# APPLICMA

## Final Report

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# SCOPE OF THE DOCUMENT

This document gives an overview of work performed within the appliCMA project which was divided into 6 workpackages WP0 to WP5. Main findings of each workpackage are described in periodic reports.

Following partners were involved in the appliCMA – project:

| Benef. no. | Beneficiary names | Beneficiary short names | Country | Date enter Project | Date exit Project |
|---|---|---|---|---|---|
| 1 Coord | Austrian Institute of Technology | AIT | Austria | 1 | 22 |
| 2 | Centre National de la Recherche Scientifique | CNRS | France | 1 | 36 |
| 3 | Eidgenössische Materialprüfungs- und Forschungsanstalt | EMPA | Switzerland | 1 | 36 |
| 4 | Technical Universität Wien | TUW | Austria | 1 | 36 |
| 5 | Jozef Stefan Institute | JSI | Slovenia | 1 | 36 |
| 6 | E.O. Paton Electric Welding Institute | EWI | Ukraine | 1 | 36 |
| 7 | Politecnico di Torino | POLITO | Italy | 1 | 36 |
| 8 | Slovenian Tool and Die Development Centre | TECOS | Slovenia | 1 | 36 |
| 9 | Genta-Platit | Genta-Platit | Italy | 1 | 36 |
| 10 | Gammastamp | Gammastamp | Italy | 1 | 36 |
| 11 | Warsaw University of Technology | WUT | Poland | 1 | 36 |
| 12 | Wolframcarb | Wolframcarb | Italy | 1 | 36 |
| 13 | Innovation Works R&D | EADS | Germany | 1 | 36 |
| 14 | Ernst Wittner GmbH | WITTNER | Austria | 1 | 36 |
| 15 | University of the Federal German Armed Forces | UniBw | Germany | 1 | 36 |
| 17 | International Tool Consulting & Management | TCM | Austria | 1 | 36 |
| 18 | LKR Leichtmetallkompetenzzentrum Ranshofen GmbH | AIT-MOBILITY | Austria | 1 | 36 |
| 19 Coord | Aerospace & Advanced Composites GmbH | AAC | Austria | 23 | 36 |
| 20 | RHP-Technology GmbH & Co KG | RHP | Austria | 23 | 36 |

(Please note: number 16 is missing as the foreseen partner IMPOL did not enter the project, and the number was blocked by the GPF-system. This partner was replaced by LKR.)

In the following chapters the main findings in the appliCMA project from each partner are described.

# 1 EXECUTIVE SUMMARY

The project "Development of wear resistant coatings based on complex metallic alloys for functional applications – appliCMA" aims at the development of a new type of coatings based on Complex Metallic Alloys (CMA). This is a family of ternary and quaternary alloys which exhibit unexpected properties. The CMAs "Al1.5Cu25.3Fe12.2B"1 and "Al59.5Cu25.3Fe12.2B3" consist mainly of metals, which show not metallic- but ceramic-like behaviour. Moreover, the bulk versions of these quasicrystals have proven outstanding properties as extremely low surface energy (wetting) and highest fretting wear resistance. The CMA AlMgB14 is known to be the hardest material after diamond.

Before the appliCMA project, these outstanding properties could not be realised as coatings. First trials to develop such coatings were not successful. The appliCMA project focused on the development of PVD deposited coatings based on these well-specified compositions. Following the mentioned outstanding properties of the 3 CMAs, the project was driven by applications for which they offer a remarkable step forward: tools for cutting, forming, extrusion dies, moulds for injection moulding, coated cooker's oven for less sticking, fretting resistant coatings for aeroplanes, but also coatings of stamps for "Nano-Imprint-Technology (NIL)".

The project was started with "lab samples" tested in lab facilities and ended with demonstrators tested in application related tests by end users. The project studied also fundamental mechanisms of the phase transitions in the manufacturing process of the targeted coatings, friction on these materials and simulation of friction in the forming applications.

The project was divided into 5 workpackages: WP1 was focused on development of coatings, WP2 on optimisation of coatings and deposition processes, WP3 on industrialisation and WP4 on applications. WP5 (fundamentals and simulations) started at the begin lasted over the whole project and was carried out in parallel in order to assist and improve the coatings development/optimisation, to characterize by fundamental analysis the produced coatings, and to support the tests technology and the HVOF process by simulation tools.

At the end of WP1 two decisions concerning deposition of quasicrystal layers were done. Firstly, to stop AlMgB14 and secondly, to stop multilayer deposition due to cracking and hollows layers. Only AlCuFeB coatings deposited at high temperature has been considered within WP2, which was optimising the coating process (assisted by results from WP5) showing the temperature required for proper ico-phase formation. Also the process itself could be fixed: deposition has to be done at high temperature, all kinds of post-annealing led to delamination of the coatings. Thus, no coatings were deposited at room temperature anymore (for which post annealing is needed).

WP3 was started with manufacturing of a target for commercial coating device at GENTA. Due to the sizes required, not one full target was made, but one consisting of "tiles". After first un-successful trials it was decided to refurbish the target by partners. POLITO and EADS tried to close gaps between the "tiles". However, these trials were stopped as the gaps could not be closed. Hence, GENTA could not take over the coatings of demonstrators. Thus, JSI was asked as backup-partner for coating, as they had setup a job coating centre. RHP manufactured new tiled targets, and JSI reported successful deposition of coatings consisting of beta- and ico-phase.

WP4 was started with manufacturing of demonstrators. Following the decision for the coating at JSI and the finalised optimisation of coating process by WP2, JSI started coating of demonstrators. Additional, demonstrators with thick coating were processed by EWI, and EADS produced demonstrators by HVOF.

Demonstrators were coated by TUW, EWI, JSI and EADS with AlCuFeB coatings (drills, mills and cutting inserts from TCM, extrusion dies from LKR, injection moulds from Wittner, punches for forming tribometer from AAC, injection moulds and forging dies from Tecos, punches from Gammastamp, bolts and an original landing gear part C-160 from EADS. All coated parts were tested by EMPA, WUT AAC and TCM on their performance in comparison with industry standard coated tools and with uncoated tools.

➔ Testing of demonstrators showed that CMA coatings improved the performance of demonstrators compared with uncoated tools and with commercial coated tools.

# 2 COORDINATOR – AIT & AAC

AAC (former AIT) was coordinator of the appliCMA project. Technically, AAC was also involved in all workpackages. AAC did analysis of coatings by lab-testing (friction, fretting tests), application testing (forming tribometer tests) and microstructure analysis (SEM, EDS, FIB) on the one hand and fundamental investigations on the other hand.

With lab-testing and microstructure results of coated lab-samples the best candidate coatings were selected for industry coating of tools and landing gear parts. Only AlCuFeB compositions exhibited good behaviour. These coatings were also micro-structurally analysed at AAC before and after field tests of end users.

AAC did application tests with respect to the vacuum suitability of 9 different coatings form JSI, which were used also for tools coating. Friction and fretting tests (both under vacuum) were performed. With SEM/FIB/EDS a detailed post test analysis was done. All samples exhibited a mean friction coefficient between 0.2 and 0.3 under vacuum, which is comparable with best CMA coatings of WP2. Regarding the fretting tests, 4 coatings are in principle suitable for tribological use under vacuum, one of them for longer time.

➔ It was found that CMA coatings improved the performance of demonstrators compared with uncoated tools.

Prof. Belin-Ferré investigated the Al electronic structure in various samples tested within the project in order to check if the electronic properties of the coatings depart or not from those of quasicrystal bulk specimens. Indeed, previous investigations on a large number of quasicrystals, approximants and related crystalline alloys have pointed out that the intensity of the Al 3p electronic distribution at the Fermi level with respect to pure fcc Al reflects the metallic character of the specimen under study (electrical resistivity for instance) and is also related to wetting with respect to pure water. Data on friction in vacuum suggests that there is also a direct relationship between friction and the intensity of Al 3p states at EF.

➔ All coatings investigated by Prof. Belin-Ferré exhibit intensities at $E_F$ that makes them comparable to good quasicrystals and approximants. The EADS coatings were the best ones with respect to electronic structure.

# 3 CNRS

During the period M12-M18, CNRS has successfully prepared i-Al-Cu-Fe-B coatings on silicon and hard metal substrates exhibiting a stoichiometry very close to $Al_{59.5}Cu_{25.3}Fe_{12.2}B_3$ (at%).

The residual stress in Al-Cu-Fe-B quasicrystalline thin films deposited by PVD on a Si(100) substrate at 560 °C using both X-ray diffraction and curvature methods was investigated. It was found that films are under tensile stress, leading to the formation of cracks and subsequent partial delamination of the film with increasing film thickness. The stress value determined by the curvature method before the appearance of cracks is close to those measured by the modified $\sin^2\psi$ method and amount approximately to 1.1 GPa. An estimation of the thermal stress component induced by the mismatch of TEC between substrate and film suggests that thermal stress is the dominant component of internal stress. Finally, the energy release rate of the channeling crack was estimated corresponding to a fracture toughness of the quasicrystalline film of about 1.7±0.4 $MPa\sqrt{m}$ . This work suggests that other substrates having a TEC close to that of the Al-Cu-Fe-B quasicrystalline phase should be preferred in the future to reduce the internal stress in the films. Stainless steel substrate is an attractive candidate in this respect if interfacial diffusion can be overcome.

Coatings from EWI, TUW and EADS were also investigated. All coatings exhibit intensities at EF that makes them comparable to good quasicrystals and approximants. However, from both investigations on 3s,d and 3p spectral distributions, the two investigated EADS coatings appear not sensitive to oxidation and in addition their Al 3p intensity at EF is of the same order of magnitude as values observed elsewhere for good quasicrystals, CNRS conclude the EADS coatings are the best ones among those they studied within appliCMA.

# 4 EMPA

Theoretical and experimental investigation of the atomic surface structure and the (local) electronic structure of complex metallic alloys (CMAs) and quasi crystals (QCs) was performed by EMPA. Goal of the investigation was to find a correlation between of the local electronic structure and macroscopic properties of this materials in particular with the electric properties and the for metals unusual surface energies making this class of materials promising for triobological applications. The main experimental tools used to investigate the surface and electronic structure was Photoelectron-Spectroscopy (XPS, UPS), Angle Resolved Photoemission-Spectroscopy (ARPES), X-ray Photoelectron-Diffraction (XPD), and high resolution Scanning Tunnelling-Microscopy (STM) and -Spectroscopy (STS). In the project the surfaces of two families of CMAs were investigated. One was the AlNiCo family with which the surfaces of 2-fold d-AlNiCo, 10-fold d-AlNiCo, and Y-AlNiCo was investigated. The other one was the AlPdMn family with which the surfaces of 5-fold i-AlPdMn, ξ'-AlPdMn and as reference that of pure Aluminium (Al (111)) was investigated.
One very important question which arises when investigating the electronic structure of CMAs surfaces is whether the surface is bulk truncated and reflects therefore bulk structure related physical properties or if the surface structure undergoes reconstruction. A first set of experiments revealed that the investigate CMAs exhibit atomic surface structures corresponding to densest atomic planes of the associated bulk model.
The investigation of the local electronic structure of the d-Al-Ni-Co quasicrystal and its approximant Y-Al-Ni-Co has shown that the Local Density of States (LDOS) in CMAs is affected much more by the complex local atomic arrangement on the scale of nearest neighbours than by a long-range ordered quasiperiodicity.
An STS study was performed to explore the origin of the remarkable electrical resistivity of CMAs. For that a new normalization method for STS data has been implemented to reveal the DOS of materials possessing a wide pseudo gap at $E_F$. A clear correlation between STS measurements of the LDOS and the electrical resistivity could be found. This result indicates that the interaction between valence electrons and the local complex local atomic arrangement plays a significant role on the macroscopic measurable electrical resistivity.
For the first time the electronic band structure of a CMA has been calculated by Tight Binding Modelling. This calculation showed that the observation of a band-like behavior of the *s-p* and *d* sates in CMA or QC, by Angel-Resolved Photoemission Spectroscopy (ARPES) (as reported in literature), cannot be associated directly to free electron like bands as in the case for “good” metals. This because ARPES does not yield, as generally accepted, in a directly information on the nature and *k*-dependent dispersion of electronic states, as demonstrated for the first time by our strict interpretation of the photoelectron emission process and our tight binding calculation of the electronic structure in case of d-AlNiCo.

In addition to the fundamental investigations on the electronic structure of CMAs, Empa has measured the roughness, thickness, micro-hardness and E-module of CMA-coatings from TUW, JSI, EWI and EADS.

