides during reactive thermal spraying of previously unreacted powder,
3. Post nitridation of the conventionally sprayed coatings with unreacted powder.

A comparison of different thermal spraying techniques (flame-, high-velocity-flame-, and plasma spraying) demonstrated their advantages while preserving or creating those kind of desired phase structures (Fig. 2).

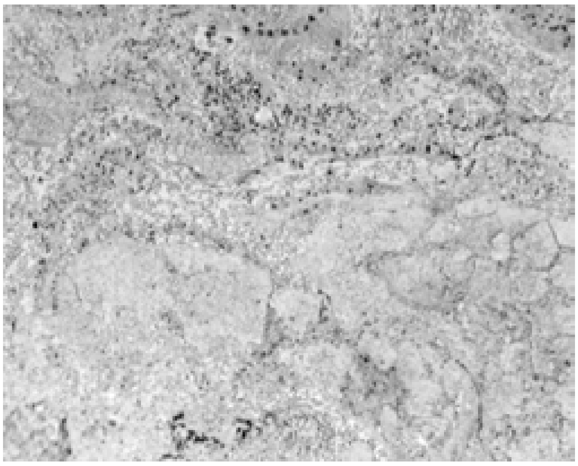

Fig. 2: Microstructure of typical thermally sprayed coatings, showing dark primary nitrides after chemical etching.

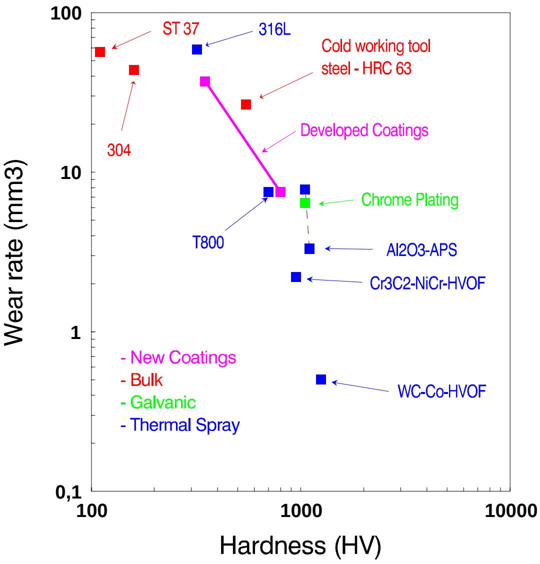

Fig 3: Volume loss rate according ASTM G75 test method of the investigated coatings and bulk materials as a function of their hardness.

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Besides the development of the new material and optimisation of the coating, wear and corrosion tests with competitive coatings (like hard chrome plating, WC-Co, etc.) were performed. A classification regarding e.g. wear resistance of generally used coatings could be done (Fig. 3).

These studies have been used to compare different kind of coating materials and processes (Fig. 4). Figure 4 shows a typical process for internal coating application.

Fig. 4: Internal coating process carried out during the project for field tests.

Field tests with real parts in their typical environment have shown the advantages of those kind of materials with simultaneous wear and corrosion resistance. The exceptional properties open a wide range of other potential applications.

Basically these alloys exhibit a:
- lower price compared to Ni- or Co-based alloys,
- easier machineability than cermets and
- higher spray rate and deposition efficiency than ceramics.

These materials bridge the gap between the mainly pure corrosion protection coatings (e.g. Al, Zn, etc.) and the pure wear protection coatings combining both advantages.

1. **Objectives** of the 95-99 research plan

The basic milestone of the first year was the development of a new nanostructured spray material which has been carried out manly at ETH-Zürich. During lots of iterative steps the properties of the **h**ot **i**sostatically **p**ressed (HIP) bulk materials have been tested. The theoretical and practical results of powder production confirmed the high potential of these new materials in terms of strength, toughness, corrosion and wear resistance (as described later).
The goal of the second year was the optimisation of the coatings with different kind of thermal spray processes by comparison of their properties with those of competitive coatings. The properties of competitive coatings have been investigated during the first and second year of the project. Those additional wear tests of standard thermal spray coating materials like WC-17Co, Al_2O_3, NiCrBSi, and galvanic chrome plating have been performed on a pin-on-disc machine. The data, which are concerned with dry sliding exclusively, have been available now for comparison with those of the newly developed stainless steel coatings. Four different wear mechanisms have been observed and corresponding wear maps correlating the load, the sliding velocity and the wear mechanisms have been established.
Together with the industrial project partners these new coatings have been subjected to vast field tests under real applicational conditions in the third year. Some new application fields have been evaluated and taken into the test procedure which are partially still under investigation.

