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THE PERFORMANCE OF WEAR RESISTANCE AND MECHANICAL PROPERTIESFOR THE TITANIUMNITRIDE

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ABSTRACT

Three body abrasion in the present study, TiN–NiMo composites were re milled to particle size of 250–315 μm and used as reinforcements for NiCrBSi alloy by plasma transferred arc hardfacing process. The manufactured hard facingalloy was characterised in terms of microstructure, mechanical properties and abrasive wear resistance. Deposition results indicate good quality thick coating with uniform distribution of hard cermet (TiN–NiMo) particles in the matrix, minimum level of hard particle dissolution and low porosity of the hard facing. Cermet particles remain in initial form and consist of agglomerates (TiN and (Ti,Mo)C grains) embedded into Ni-based matrix. The mechanical properties of the TiN and (Ti,Mo)C phases measured by Nano indentation are very similar exhibiting a narrow distribution. The nano-scratching test reveals excellent bonding between the matrix and cermets in the hard facing. No crack propagation was found in the interface matrix/hard phase region. The abrasive wear results ensure the promising features of TiN–NiMo reinforcements for Ni-based alloys. Produced coatings showed excellent performance under high-stress abrasion with wear values lower than for industrially used WC/W2C reinforced coatings.

I. INTRODUCTION

Coatings and surface treatments have proved to be a successful approach for increasing machinery lifespan by preventing severe wear and corrosion of working tools [1–3]. One of the attractive surface treatment methods is hardfacing by welding technique. This method offers the ability to apply thick protective coatings metallurgically bonded to the substrate material. Many hardfacing techniques such as laser cladding, gas-tungsten arc welding (GTAW), gas-metal arc welding (GMAW) and plasma transferred arc (PTA) are widely employed for deposition of a protective layer on a surface of a bulk material subjected to severe working conditions [4–6]. The most common coatings dapplied by hardfacing are metal matrix composites (MMCs) consisting of Ni, Co or Fe-based matrix, and reinforced with hard ceramic particles such as tungsten carbides

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[5,7,8]. Tungsten carbide based hard metals are widely used in tribo-conditions because of their high abrasion and combined impact/abrasion wear resistance [9,10]. However, due to their poor oxidation resistance at elevatedtemperatures, WC-based composites are a less than ideal choice fortooling parts exposed to temperatures exceeding 550 °C [11].Titanium Nitride (TiN) can be considered as an attractive reinforcementfor MMCs because of its high hardness, quite low density,good oxidation resistance and high wear resistance in erosion andabrasion environments [12–15].Several attempts have been made to apply titanium carbide powdersby hardfacing using different processing methods. For the powder feedingmethod, TiN-based powder and metal matrix powder are deliveredinto the laser or plasma beam, melted and deposited onto the substrate[4,5,16]. This method enables a uniform distribution of primary hardphases in the matrix and results in low carbide dissolution. Alternativemethods include mixing TiN and metal matrix, pre-placing the powdermixture on the surface of the substratewith the help of an organic binderand forming a coating layer to be cladded [17,18]. The coatings depositedby these techniques are mostly characterised by formation of a gradientdistribution of hard phase and are highly affected by dilution and its influenceon the microstructure of the final product.A promising method for the reinforcement of metal matrix with TiNparticles using laser cladding involves in-situ synthesis of TiN by reactionof titanium and graphite during laser processing [19,20]. Such hardfacingsare characterised by excellentmetallurgical bonding between the coatingand the substrate and the high quality of the depositedmaterial. However,because of TiN's low density, a uniform distribution of hard phases isnot easily achieved. During solidification, the TiN particles show a gradientdistribution in thematrix with respect to size and volume fraction[20].Although titanium carbides are widely applied as reinforcementsusing different cladding technologies, there is a lack of information

about processing of recycled TiN-based cermets as reinforcements for anickel-based matrix with the PTA process. In the present study, titanium carbide reinforced hardfacings have been produced by the PTA technique using the powder feeding method.The precursor materials used were re-milled TiN-20% Ni:Mo (2:1)cermets added into the NiCrBSi matrix alloy. The coatings have been deposited onto an austenitic steel substrate. The main objectives of the work were: (i) to deposit NiCrBSi hardfacing coatings reinforced by TiN–NiMo cermet particles; (ii) to examine the microstructureand mechanical properties of the developed hardfacings; and (iii) tostudy the wear resistance of the coatings under three body abrasive wear conditions.