# 5 TUW

TUW as “research coater” coated more than 100 samples and cutting inserts during the project by means of PVD. On the 2nd hand, TUW did investigations on influence of deposition power, working distance, substrate temperature, working gas pressure and bias voltage on the coating performance. With the findings optimised deposition parameters for deposition of AlCuFeB coatings on different substrates (epitaxial Si, hard metal WC-Co, steel K600, steel K890 and ceramic Al995) could be determined. The Adhesion of the AlCuFeB coatings was found to be very good for all substrates except Si. Within the error of measurement, the chemical composition of the coatings is independent on the substrate material and in average: 59.7 ± 2.6 at% Al, 27.3 ± 2.0 at% Cu and 10.0 ± 0.8 at% Fe. The O content is about 7 at% and the C content about 6 at%. Investigations of the microstructure of the coatings by Transmission Electron Microscopy revealed that they can be considered as nanocomposites of quasycrystalline grains which are embedded in an amorphous matrix.

This special microstructure may be responsible for the very promising mechanical, tribological and adhesive properties of the PVD deposited coatings which could be shown in first tests on cutting inserts and Nanoimprint Lithography (NIL) moulds.

# 6 JSI

At beginning of the appliCMA project it was planned that JSI acts as "research coater" for coating of multilayers. JSI has deposited multilayers with the overall stoichiometry $AlMgB_{14}$. After post-annealing, the multi-layers homogenisation was well advanced, but not fully completed. High oxygen content was found in the coatings too. After WP1, it was decided to stop multilayer and AlMgB14 deposition. In meantime, JSI had set up a new coating apparatus capable of depositing CMA directly in their job-coating centre and was asked in Dec. 2010 to act as second industrial coater for deposition AlCuFeB coatings on demonstrators and tools. Therefore, all planned effort for JSI in WP5 was also switched to WP3 and WP4 (for coating of demonstrators and tools).
JSI coated as "industrial coater" successfully demonstrators like forging dies, injection moulds and punches. The following tools were also coated successfully by JSI: 28 punches, 12 mills, 10 cutting inserts, 8 drills, 6 injection moulds, 4 mills and an extrusion die.

# 7 EWI

EWI as “research coater” coated 40 discs and mills, punches, moulds and extrusion dies during the project.

Different interfaces were integrated because diffusion barrier play a very important role especially for Hard Metal and W – containing steels.

EWI performed investigations on the influence of substrate temperature on roughness and microstructural characteristics of coatings, phase transformations at their heating and analysis of the factors influencing the cracking susceptibility and coating delamination from the substrate. X-Ray diffractometry and transmission electron microscopy were used to show that with lower substrate temperature the crystallites are refined, and their size can reach nanoscale. It is established that at heating of such coatings a cascade of phase transformations takes place, which is completed by formation of a quasicrystalline structure at temperatures above 700 °C. Addition of boron atoms to Al-Cu-Fe alloy precipitations form on grain boundaries, which are assumed to be $AlFe_2B_2$ borides. Substrate temperature affects not only the microstructural characteristics of quasicrystalline coatings, but also coating surface roughness. A change of growth texture of quasicrystalline phase grains is also observed. It is assumed that the change of coating roughness can be due to the change of crystallite growth texture. Important aspects in practical terms are preservation of coating integrity and high strength of adhesion to the substrate. Proceeding from earlier conducted research, it was established that in a number of cases the coatings have cracks or delaminate from the substrate (s. Del231). It is shown in the study that in the case of brittle coatings a “critical thickness” exists, at which cracking is a stress relaxation mechanism, advantageous in terms of energy, for stresses due to a difference between linear coefficients of thermal expansion of the coating and substrate. Conducted calculations were the basis to determine the critical values of coating thickness, which eliminate cracking and their comparison with experimental results was performed. It is shown that application of buffer layers does not lead to any significant increase of critical thickness of coatings; however, it allows lowering the probability of their delamination from the substrate.

# 8 POLITO

Within WP2, POLITO has investigated 6 coatings deposited by TUW with scratch tests, Micro- and Nano-hardness and wear testing. With all samples the same types of cracks were observed, which are typical of brittle materials. It's a combination of Chevron and Hertzian cracks, leading to complete fracture of the coating.

Cutting tests of mills on AISI 1045 steel have been performed by POLITO within WP3 and WP4, (I only loaded MM and costs to WP3. I don't remember to have participated to the WP4 report. Can we skip WP4 here?) in order to explore the performance of the quasicrystal coatings. The cutting tests have been carried out in milling, with two cutter mills, 10 mm in diameter, with cutting speed ranging between 100 and 200 m/min.

The results show that the quasicrystal behaviour is taylorian, in terms of tool life vs. cutting speed. Further, wear analysis shows that the coating is almost completely worn away at the end of the cutting tests.

➔ However, it can be pointed out that the quasicrystal coatings improve tool performance with respect to the uncoated tools.

➔ Compared with commercial coating, the quasicrystals do not perform better at low cutting speed, whereas at high cutting speed (200 m/min) they perform better in terms of tools life.

➔ Performances in terms of surface roughness and hardness do not show significant differences with respect to the uncoated tool and to the commercial coating.

Within WP5, POLITO simulated the metal cutting process. Fundamentally, metal cutting process has being considered as a deformation process where deformation is highly concentrated in a small zone. Thus, chip formation in milling process has been simulated using Finite Element Method (FEM) techniques developed for large deformation processes. The main advantage of using such an approach is to be able to predict chip flow, cutting forces, and especially the distribution of tool temperatures and stresses for various cutting conditions. However, material flow characteristics, or flow stresses, at high temperature and deformation rates are required to make predictions with FEM-based simulations.

In this project, simulation of end-milling process has been performed by using FEM-based commercially available software, Deform-2D, which makes use of an implicit Lagrangian formulation.

Simulations were carried out in the same conditions of experimental tests conducted at POLITO, for dry lubrication condition. In particular, milling operations were performed on an AISI 1045 steel specimen with rectangular shape (50X50X260 mm), in down-milling direction.

A comparison between experimental and numerical forces, in terms of minimum and maximum Fx and Fy for all investigated cutting speeds show that the forces are always in the same range. A general effective prediction of forces is given by the numerical model. Errors in the prediction are mainly related to the simplification introduced with 2D simulation and to the difficulty to model correctly contact conditions at the chip-tool interface.

# 9 TECOS

TECOS' role in the project was to transfer all the gains and scientific breakthroughs to the industry and practical applications.

The first task was to gather data what are the specific needs of individual end user of hard metal coatings. After checking the competences and data provided by other project partners it was established that the requirements for cutting tool are well known but data for polymer processing and metal forming tools are missing. Therefore special emphasis was given to the data from forming processes.

In the second task TECOS concentrated for the preparation of the testing tools and the testing procedures. The drawings for the injection moulding testing mould were done together with the selection of the material and the testing procedure. Similar was done also in the field of hot forging. A procedure from the industry was taken, where many problems with the surface failure of the punch and die were arisen. With the new coating that will be developed in the scope of the appliCMA project this problem will be hopefully solved.

In the third task TECOS real injection moulding and hot forging was done to compare the behaviour of new coating to the existing classical ones. For the injection moulding four different set up of cavities were prepared: one with reference TiAlN coating, one with AlCuB double rotation coating and one with AlCuB triple rotation coating. One was left empty for the benchmarking. 30.000 test runs were made and then inserts were sent to JSI for final evaluation. There optical and topographical measurement all the surfaces were performed. The final conclusion is that AlCuFeB coatings are comparable with classic TiAlN coatings.

at hot forging In order to evaluate the new coating punches several different coatings were deposited for testing. Because there are already solutions with classical coatings, it was imperative to prepare also test pieces with this kind of coating in order to objectively evaluate new quasi-crystal coatings. The results clearly showed that the new coatings have great advantages over the existing one because in case of thick coatings they more than double the number of forged pieces.

# 10 GENTA-PLATIT

Within WP3 it was planned to develop and manufacture target(s) for the industrial coater GENTA. This was finalised in autumn 2010. GENTA performed coating trials on this target, but had to stop due to malfunction (reported in minutes of meeting Dec. 2010). It was then decided to repair this target: using plasma spraying process (EADS) the gaps should be filled. This was done until Mar. 2011: then the re-coated target was re-machined for proper surface. Here, again gaps appeared beneath the plasma spraying top coat. GENTA reported at Meeting M06 that even the repaired target cannot be used.

# 11 GAMMASTAMP

Gammastamp delivered punches to be coated by industrial coater within WP4 on the one hand and field tested coated punches and stamps with AlCuFeB and nano-structured coatings (TiAlSiN) on the other hand.

Results were good meeting the requirements of 90,000 strokes with the quasi crystalline system AlCuFeB. Excellent results were obtained with TiAlSiN coatings exceeding the 90,000 strokes state of the art number. A maximum of impressive 202,000 strokes were achieved.

# 12 WUT

Contact angle, anti sticking measurements of coatings were performed by WUT on the one hand, fundamental studies of coatings devoted for Nanoimprint Lithography were carried out on the other hand. Following criteria have been used to estimate the properties of the coatings:

- surface topography optimized looking for minimization of friction and adhesion in particular
- friction and adhesive , anti-sticking properties identified by pull-off force measurements
- nanowear resistance
- naoscratch resistance
- nanomechanical properties (nanohardness, Young`s modulus) studied by nanoindentation
- wettability: contact angle, surface energy.

WUT found out that CMA coating film is not enough for imprinting because the adhesion is little bit strong to for nanoimprint lithography. The adhesion is stronger than that of the sticking force between PMMA and the coating film, so the PMMA is peeled from the Si substrate. Next, at the 'hot embossing' to PMMA plate directory and measure the de-moulding force there were problems with the removal of the PMMA resist from the silicon substrate. More control of the surface energy of the CMA film is needed in the direction of its further decrease. However other important problems should be solved connected with the interface Si-CMA material of the coatings, its uniformity on the working walls of the Si moulds, mechanical interlocking and roughness problems should be taken into consideration in future studies. The general conclusion is such that the CMA coatings are very interesting candidates to be applied in NIL technology, however it needs further deep studies of the reasons of the partial failure and partial success of their application for NIL moulds.

# 13 WOLFRAMCARB

Wolframcarb produced hard metal mills, punches and rectangles to be coated with CMA by different coaters.

# 14 EADS

In the first half of the project, EADS was carrying out experiments to develop suitable coating parameters for a homogeneous coating process by use of two HVOF processes providing good adhesion to the substrate.

In the beginning feedstocks consisting of powder blends were deposited onto test samples unless Cristome F1 powder was available in sufficient amount. Furthermore an own powder charge was prepared and compared with the F1 feedstock. Two different HVOF techniques were investigated and the spray parameters optimized to achieve quasi crystalline coatings. The icosahedral phase was detected by XRD in the as-sprayed condition together with a beta phase. Latter disappeared after post heat treatment. Thus the pure ico phase remained in the coating. One HVOF technique comprised a liquid fuel while the other used a gaseous one. With the liquid fuel driven gun all test samples as well as the demonstrator parts were coated. Tribological tests carried out on test specimens revealed a good performance especially when the as sprayed samples were mechanically finished in a post step.

Within the project EADS tried to repair a sputtering target (filling of gaps using the HVOF spraying method).

EADS as the work package leader of WP4 has its main role in the second half of the project. It coated 20 bolts and an original landing gear part C-160 with CMA coating successfully!

# 15 WITTNER

Wittner produced two sets of injection mould demonstrators to be coated:

- 1 set (2 pieces) K600 for EWI-coating
- 1 set (2 pieces) K600 for JSI-coating

Furthermore, Wittner did field tests (production of 10000 pieces) on mould 1 coated by EWI. For reference, the same mould was tested in uncoated state.

➔ The wear of the coated mould was lower than the wear of the uncoated reference mould.

Wittner recommended the developed coating to their customers for serial tools under the following conditions:

- production of more than 1 Mio. pieces (mass production)
- abrasive materials contents between 30 and up to 50 % reinforcing filler additives (glass or carbon fiber)
- limited to high-tech polymers to achieve a good balance between increased efforts and financial output for a manufacturing company like in the case of company Wittner

# 16 UNIBW

The Institute for Plasma Technology at the Universität der Bundeswehr München (UniBw, University of the Federal Armed Forces Munich) had two major tasks in the appliCMA project.

The first task has been to set up a simulation tool for the HVOF (High Velocity Oxy Fuel) process. Here the emphasis was put on two aspects. The simulation should be

- simplified enough to be operated simultaneously to the spray process itself in order to estimate the influence by modifications in the torch and injection parameters on the resulting deposited coating,
- should incorporate enough physical details to yield reliable results for temperature and velocity of the injected particles impinging on the coating.

The model consists of two parts, one regarding the supersonic compressible gas flow inside the HVOF gun, and the other calculating the interaction of the injected particles with the gas jet. In the thus constructed model, the simplifications of these two simulation parts are to be checked separately by diagnostics tools applied on the gas jet (emission computer tomography) and on the particle flow (Laser Doppler Anemometry). The output of the diagnostics results as well as the modeling of the spray process will be subsequently used to develop a coating deposition model to estimate the deposition efficiency, porosity, roughness and eventually the quasicrystalline content in the sprayed coating.