3. Results

3.1 Materials Development:

3.1.1 First Alloy: Austenitic Iron Based MMC Containing Primary Vanadium Nitrides

Primary nitrides are VN precipitates which are formed during a nitriding process performed in a rotary furnace. They grow in size depending upon the process parameters during HIP compaction. Figure 1 illustrates how the mechanical properties of these nitrides containing nickel free materials compare with those of similar stainless steels which are precipitation free.

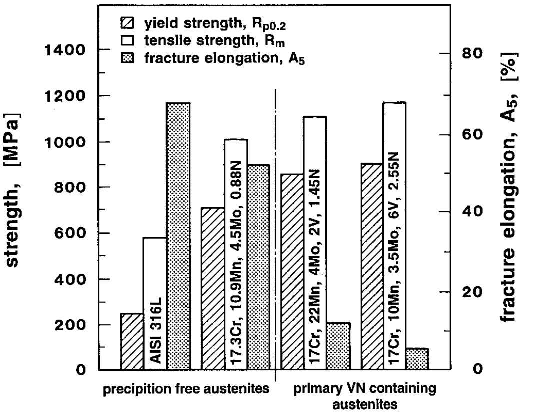

Fig. 1: Mechanical properties of nickel free austenitic alloys containing primary nitrides.

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3.1.2 Second Alloy: Austenitic Iron Based MMC Containing Primary and Secondary Vanadium Nitrides

This important group of VN strengthened stainless steels are materials containing the above mentioned primary nitrides (Figure 2a) as well as an additional family of extremely small nitrides of 1-10 nm in size (Figure 2b). The secondary VN-hardening phase is formed when a hardening treatment (quench and temper procedure) is applied after consolidation.

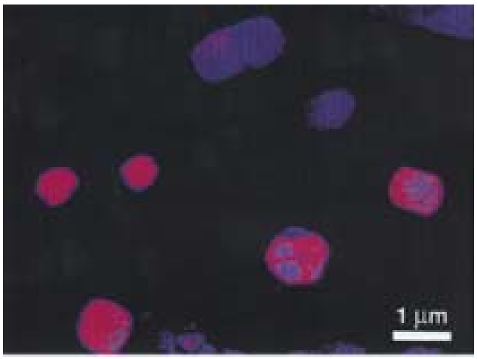

Fig. 2a: TEM-Image showing primary nitrides of µm size.

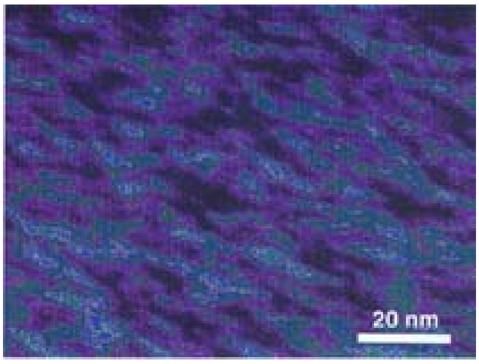

Fig. 2b: TEM-Image showing secondary nitrides of nm size.

The strengthening through secondary VN is illustrated in Figure 3. Compared with the material without secondary nitrides the yield strength was improved from 530 MPa to 880 MPa when hardened for 100 h at 600°C, while the fracture elongation was held above 15% - even after hardening. The toughness was measured using the impact test and it was found that the impact energy (ISO-V specimen) was reduced from 25J to 15J through ageing at 600°C.

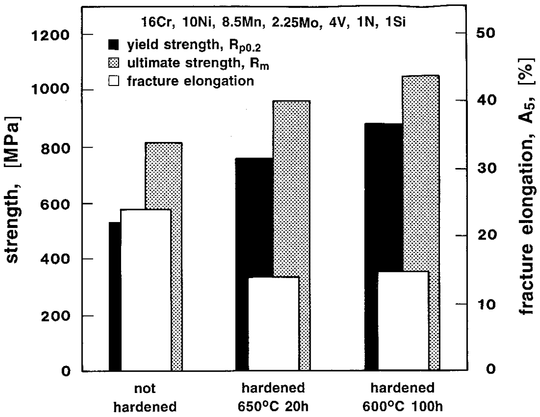

Fig. 3: Mechanical properties of the nitride hardened austenitic MMC with 4 wt-% of vanadium.

The effect of the nitrides on the high temperature strength is summarised and compared to commercial wear resistant stainless steels in Figure 4. The high thermal stability of the austenitic matrix strengthened through the primary and especially the secondary VN results in a high strength across the entire temperature range.