II. EXPERIMENTAL DETAILS

2.1. Powders

Pre-processed powder of titanium carbide based and nickel–molybdenum bonded cermet particles was used in the presentstudy. These cermet particles were re-milled from the bulk ofTiN-20 wt.% Ni:Mo (2:1) and then sieved to obtain the fraction 150…310 μm using collision milling method. To obtain cermet particleswith the predetermined granulometry, multistage milling (up to 16times) was used [21]. A representative SEM micrograph of the powderis shown in Fig. 1. NiCrBSi alloy powder (0.2% C, 4% Cr, 1% B, 2.5% Si,2% Fe, rest Ni) with particle size of 50 … 150 μm was used as a matrixmaterial for the PTA process.2.2. Plasma transferred arc hardfacingPTA hardfacing of TiN–NiMo particles in combination with NiCrBSimatrix was carried out using a EuTronic® Gap 3001 DC apparatus.Austenitic stainless 1.4301 steel was used as a substrate. The coatingthickness was set to 2.0–2.5 mm. The coating of the identical matrixalloy with the same volume

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percentage of WC/W2C reinforcements(Castolin Eutectic EuTroLoy PG 6503 alloy) was used as referencematerial for the wear testing.

2.2. Characterisation

Prior to testing, the samples were cut from large pieces, ground andsubsequently polished using 1 μm diamond paste. A comprehensivemicrostructural evaluation of the plasma hardfacing was performedby optical microscopy (OM) with a digital camera (MEF4A, LeicaMicrosystem) and scanning electron microscopy (SEM Philips XL 30FEG), equipped with an energy dispersive X-ray analyser (EDX) withDual BSD detector and operating at an accelerating voltage of 20 kV.For EDX quantification the standardless EDAX ZAF quantification methodwas used. The microstructural examination (OM) was conducted on thesamples etched with a solution of HF and HNO3 in volume ratio 1:12 at room temperature for 2 s.X-ray diffraction (XRD) experiments were performed on an X-Pert powder diffractometer (PANalytical, Netherlands) in continuous mode using CuKα radiation in Bragg–Brentano geometry at 40 kV and 30 mA. The diffractometer was equipped with a secondarygraphite monochromator, automatic divergence slits and a scintillation counter.The hardness was determined by standard Vickers hardness testingat a load of 50 kgf (HV50). Average hardness values were calculated from8 indents per specimen. The choice of such a high load was conditioned by themicrostructural features ofmultiphase hardfacings,where under load of 10 kgf (10HV) a large scatter of hardness values for similar multiphase structures was obtained [22].To evaluate the mechanical properties of constituent phases,nanoindentation measurements were performed using a Hysitron Triboindenter TI900 (Minneapolis, MN, USA) equipped with a diamond Berkovich indentation tip with 100 nm tip radius. The load cycle comprised loading for 5 s to reach the peak load of 10 mN and subsequent unloading for 5 s. The load vs. depth curves were analysed to determine the reduced elastic modulus and hardness using the procedure described elsewhere [23].Nano-scratch testing was also performed with the Hysitron Triboindenter TI900 using the Berkovich tip as described above. The load during the scratches was set to a constant value of 5 mN. The length of all scratches was 20 μm with a scratch rate of 0.2 μm/s.2.4. Wear testing The abrasive wear performance was evaluated using three-body abrasion tester by variation of testing conditions: a) use of a dry-sand rubber wheel according to ASTM G65 requirements; b) application of a steel wheel to simulate high-stresswear behaviour of materials. Rotation speed, normal load and sliding distance were kept constant at 200 rpm, 130 N and 4309 m, respectively. Ottawa silica sand with particle size of 212–300 μm was used as abrasive. Before and after testing each specimen was cleaned with acetone, dried and weighed. At least three testswere run for each material to determine thewear resistance.

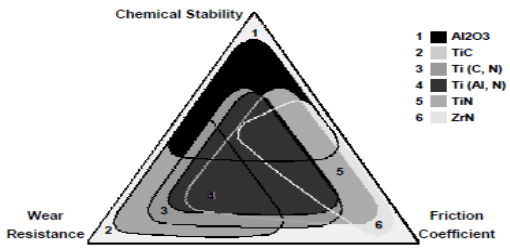

Figure 8: The Main Properties of Various Coating Layers.