The second task has been to develop and employ a sophisticated diagnostics system that will be comprised of particle flow characterization and flame analysis using tomography and laser based imaging. Results of the experimental investigation are supposed to include shape, speed and density of the particle flow as well as parametric controlled process adjustments. Experimental results are supposed to be used to verify the modeling results to obtain a fully understood deposition process.

In addition to that a Filtered Cathodic Vacuum Arc deposition method (FCAPD) for production of thin AlCuFeB-coatings has been explored.

# 17 TCM

TCM served as deliverer of demonstrators (cutting insert plates, drills, mills) and as industrial field tester.

Within WP3 TCM did field tests with cutting inserts coated by TUW. TCM performed also field tests with cutting inserts coated from JSI within WP4; for comparison, the results from the industrial coated cutting inserts can also be found in this document.

With 40 cutting inserts workpieces from aluminium grade EN AW-6082 were machined. 10 cutting inserts were coated by TUW, 10 inserts were coated by JSI. For reference, 10 uncoated and 10 cutting inserts coated with commercial available $TiB_2$ coating were tested under the same conditions.

Due to the low Si-content in the Al-grade, there was constantly noticed the well-known problem of building – up edge effect on the polished surface of the test inserts. Furthermore a difficult forming of the chips throughout the test series was noticed. Ribbon chips were formed during the turning tests which led to a disturbing of the turning process and consequently the process reliability was affected. The used cutting data are state of the art values, approved by machining Al-parts in the modern high level industry.

The end of tool life had been defined by a rapid increase of the cutting forces and deterioration of the workpiece surface. It was reached at 31 pcs.

➔ After the turning test series with the Al workpieces, it can be summarized that the new developed AppliCMA AlFeCuB coating performs as well as the reference coatings currently available on the market.

➔ Regarding the cutting force the best results were obtained with coatings from TUW. As expected, the worst result was achieved with the uncoated inserts.

# 18 LKR (AIT-MOBILITY)

Within WP4, LKR delivered extrusion dies to be coated by industrial coaters. Based on the investigations at LKR (casting, turning and extrusion of aluminum) it has to be stated that no positive evaluation for CMA-coatings in aluminum extrusion can be given and the usage of CMA-coatings in its industrial applications is hardly recommended. For further improvement of extrusion process introducing a coating into the process another coating system, e.g. CrN, is more suitable than a CMA coating system. Nevertheless the work being done in this task enabled the establishment of other technical and scientific expertise regarding the investigated processes of DC-casting, turning and extrusion and their interactions when processing aluminum alloys, which will be the basis of further research at those fields.

Based on the obtained results the goal of LKR in WP5, the development of a proper simulation model of a turning process with coated tools within the commercial FE-code DEFORM., can be declared to be mainly reached, since the differences between the simulated coating systems could be attributed to differences in the physical behaviour between the coating systems and also for the cutting forces a good match between simulation and experiments was achieved. The lack of fit regarding feed forces could be explained by the complex material flow which couldn't be described with two-dimensional FE-based process simulation. In this case to obtain a better fit a three-dimensional model should be established instead. For reaching this goal several tasks – establishment of a basic model setup, following enhancement of mesh quality, introduction of coating into model setup, interaction test methods-materials properties and expansion of the set of evaluation criteria – were conducted.

# 19 RHP

Because of problems of the planned industrial coater (Genta), JSI was asked to act as second industrial coater. They had setup a job-coating centre offering an industrial sputter coating device. Begin of 2011 RHP manufactured a tiled target for this device. After successful use for first coating trials, RHP produced a second target for use in WP4.

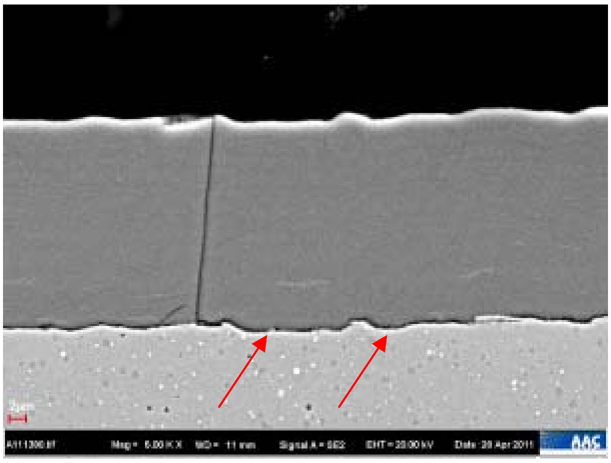
➔ AlCuFeB targets can be prepared by RHP – depending on the manufacturing process - in metallic type and ceramic structure

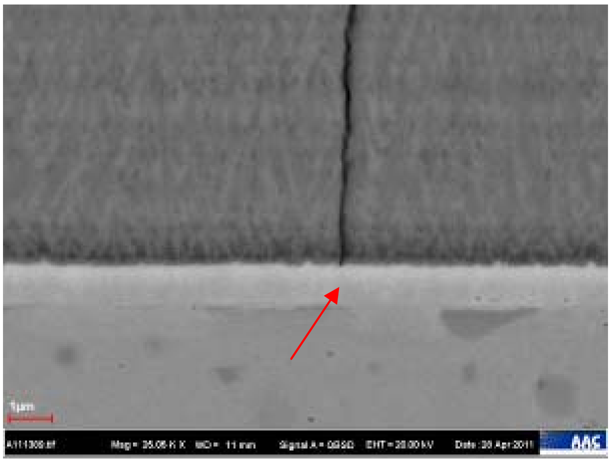
➔ Metallic targets are more preferable for sputter deposition processes since they allow the use of DC sputtering

➔ Segmentation of targets is no problem for sputter deposition process (e.g. CEMECON type equipment)

# 20 ANNEX: PUBLISHABLE PICTURES

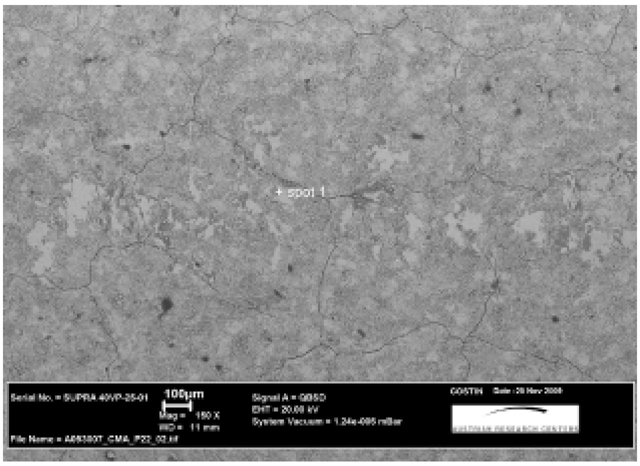
Research coatings - cracks:

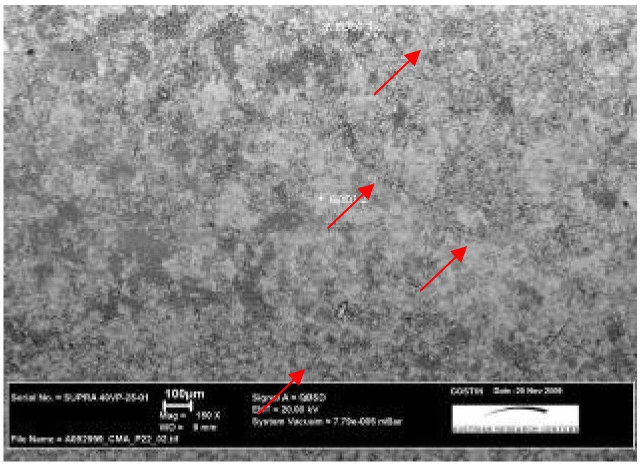




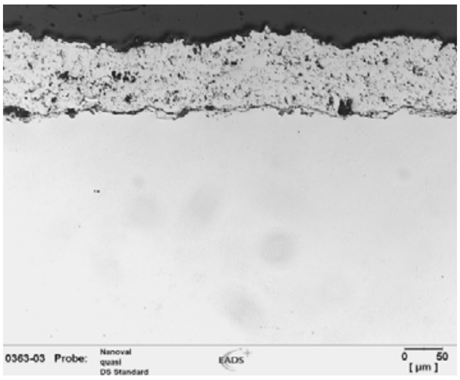
Left- coating deposed on steel K890 without interlayer - crack propagates along interface; coating –to-substrate. Right – coating deposed on steel K890 with Ni interlayer - crack stops on interlayer.

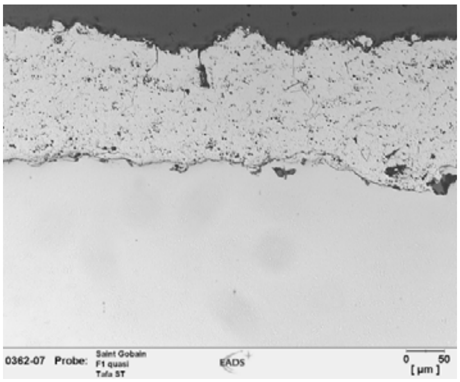
Research coatings – EADS – different powders:



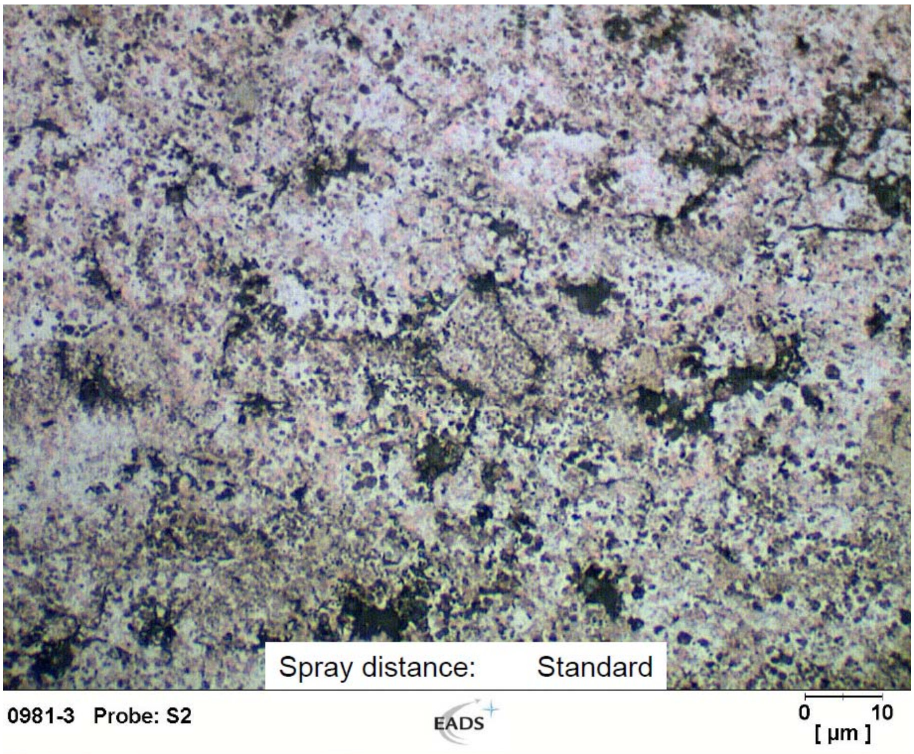




Left – Coating prepared from Crsitome 1 powder. Right – coating prepared from Nanoval powder.




The Nanoval powder gives a finer particle distribution but a darker appearance compared to the Cristome F1 powder. This is due to the higher oxidation sensitiveness of the smaller feedstock fraction. Both coating show a homogeneous morphology and a good adherence to the substrate.




Detailed image of a Cristome F1 coating applied by HVOF showing a homogeneous particle distribution in alloying elements.