The wear properties of the new alloys were investigated on two different variations of the MMC; one containing 4 wt-% vanadium the other with 9 wt-% vanadium by means of measuring abrasion using the dry sand/rubber wheel apparatus (ASTM G-

65, B-611). Figure 5 illustrates that the higher the fraction of primary VN precipitate is, the higher the wear resistance is.

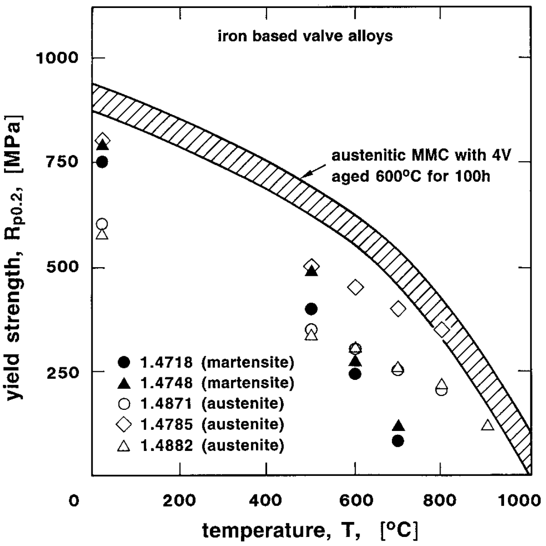

Fig. 4: High temperature behaviour of the hardened alloy with 4 wt-% of vanadium.

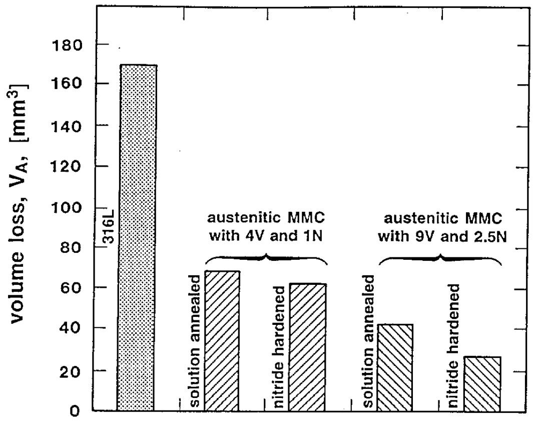

Fig. 5: Non-corrosive wear (ASTM G 65) of the austenitic MMC.

The corrosion resistance of materials containing secondary VN was tested on the alloy with 4 wt-% V containing 0.95 wt-% nitrogen using the pitting corrosion potential, E_p (Figure 6). In the solution annealed state the E_p-value was approximately 825 mV higher than that of both AISI 316L (795 mV) and AISI 304 (480 mV). The ageing of 600°C for 100 h and 650°C for 50 h decreased the value to 670 mV and 680 mV respectively, falling below the resistance against pitting corrosion of AISI 316L while still remaining above AISI 304.

3.1.3 Discussion of the Influence of Secondary, Nanometer Sized Nitrides

When consolidated the newly developed powders assigned for thermally sprayed protection coatings lead to an austenitic matrix combined with primary and secondary nitrides. The mechanical properties are characterised by a strong increase in strength and wear resistance. The EDX measurements showed that the formation of the secondary nitrides through ageing at 600 to 650°C did not lead to a segregation of the elements chromium and molybdenum. These elements are instrumental for the corrosion resistance of the material. The pitting corrosion behaviour of the hardened MMC therefore remain above that of alloys traditionally regarded to have a high pitting corrosion resistance. These materials may therefore be regarded as hardenable corrosion resistant austenitic iron based MMC.

3.2 Thermal Spraying of the New Material

These new kind of alloyed materials can be applied as a surface coating by thermal spraying following three different routes, as described in Figure 7. One of the most attractive way is the reactive spraying (Fig. 7, route 1) which saves one production step during the application. Therefore reactive thermal spraying is described more detailed. The second possibility (Fig. 7, route 2) is the most common way of coating application because of the easier process control of conventional thermal spraying. Conventional thermal spraying with a post annealing process (Fig. 7, route 3) is typically used with self fluxing Co-, and Ni-based alloys of relatively low melting point (temperature range: 1'000°C - 1'200°C). This post annealing process can influence the mechanical properties of the substrate negatively.