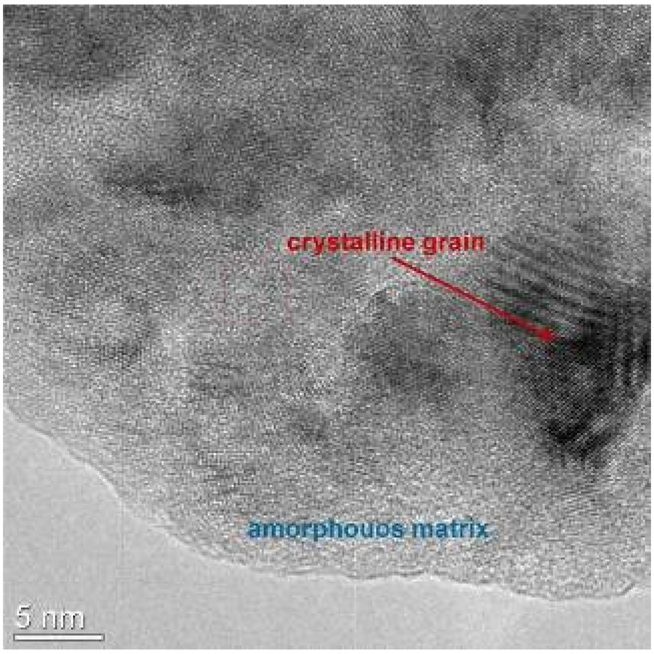
## Research coatings – tribological performance:

| Substrates | Best Coatings for friction tests in Air | |
|---|---|---|
| K600 | QCMA_EWI_05 | AlCuFeB (EWI - 600°C, 65 µm) 90/10% ico/beta |
| V134 | QCMA_EAD_001 | AlCuFeB (HVOF) - 3H/600°C/Vac 100%ico Post Ann.: 3H/600°C/Vac |
| K10 | QCMA_EWI_21 | Ni + AlCuFeB (EWI-540°C,1.5+9µm) 60/40% ico/beta |
| K110 +Ni (2µm) | QCMA_EWI_027 | AlCuFeB beta phase -- Al 36.67 Fe 18.46 Cu 44.87 w% |
| K110 +Ni (1.5µm)+Cu (2.5µm) | QCMA_EWI_028 | AlCuFeB beta+omega phase -- Al 44.73 Fe 19.54 Cu 35.74 w% |
| K110 +Ni (1.5µm)+Cu (2.5µm) | QCMA_EWI_30 | AlCuFeB 70/30% ico/beta |
| K110 + Cu (2µm) | QCMA_EWI_31 | |
| K110 + Ni (2 µm) | QCMA_EWI_32 | |
| K110 + FeNi (1.5 µm) | QCMA_EWI_33 | |
| W300 | QCMA_EWI_05 | AlCuFeB (EWI - 600°C, 65 µm) 90/10% ico/beta |
| K890 | QCMA_TUW_059 | AlCuFeB (Q23, PVD 100W 550-600°C, 2.5 µm) |

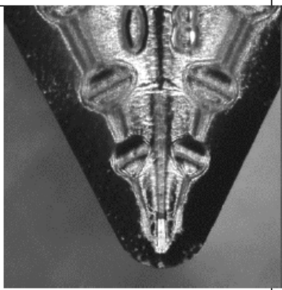
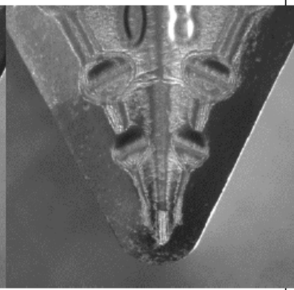
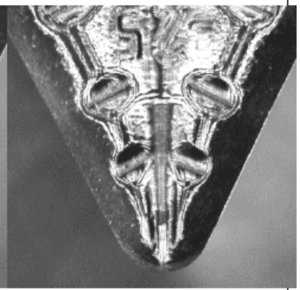
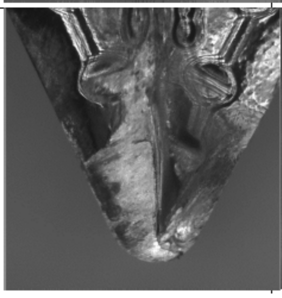
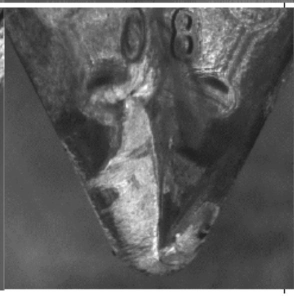
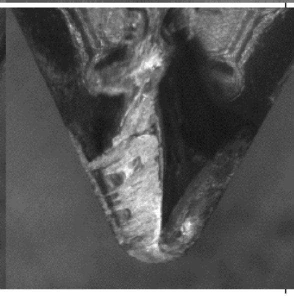
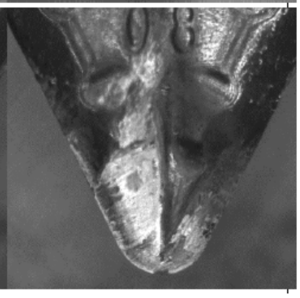
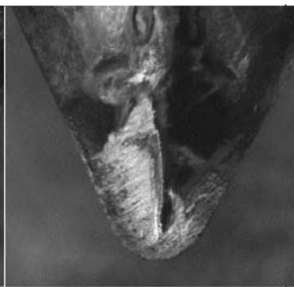
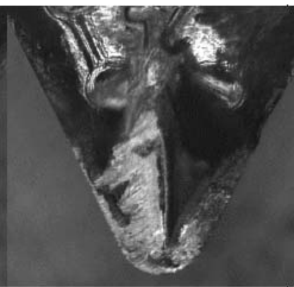
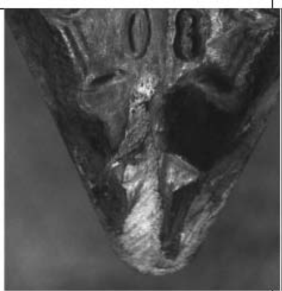
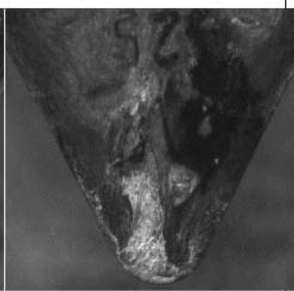
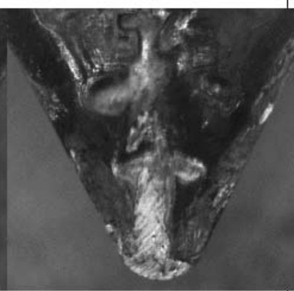
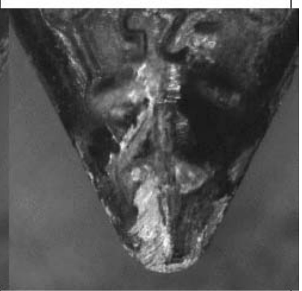
| Substrates | Best Coatings for friction tests under Vacuum | |
|---|---|---|
| V134 | QCMA_EAD_002 | V134 / AlCuFeB (DJ Standard) - 3H/600°C/vac 100%ico Post Ann.: 3H/600°C/Vac |
| K600 | QCMA_EWI_05 | K600 / AlCuFeB (EWI - 600°C, 65 µm) 100%ico |
| | QCMA_EWI_07 | K600 / AlCuFeB (EWI - 620°C, 9 µm) 80/20%beta/ico |
| K10 | QCMA_EWI_21 | K10 / Ni + AlCuFeB (EWI-540°C,1.5+9µm) 60/40% ico/beta |
| | QCMA_TUW_063 | K10 / AlCuFeB (Q23, PVD 100W 550-600°C, 2.5 µm) |
| K890 | QCMA_TUW_071 | K890 / AlCuFeB |
| K600 | QCMA_TUW_073 | K600 / AlCuFeB |
| W300 | QCMA_EWI_026_1 | W300 / AlCuFeB omega-phase -- Al 45.5 Fe 12.27 Cu 45.24 w% |
| K110 +Ni (2µm) | QCMA_EWI_027 | K110 +Ni (2µm) / AlCuFeB beta phase -- Al 36.67 Fe 18.46 Cu 44.87 w% |

## Research coatings – microstructure by TEM (TUW):

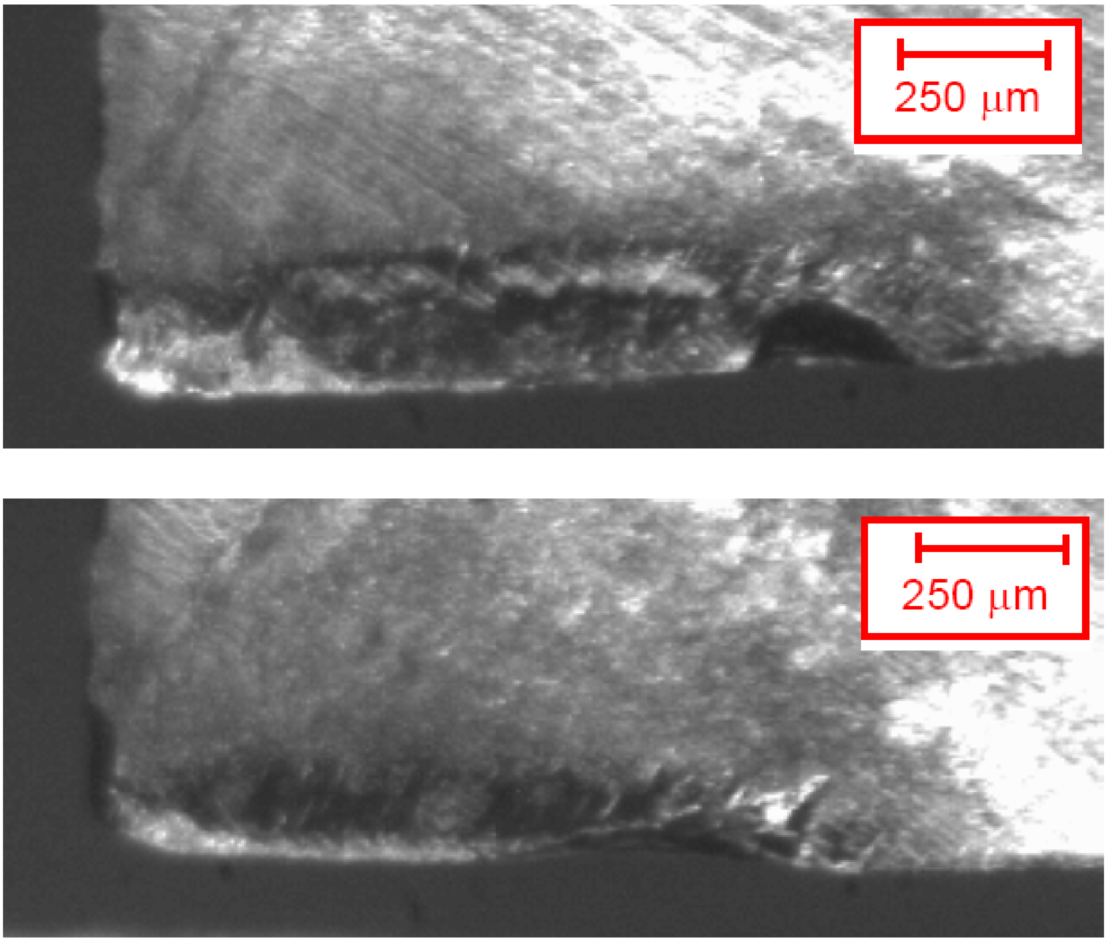
Investigations of the microstructure of the coatings by Transmission Electron Microscopy at TUW revealed that they can be considered as nanocomposites of quasycrystalline grains which are embedded in an amorphous matrix, as the figure below shows.



Industrial coatings – Comparison of the used cutting edges during turning field tests:

| | Uncoated | AluSpeed coated | „JSI" coated | „TU Vienna" coated |
|---|---|---|---|---|
| Tool as manufactured New tool |  |  |  |  |
| First cutting: Machining length: 180 mm Cutting depth: ap 2,5 mm Cutting speed:. vc 300 m/min Feed rate: fu 0,25 mm/U |  |  |  |  |
| After turning 3l aluminium bolts: Cutting insert Nr. 1<br><br>Machining length 16560 mm Cutting depth ap 2,5 mm Cutting speed:. vc 300 m/min Feed rate fu 0,25 mm/U |  |  |  |  |
| After turning 3l aluminium bolts: Cutting insert Nr. 2<br><br>Maching-length: 23760 mm Cuttings depth ap 20 bolts wih ap 2,5 mm 12 bolts with ap 1,25 mm Cutting speed. vc 300 m/min Feed rate fu 20 bolts with fu 0,25 mm/U 12 bolts with fu 0,30 mm/U |  |  |  |  |

POLITO: tool wear vs. cutting time

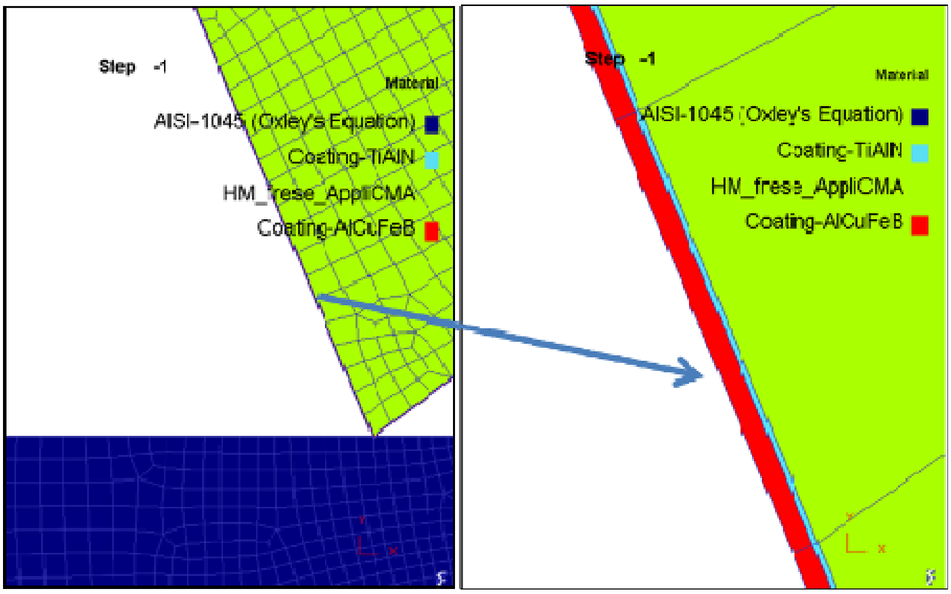



T1

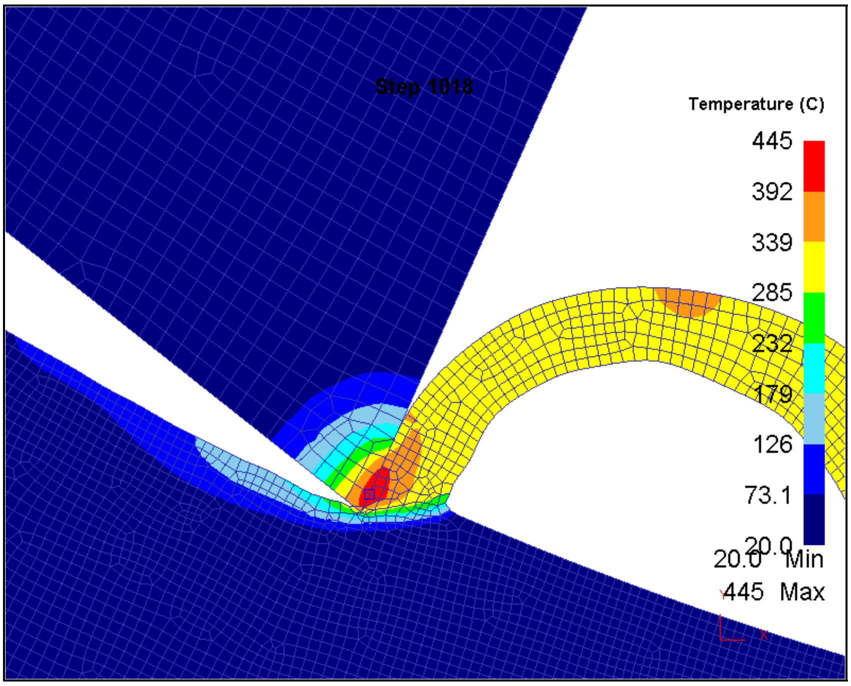
T2

Tool rake after 14 min of cutting time, tool 3, cutting speed = 200 m/min and cutting feed = 0.10 mm/tooth, dry cutting. T1: cutter 1; T2: cutter 2.

POLITO: FEM simulation

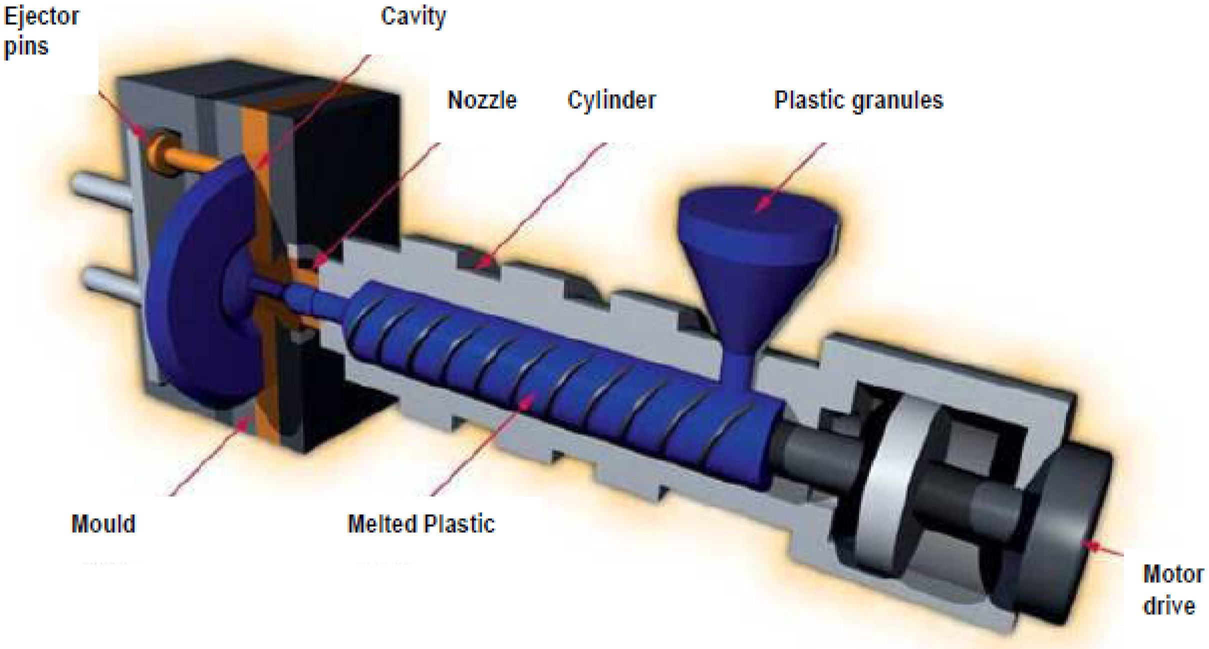



Detail of FEM model setup: coating system.



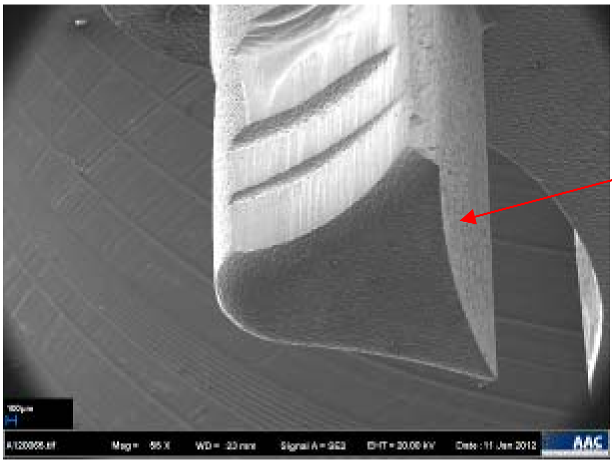

Temperature distribution in the tool (V=150 m/min).

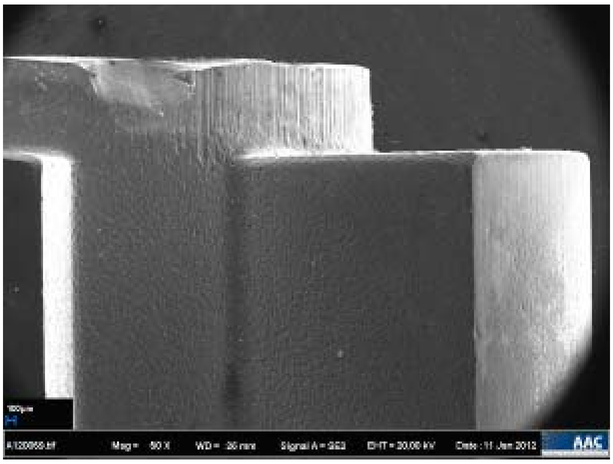
Wittner: injection moulding



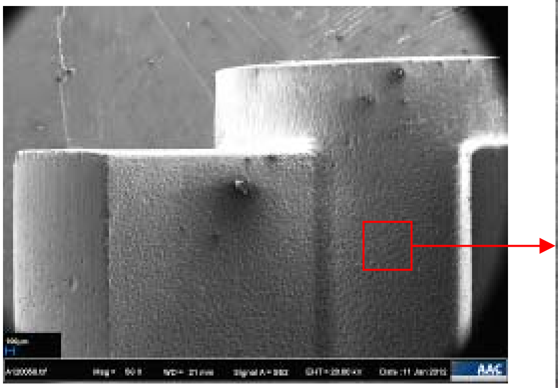

Injection moulding facility

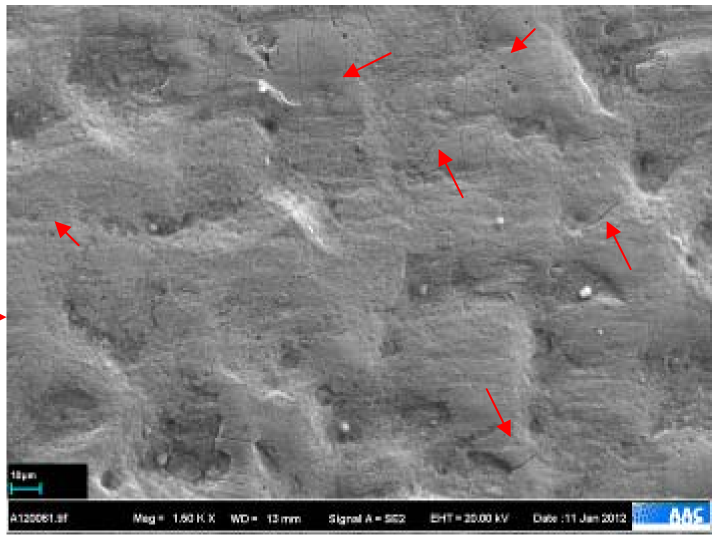
Injection mould after production of 10000 pieces



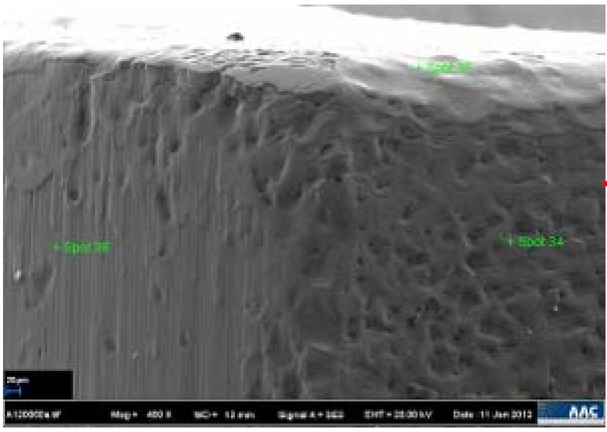


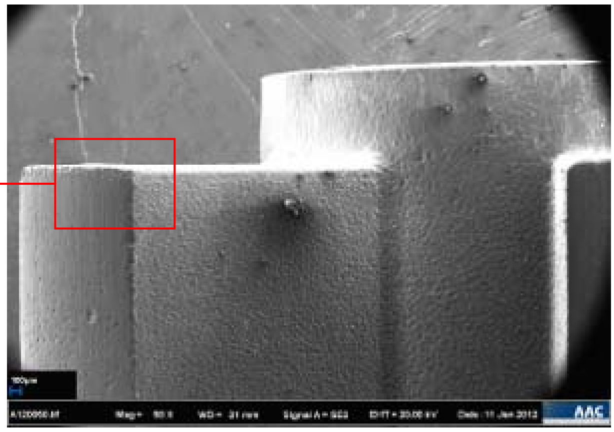
Injection mould investigated in HR-SEM at AAC

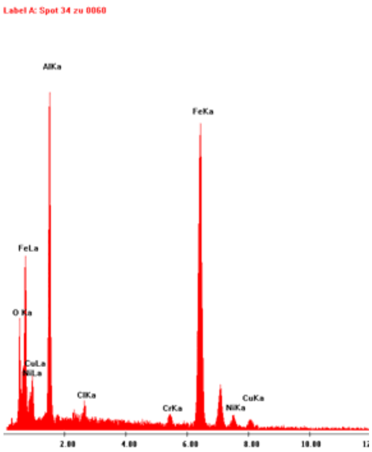


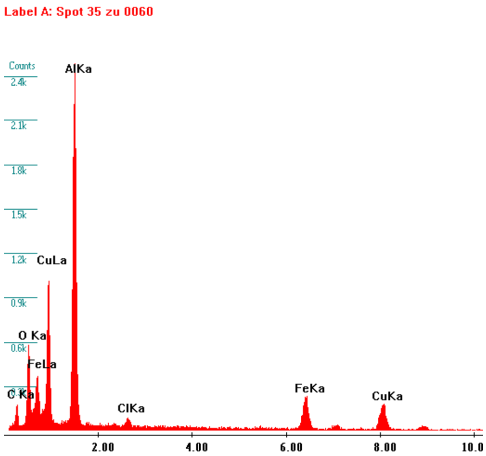


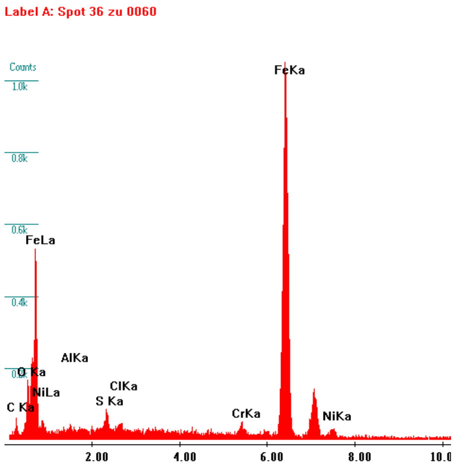
A mould element – cracks in the coating (e.g. marked by arrows)