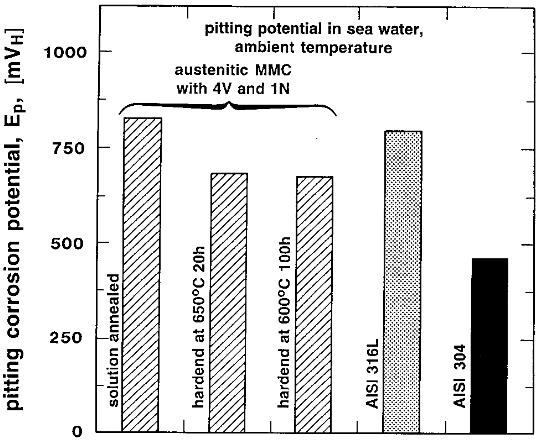

Fig. 6: *Pitting corrosion behaviour of the alloy with 4 wt-% vanadium.*

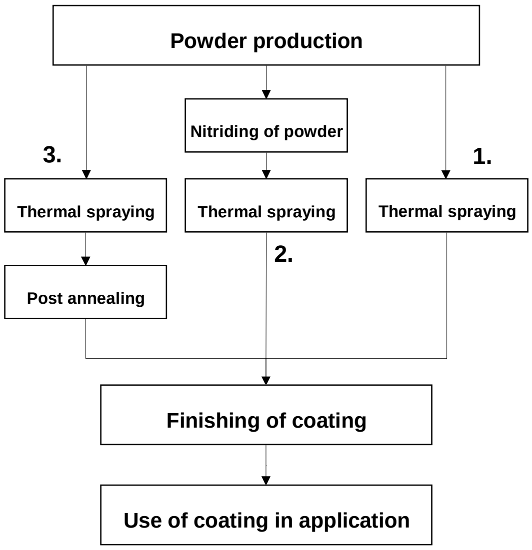

Fig. 7: Three routes of coating application by principle:
1. Reactive thermal spraying,
2. Conservative thermal spraying of preliminary nitrided powder,
3. Conservative thermal spraying and post annealing.

The reactive thermal spraying process itself (Fig. 7, route 1) can be performed in three different ways. All techniques of thermal spraying have been used for reactive spraying. The most efficient and promising way was the reactive plasma spraying using a vacuum plasma spraying (VPS) equipment. The VPS-process offers the advantage of a wide field of parameters which comprehends all of the parameters of the other spray techniques. Furthermore the VPS-process is performed in a chamber which offers the possibility to spray a Fe-based coating without oxides resulting in an improved corrosion resistance.

The reaction with nitrogen during spraying can take place
- during the flying of the spray particles in an Ar/N_2-rich plasma,
- using N_2 as a powder carrier gas or
- by creating a N_2-rich environment in the VPS-chamber or at least near the substrate.

To clarify the basic efficiency of the nitrogen absorption all three above mentioned types have been carried out. The results have shown that the most efficient way of N_2-alloying was the use of an Ar/N_2-plasma. The nitrogen content of the coatings obtained this way are presented in Figure 8 as a function of spray powder grain size ranges and of the total electric input-power (EPI) to the plasma, which could be varied by the Ar/N_2-composition and the plasma current.
When spraying the powder of -90+45µm, the increase in N_2-content in the coating with respect to EPI is marginal as compared with spraying finer powders. While spraying with an EPI of P_c = 44.8kW the resulting N_2-content of the fine fraction with -25+5µm is close to the maximum value reached in this experiment. Changing the EPI

from P_c = 44.8 to 46.8kW using the -45+25µm powder yields a dramatic increase in the N_2-content of the coating from about 1 wt-% to more than 3 wt-%.
The particles of the finest size range (-25+5µm) could reach their maximum heat up at an EPI slightly above P_c = 44.8kW, as indicated by the high N_2-content of the coating close to the maximum value reached. The maximum N_2-content of about 3 wt-% in a coating can only be achieved spraying with the medium size range (-45+25µm) with the maximum power during this experiment.
The basic knowledge about the influence of the spray powder grain size range on the resulting coating properties was an important point of view to manufacture an available spray powder for the different processes used by the industrial partners. The up-scaling of powder production for the required amounts used for the field tests was successfully done to an industrial powder supplier during the project.

Usually the weight loss or volume loss versus wear length or time is used to demonstrate the wear behaviour as a function of different spray parameters or different coating materials. Presenting the wear rate (volume loss) as a function of the hardness provides the advantage of a general overview in the wide field of wear behaviour of different materials and coatings in comparison to each other. The N_2-content is the primary property of the coating and therefore influencing all of the other properties of the coating like wear or corrosion resistance. At this point of investigations the results of the austenitic and the martensitic coatings are given in the range from 0% up to the maximum nitrogen content, with which the maximum hardness have been achieved in this study.
An increasing nitrogen content of the coatings yields an increasing hardness and amount of precipitations and wear resistance, as shown in Figure 9. The improvement of the wear resistance of the austenitic coatings is superior compared to the martensitic coatings. With the maximum nitrogen content the wear resistance of both types of coatings is similar. In general, it was found that the wear resistance increases with the hardness up to value of about 800HV. A further improvement of wear resistance could be only achieved by a reinforcement of the coating by hard phases or precipitations. At this stage of investigations the wear resistance of the developed Fe-based coatings is comparable to an atmospheric plasma sprayed (APS) Al_2O_3-coating and the galvanic chrome plating, as shown in Figure 9.