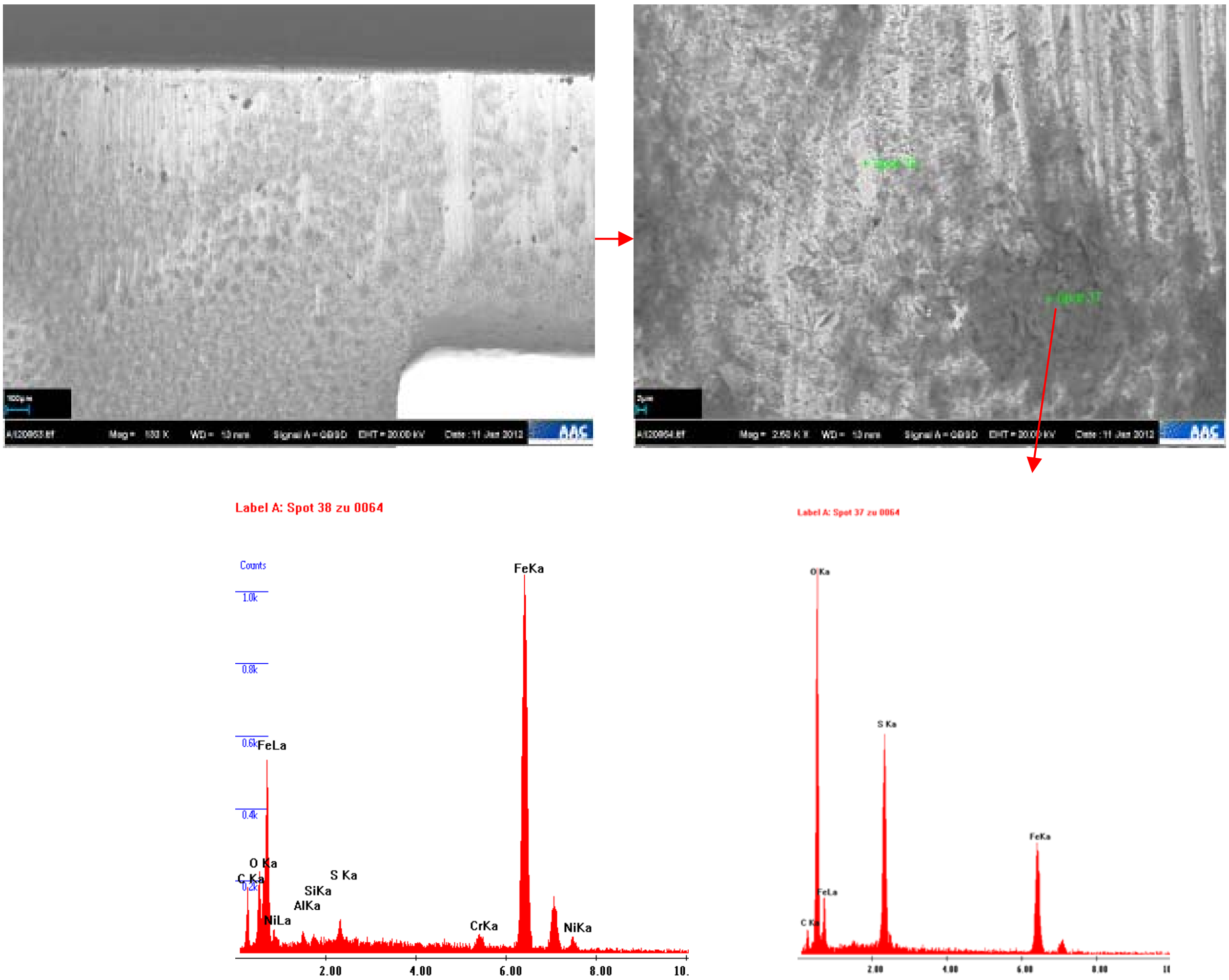





Images of a corner show a distribution and topography of the coating on three walls of a mould element (in images – top, left and right wall). According to the EDS analysis the left wall does not exhibit coating (spot 36 - Fe, Cr and Ni peaks originate from mould steel). The top and right wall show coating whose chemical composition differs strongly from that of quasi-crystals (spot 35 – see semi-quantitative analysis, spot 36). Additionally, Cl and S (spot 36) have been detected on the surface.

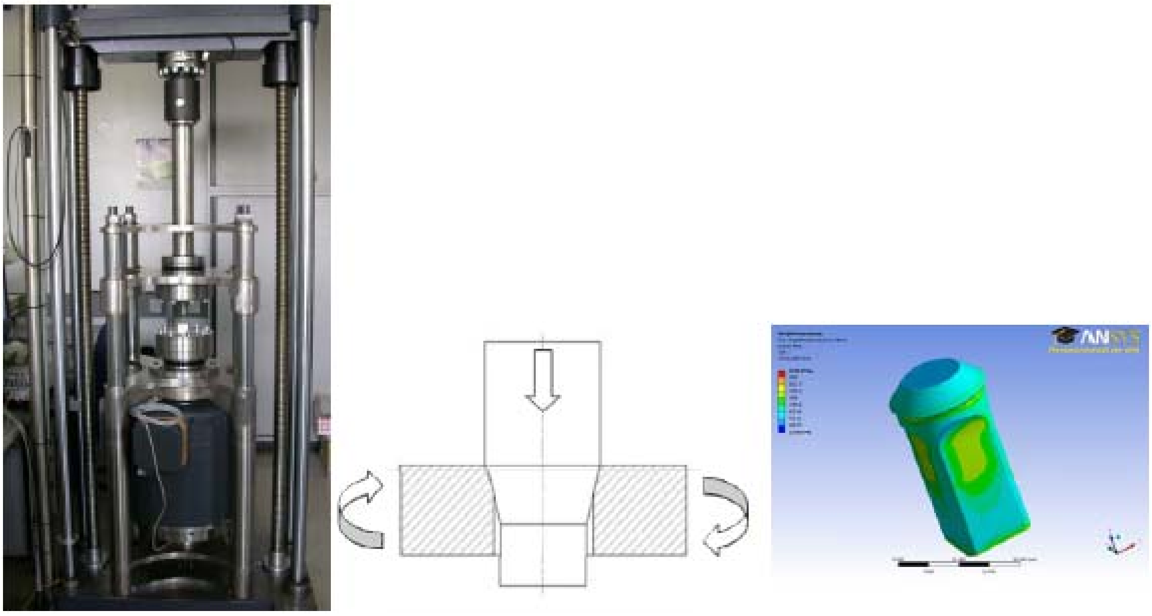



Left: a mould element - slight wear of the surface. Right: EDS analysis from a dark phase present on the surface (spot 37) and from a worn area (spot 38). According to spectrum 37 the dark phase consists of O, S and small amount of C (these elements may refer to residuals of an injected plastic). Fe signal in this spectrum originate from steel. According to spectrum 38 there is no coating within the worn area. The signals from Fe, Cr and Ni correspond with the composition of mould steel.

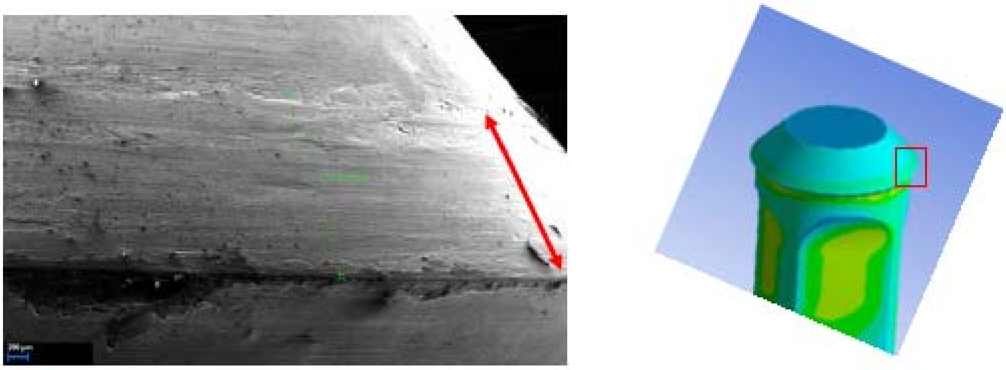
Summary – Mould:

- the mould elements are only partly coated
- the chemical composition of the existing coating differs strongly from the composition of quasi-crystal phase
- the coating exhibits cracks,
- the wear traces within the contact areas are marginal, within the traces the coating does not exist anymore
- on the surface O-, S-, C-containing phase has been identified (it may correspond to residuals of an injected plastic)
- on the surface Cl has been detected frequently

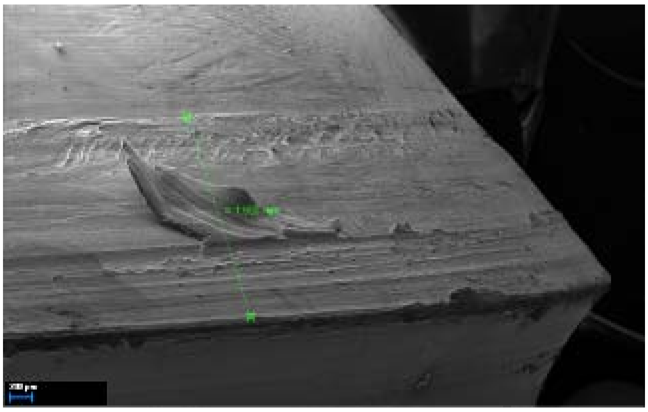
AAC: forming tribometer tests



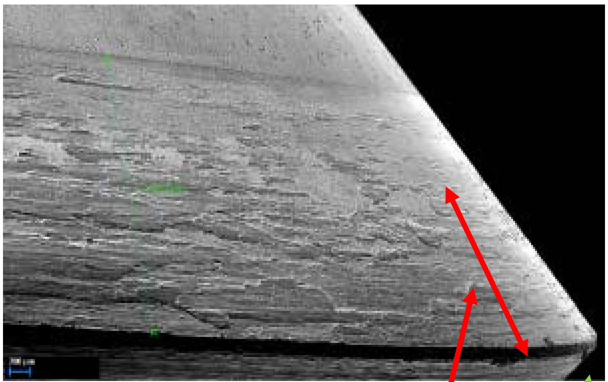
Left: Forming tribometer, Middle: principle of motion of the punch (axially down) and the bush (rotating), Right: specimen (Punch = tool on top, Bush = work piece bottom).



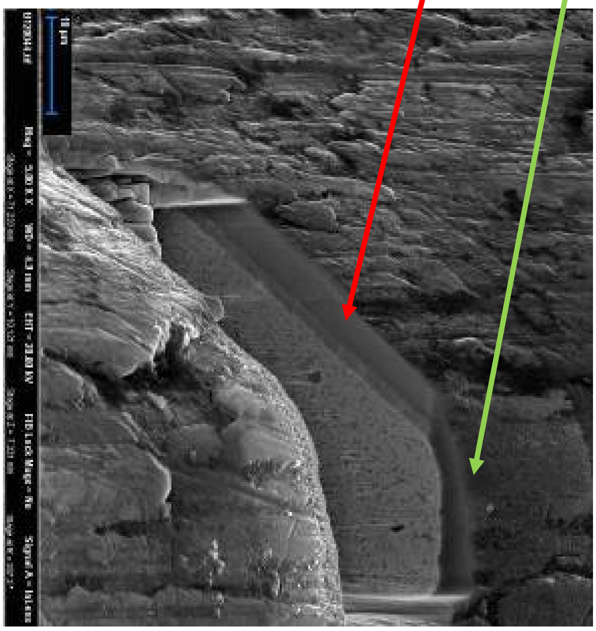
W300 nitrided: contact area width (~2mm, arrow) fully covered with aluminium transferred from counter bush



W300 with out any treatment: heavy adhesive transfer from bush,

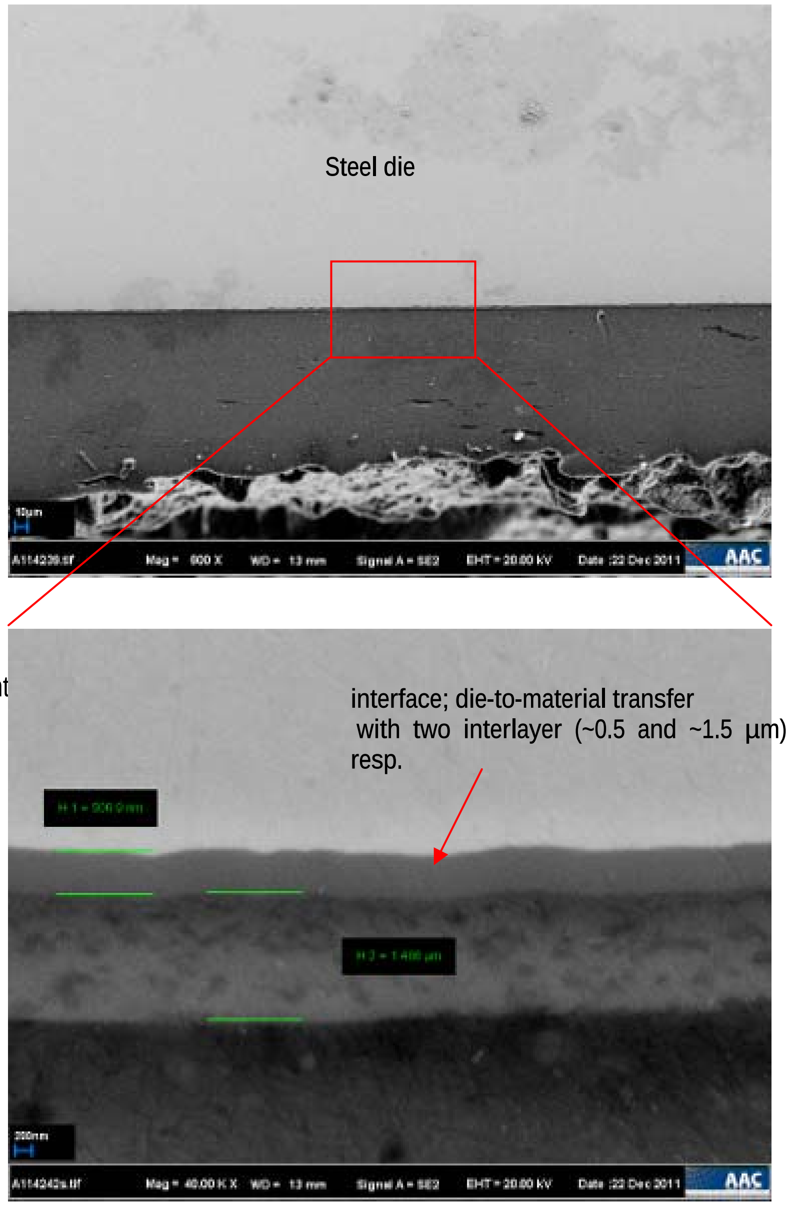


WC-Co CMA coated by JSI (AlCuFeB): Left survey of contact area, partly transferred layer, but not fully covered, coating still visible between transfer parts.

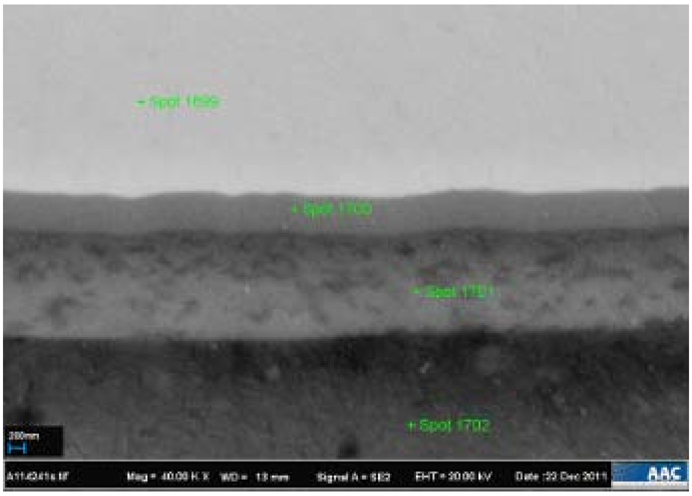


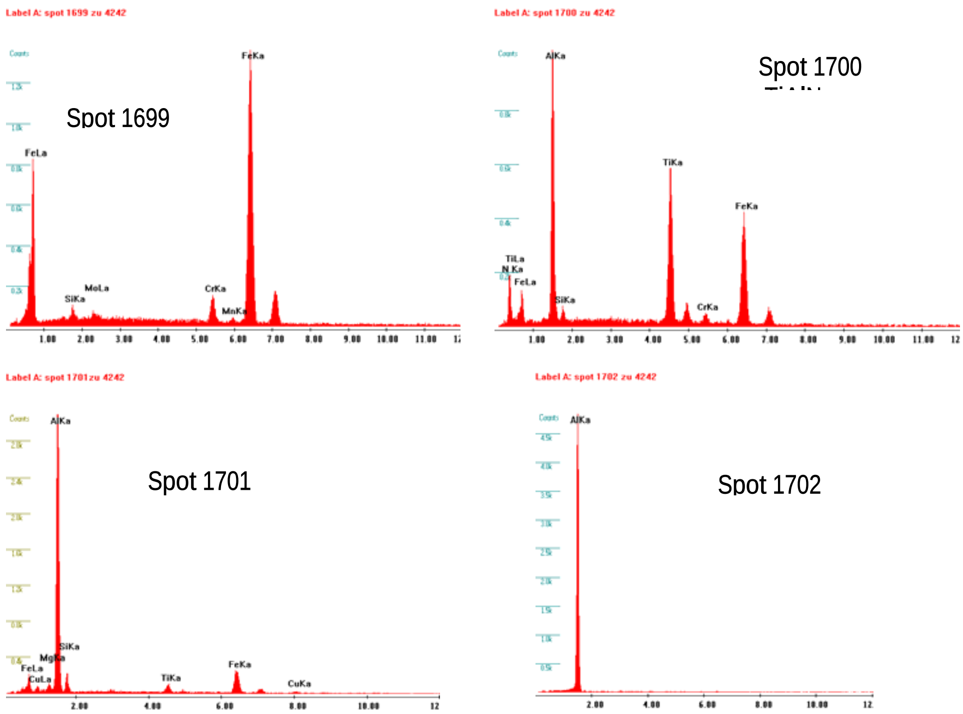
Detail of previous image: on the conical area still CMA-coating is visible, on the outer edge not any more (green arrow).

HR-SEM investigations on a coated extrusion die




A side of the extrusion die with a small amount of the material transfer and two interlayer (~0.5 µm, ~1.5 µm) between the mould and the material transfer



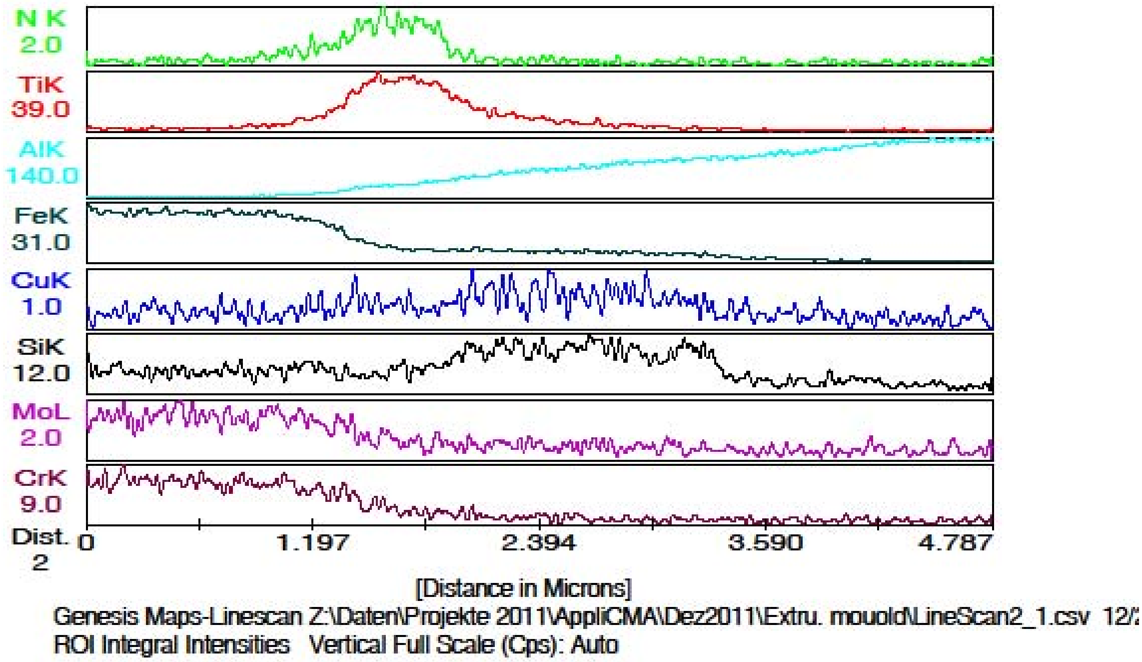

EDS analysis of the

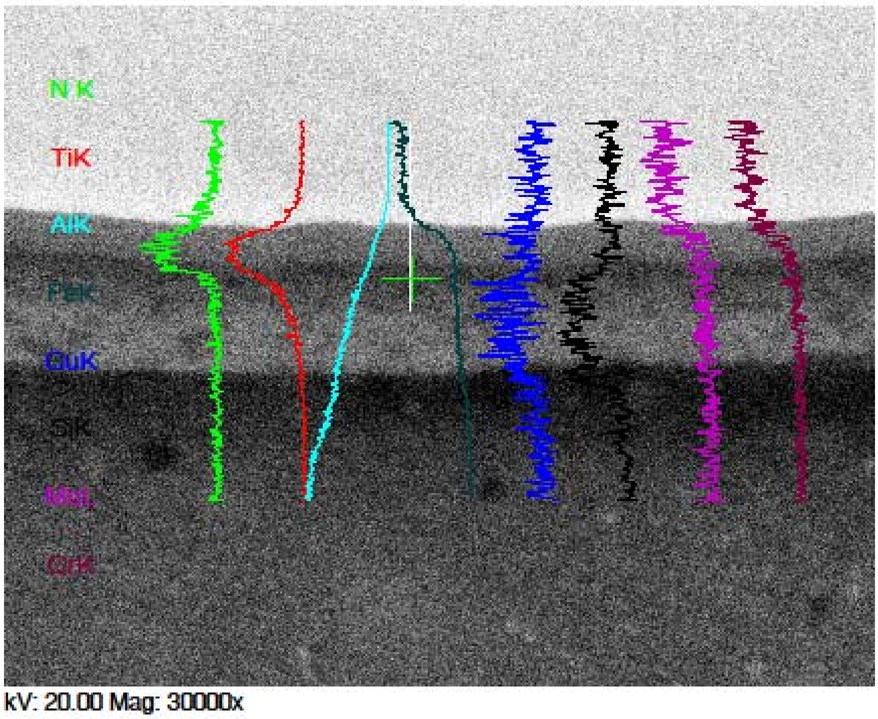
- **extrusion die** (spot 1699 – steel containing Cr, Mn, Mo and Si),

- **interlayer 1** (spot 1700 - containing Ti, Al and N. Fe, Cr and Si signals may originate from steel. A diffusion of these elements from steel towards interface is most likely

- **interlayer 2** (spot 1701 – interlayer 2 consisting predominately of Al and a small amount of Fe, Si, Cu and Mg. Al, Fe and Cu refers to former QC composition, Si and Mg originate most likely from Al alloy),

- **material transfer** (spot 1702 - material transfer consisting of a Al alloy, alloying elements such Si and Mg diffused most likely in to QC coating.




EDS line-scan showing an element distribution along the interface between the mould and the material transfer. Note a distinct diffusion along the interface between the steel mould and the material transfer from an Al alloy – as already indicated above.