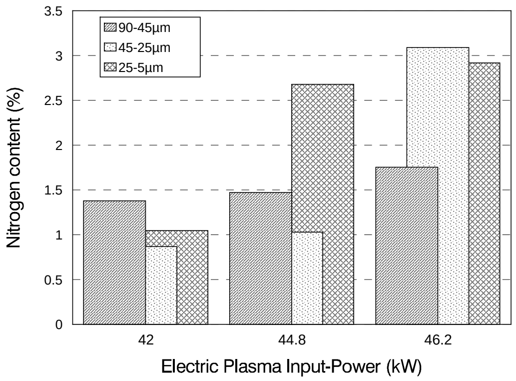

Fig. 8: N_2-content of reactive VPS-coatings as a function of the EPI using the Ni-free austenitic alloy in different powder size ranges (see legend).

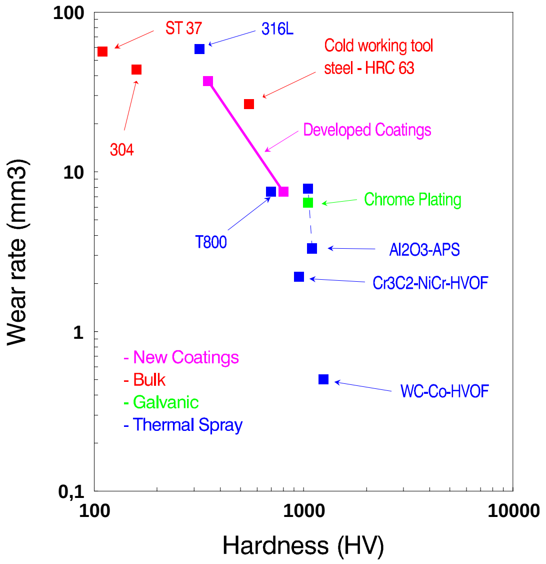

Fig 9: Volume loss rate according ASTM G75 test method of the investigated coatings and bulk materials as a function of their hardness.

These results demonstrate that the wear resistance is not a function of the hardness of the coatings and bulk materials alone. This could be an important fact in future if thermal sprayed coatings are used to replace other coatings like hard chrome plating.

3.3 Additional wear tests with dry sliding on competitive coatings

The additional wear testing of standard coating materials like WC-17Co, Al_2O_3, hard chrome plating and NiCrBSi had been performed on a ball-on-disc machine at EIV. The ball material was hardened steel 100Cr6 for all the tests. While the wear mechanism in the steady state condition was about the same for all five disc materials tested, i.e. substrate steel 100Cr6, WC-17Co, alumina, hard chromium and NiCrBSi, and consists of abrasive-oxidative wear, the wear type at the beginning of the tests was of four different kinds:

1) adhesive wear associated with material transfer from the ball to the disc,
2) adhesive wear with material transfer occurring simultaneously to the disc and to the ball,
3) microcutting and material transfer from the ball to the disc and
4) adhesive wear with material transfer from the disc to the ball.

Figure 10 shows the total wear volume (of the ball plus the disc) per unit sliding distance W_{total}/s. Figure 11 shows the friction coefficient f as a function of the load using a constant sliding velocity of 0.42 m/s. The wear volume increases significantly with increasing load. The alumina coating leads to the best wear results. The highest wear rate was obtained for the WC-17Co coating, due to the strong microcutting effect induced by the carbides at the beginning of the wear process. On the other hand, the hard chromium leads to the lowest values of the friction coefficient for all applied loads, the NiCrBSi coating to the highest ones.