## Demonstrators and tools for coating


Drills at JSI


Mills


Cutting inserts

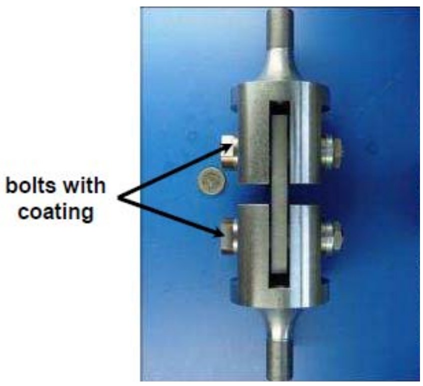

Injection moulds


Punches for forming tribometer

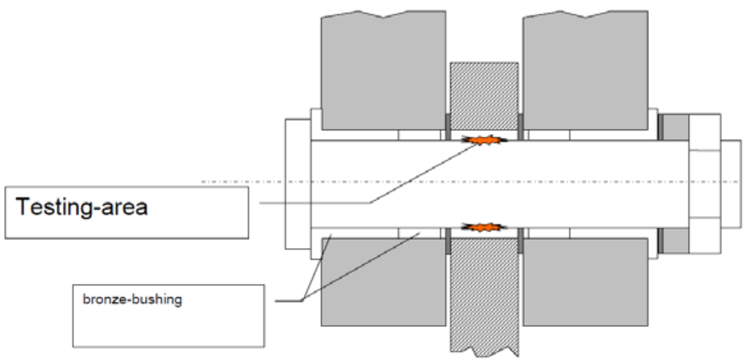

Injection mould (“Lego”)


Forging dies


Punches



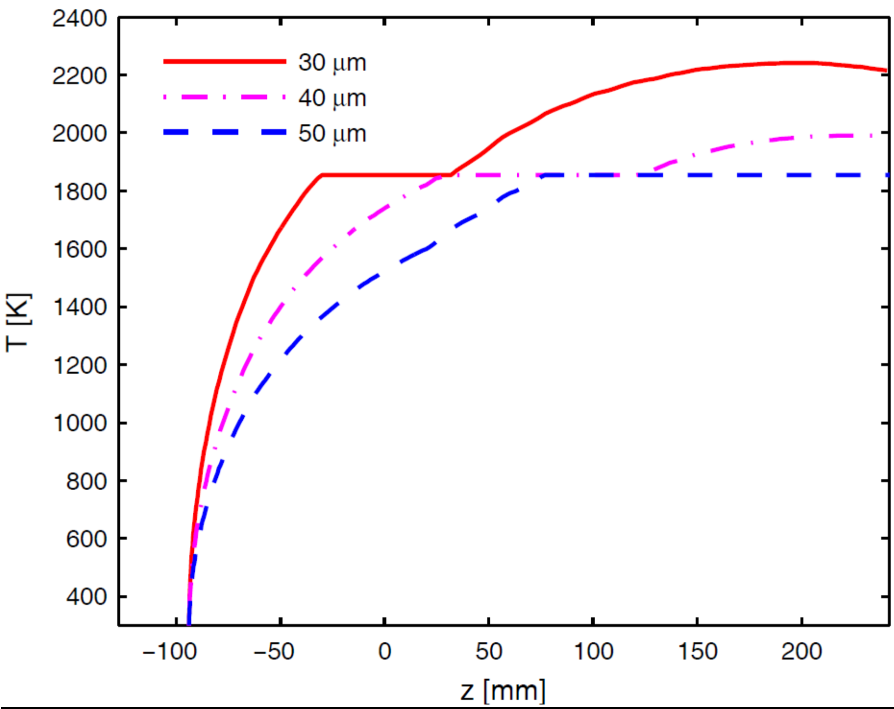
Bolt-Bushing-Set-Up of the dynamic tensile tester with insertion of two coated bolts (EADS)



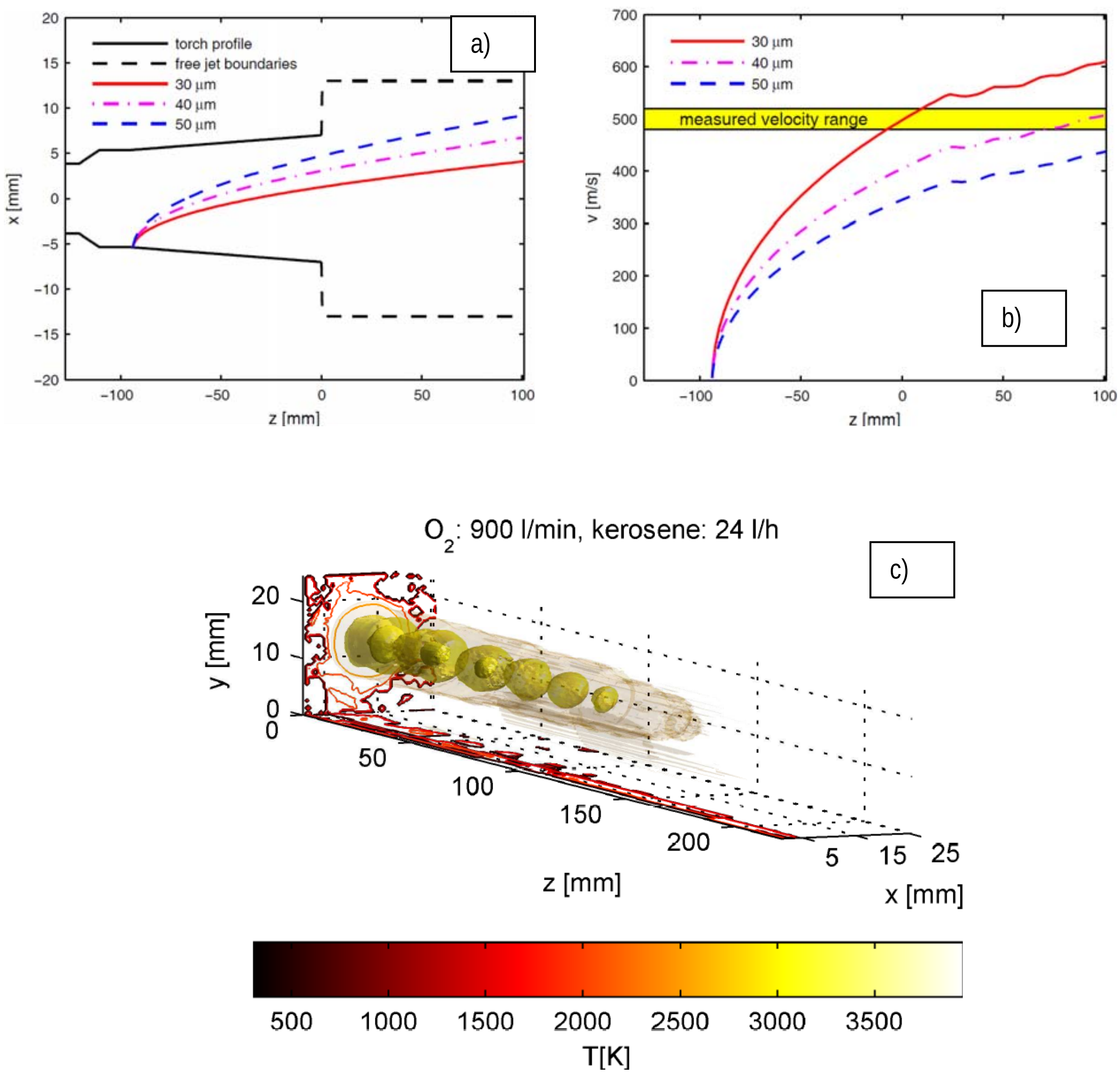
Principle of Bolt-Bushing-Test set-up (EADS)

Landing gear part (EADS)

<u>Numerical simulation of particle trajectories in a HVOF jet based on the tomographic reconstruction of the gas flow:</u>




Tomographic reconstruction of temperature distribution; GTV K2 gun operating with 24l/h kerosene and 900l/min O2

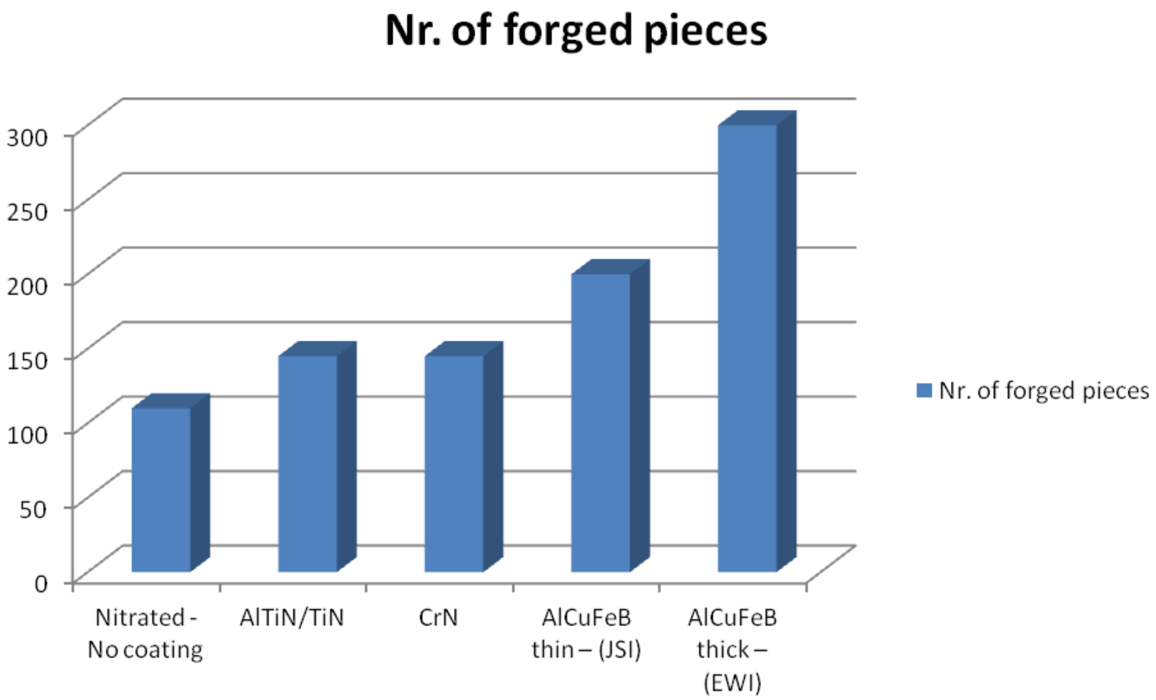



Surface temperature (a), axial velocity (b) and trajectories (c) of 316L-stainless steel powder particles of di erent diameter d with an injection velocity of 22 m/s into a GTV K2 gun operating with 24l/h kerosene and 900l/min O2

<u>TECOS – Hot Forging</u>

Hot forging process of imbus screw

Punch, with which the forging is done. The second picture shows the wear of the punch after 150 strokes.

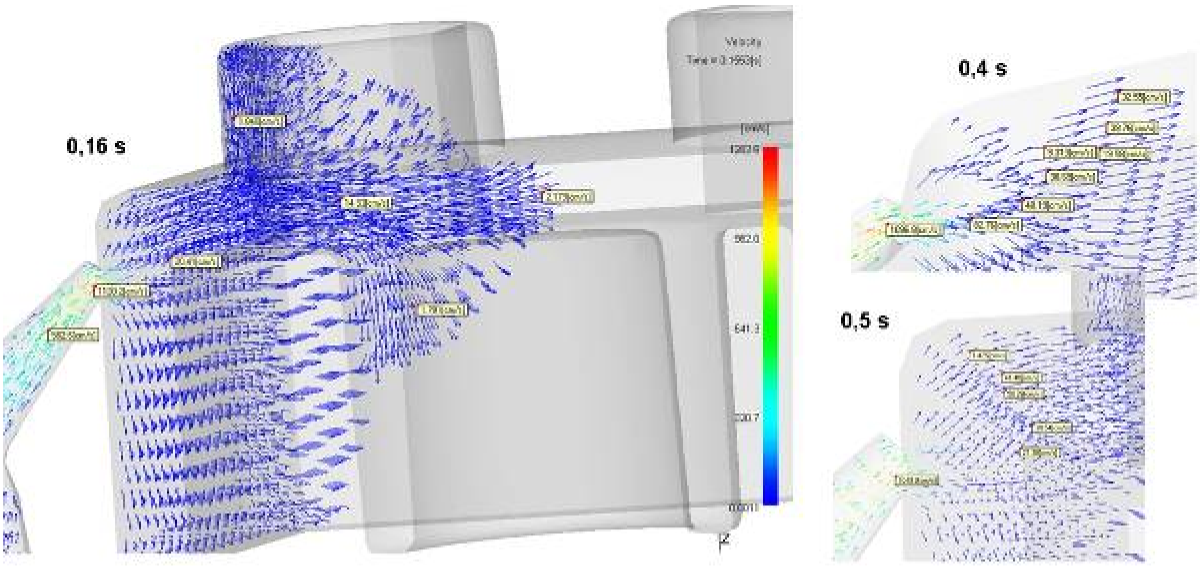



Number of forged pieces in dependence to the coating type

The punches with AlCuFeB coating after forging. On top surface the coating got inflated, but this didn't have influence in quality of the inbus screw.

<u>TECOS – Injection moulding</u>

One lower and upper insert




Velocity profile in the mould cavity