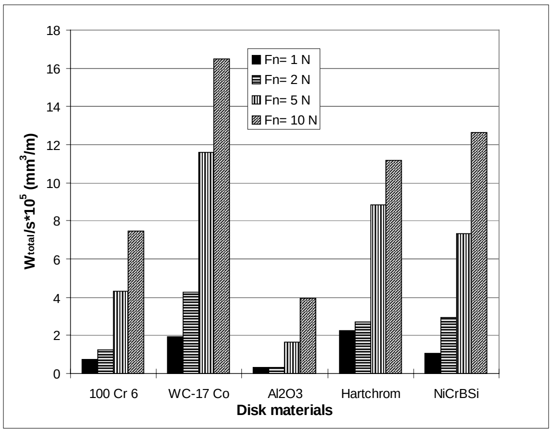

Fig 10: Comparison of total wear losses of different disk materials, e.g. hardened steel 100Cr6, uncoated and coated by WC-17Co, Al2O3, hard chrome or NiCrBSi (v= 0.42 m/s).

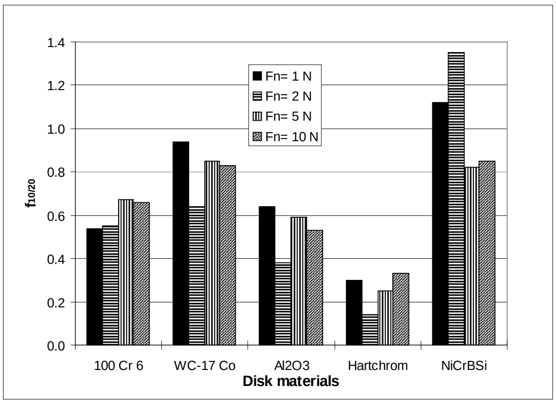

Fig. 11: Comparison of friction coefficient f10/20 of different disk materials, e.g. hardened steel uncoated and coated by WC-17Co, Al2O3, hard chrome or NiCrBSi (v= 0.42 m/s).

3.4 Corrosion tests

To characterise the corrosion behaviour of the coatings electrochemical measurements and salt spray tests according ASTM B117 and DIN 50021 have been carried out (Figures 12a-c).

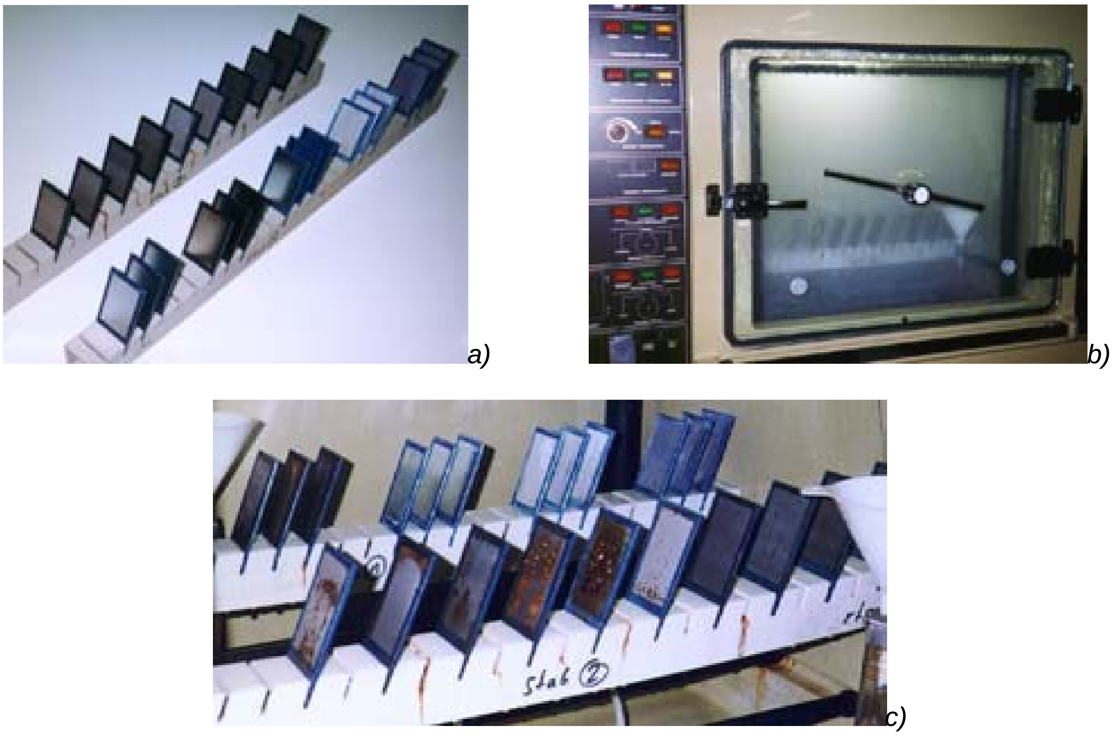

*Fig 12: Different coated samples a) **before**, b) **during**, and c) **after** salt spray testing.*

Beside the pure corrosion resistance of the bulk materials, phenomena's like corrosion between coating and substrate due to porosities (Figure 13a) have been studied to improve the density of the coatings and final corrosion resistance (Figure 13b).

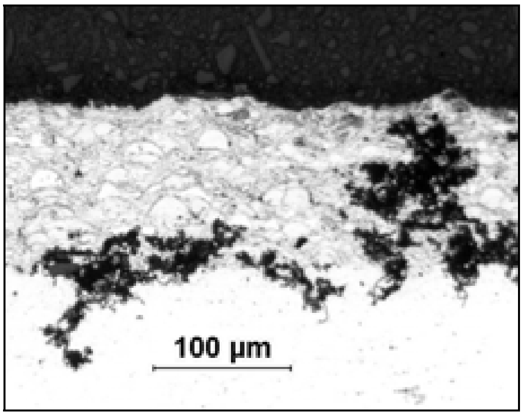

Fig. 13a: Example of corrosion marks between relatively porous coating and substrate after salt spray test (from top to bottom: epoxy, coating, steel substrate).

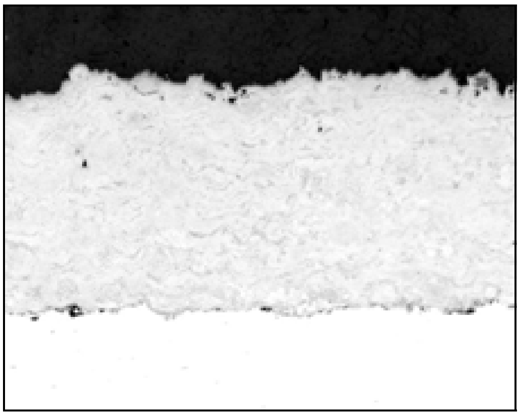

Fig. 13b: Example of a vacuum plasma sprayed dense coating (from top to bottom: epoxy, coating, steel substrate).

Polarisation curves

Potentiokinetic polarisation curves of the standard stainless steel AISI 304 as well as the WC-17Co, the Al_2O_3 and the hard chromium coatings show that the alumina and the hard chromium coatings remain passive in the solutions of pH 3, 5, 7 and 9 (the latter for hard chromium only) without and with NaCl, while the stainless steel 304 is

passive in all solutions without NaCl, but shows pitting in the NaCl containing solutions. The WC-17Co coatings show by far the worst corrosion resistance of all the materials tested. Potentiokinetic polarisation curves of coatings of the standard stainless steel AISI 316L as well as three stainless steels newly developed at the ETHZ were determined in solutions of pH 3, 5 and 7, without and with 3 wt-% NaCl.
The accelerated immersion tests were performed in a solution with pH 1 without NaCl and at a temperature of 50°C. The materials tested were the substrate steel 100Cr6 as well as the WC-17Co, the alumina and the hard chromium coatings. The corrosion rate has been determined by the chemical analysis of the metallic ions in the solution as a function of time. The low corrosion resistance of the WC-17Co coatings as shown by the polarisation curves have been confirmed in the immersion tests. The corrosion rate of the alumina coating is faster than that of the hard chromium, but still significantly lower than that of the WC-17Co.

3.5 Field tests

Several machine parts of the industrial project partners have been coated (e.g. Figure 15a-c) for increasing the service life time of the components and to show the potential of those coatings known from laboratory measurements now in field tests.

Fig. 15a: Slurry pump elements (top: as sprayed, bottom: finished)

Fig. 15b: Rope rollers and guidance for trucks

Fig. 15c: High pressure cylinder during internal coating.

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The advantages opened further applications for this new coating materials. Basically these alloys exhibit a:

- lower price compared to Ni- or Co-based alloys,
- easier machineability than cermets and
- higher spray rate and deposition efficiency than ceramics.

These materials bridge the gap between the mainly pure corrosion protection coatings (e.g. Al, Zn, etc.) and the pure wear protection coatings combining both advantages.

3. Synergies (cooperations)

The synergies between the project partners lead to a further collaboration for evaluating other applications now available through the exceptional characteristics of those coatings. The involved coating shops and their clients offered good opportunities for testing these coatings to compare them to conventional ones. These connections lead to a larger group of interested persons and companies giving a reliable and vast knowledge out of the field experiments.

In other fields like conventional galvanising, thermally sprayed coatings can give additional advantages, as shown during the project.

4. **Present or foreseeable impact** on the market position/situation of the industrial partners

In case of internal thermal spraying for chambers of high pressure tank guns **(confidential!)** it will take additional investigations until a product will be available on the specific market. This additional development will be done separately after the completion of the WF-PPM project because of the specific interest on this application.

For the coating shops this new powder offers a potential tool replacing a lot of other „conventional“ powders used before. The advantage of an inexpensive material and the simultaneous wear and corrosion resistance opens a wide field of potential applications. The ongoing tests show that these new type of coatings will not only be restricted to the allocated applications. Many possible partners showed interest in this development for their products requiring high wear and simultaneous corrosion resistance. Further applications in printing and chemical industry, environmental technology, and other areas will profit from these investigations. Further tests have to prove the reliability of these coatings in vast field tests until other products can be realised.

5. **Impact** of the project on Swiss research and Swiss economy

This project demonstrated within three years the transferability of basic materials research and development to an industrial production level. Materials knowledge at university level combined with industrial demands lead to some exemplary applications within this time frame. Beside those first field tests further confirmations have to be received until a noticeable impact on the Swiss economy can be seen in the near future.

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6. **Position and distinctiveness** of this research on the Swiss and international scene (before and after the project)

The activities in this project have been unique in the Swiss -, and international scene. Usual particle reinforced thermally sprayed coatings like e.g. WC-Co consist of many micron large particles. As it is known that with decreasing size of hard phases the wear rate decreases, this new type of coating brings together both advantages.

To continue with the competitiveness of the project partners in the market, patent claims have been made for the newly developed materials as well as for the processing and application of those coatings.

7. **Outlook, future work** (*e.g.* academic or industrial research, networks, follow-up projects, products, start-up companies etc.)

Out of this ending collaboration smaller project groups will be formed focused on specific questions. The academic materials research on precipitations will of course be continued at ETHZ, where the profound knowledge on nitrided steel is a research topic for many years. EMPA will continue accompanying the extensive field tests done at their own place and at the job shops within new projects. Knowing more about this new kind of coating material through broad tests, confidence will be given for other applications where profound reliability is requested. Therefore new field tests with other companies are under investigation.

8. Comments on this report

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9. List of

- publications, broken down among following categories :

\- proceedings with peer review

[1] Bähre, W.-F. u. C. Solenthaler, et al.: **Hardenable Austenitic Iron Base Metal-Matrix-Composites**, Proceedings of PM Tech '97 (1997), p. 12.
[2] Brandt, O. C. u. S. Siegmann, et al.: **HVOF- and VPS-Coatings Using Nanostructured Iron-Based Alloys**, Proceedings of 1st United Thermal Spray Conference - Thermal Spray: A United Forum for Scientific and Technological Advances (1997), p. 875-876.
[3] Brandt, O. u. S. D. Siegmann: **VPS Coatings Using Nanostructural Iron-Based Alloys**, Proceedings of 15th International Thermal Spray Conference - Thermal Spray: Meeting the Challenges of the 21st Century 2 (1998), p. 1249-1253.

\- theses

[1] Bähre, W.-F.: **Metallurgical and Technological Advances in Powder Metallurgically Produced High Nitrogen Austenitic Iron Based Materials** - No. 12478, Institute of Metallurgy (1997), p. 125.

- other (*e.g.* talks, posters at conferences, …)

  [1] Bähre, W.-F. u. C. Solenthaler, et al.: **Hardenable Austenitic Iron Base Metal-Matrix-Composites**, PM Tech '97, Chicago, USA (1997).
  [2] Brandt, O. C.: **HVOF- and VPS-Coatings Using Nanostructured Iron-Based Alloys**, 1st United Thermal Spray Conference (1997).
  [3] Brandt, O.: **VPS-Coatings Using Nanostructural Iron-Based Alloys**, 15th International Thermal Spray Conference - Thermal Spray: Meeting the Challenges of the 21st Century (1998).
  [4] Brandt, O.: **Ausscheidungsverstärkte Schichten aus Eisenbasislegierungen im Vergleich mit konventionellen Schichtsystemen**, EMPA Seminare (1998).
  [5] Brandt, O.: **Ausscheidungsverstärkte Eisenbasislegierungen als thermisch gespritzte Schicht: Herstellung und Eigenschaftsprofil**, 44. Metallkunde-Kolloquium - Werkstoffe: Einsatz und Entwicklungstendenzen (1998).

- patents

  [1] CH-Patent pending
  [2] EU-Patent pending

- spin-offs, broken down among following categories :
- products on market
- companies (start-ups)
- projects
- results (by-products)
- other

- awards and prizes

Best paper award for:
Bähre, W.-F. u. C. Solenthaler, et al.: **Hardenable Austenitic Iron Base Metal-Matrix-Composites**, Proceedings of PM Tech '97 (1997), p. 12.

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