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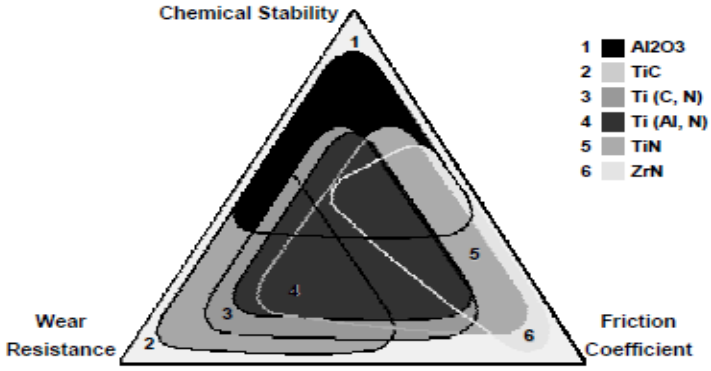

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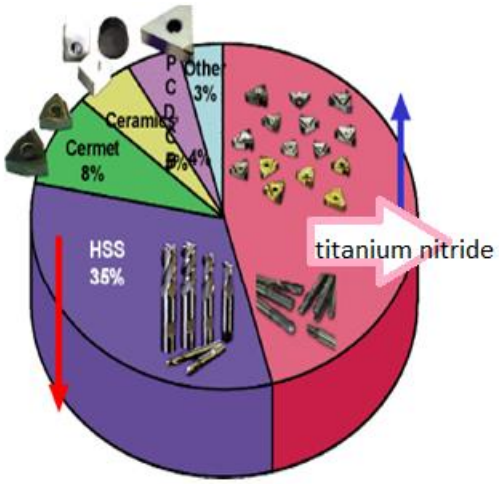

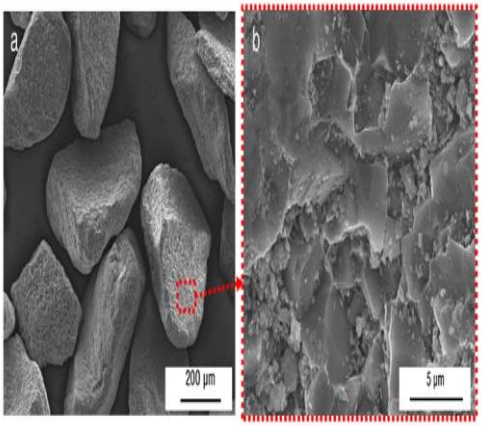

Fig. 1. SEM images of TiC-NiMo particles: (a) overview; (b) surface of the particle.

III. RESULTS AND DISCUSSION

3.1. Deposition

Deposits of the TiN–NiMo and NiCrBSi alloy powders in the ratio of40:60 vol.% were processed onto an austenitic stainless steel substrate.The selection of proportion for PTA hardfacings can be attributedto the low density of TiN-based reinforcements, where 40 vol.% of hardphaseswas suggested to be optimal for uniformhard particles distribution[24].Two separately controlled powder feeders were used for the adjustmentof the required powder ratio. The powders were transported. internally through the welding torch with the help of a carrier gas and then introduced into a molten weld pool which after solidification formed a metallurgically bonded layer on the surface of the base metal as schematically shown in Fig. 2.Optimised hardfacing process parameters are listed in Table 1. The parameters of deposition of TiN–NiMo phase are influenced by certainporosity; high welding energy (welding current up to 100 A and high plasma gas flow rate) is required to overcome this problem and minimize porosity level in a welding seam. Due to low density of TiN–NiMo reinforcements (~5.5 g/cm3), which is significantly lower than density of nickel-based alloy (~8.5 g/cm3), cermet particles float upward in themolten pool during solidification and almost no cermet particles remain at the close proximity to a coating base. The high carrier gas flow and pressure rates were found to improve the distribution of hard particles during deposition.Fig. 3 illustrates the TiN–NiMo reinforced NiCrBSi weld overlay.The OM examination reveals a uniform distribution of hard phasesin the matrix, negligible porosity of

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the hardfaced layer and overall good quality of the welding seam with minimal dilution with the substrateof less than 5% according to the quantitative analysis. The obtained coating seems to be metallurgically well bonded to the austenite substrate.

3.2. Microstructural analysis

Fig. 4 illustrates the microstructure of the cermet particle reinforced hardfacing. The following apparent phases were detected: dendritic Ni-based matrix, TiN-based precipitates of less than 2 μm in diameter,and TiN–NiMo cermet grains. Both hard phases were homogeneously distributed throughout the matrix. The nickel binder in the cermet particle is assumed to protect the primary carbides from dissolution.The XRD pattern of TiN–NiMo reinforced NiCrBSi hardfacing is presented in Fig. 5.

The analysis reveals five crystalline phases:

Ni-rich dendritic matrix — γ(Fe,Ni); (Fe, Ni, Mo)23B6, which is the most probable Fe–Ni–B hard phase located in dendrites with sometraces of Mo in the crystal lattice; TiC phase; non-stoichiometric carbide Ti0.92Mo0.02N0.6; and (Mo, Ti)N. Formation of solid solutions ofMo in the TiN lattice results in development of so-called core-rim structured grains consisting of a TiN core surrounded by the rim of(Ti,Mo)C [25–27].Fig. 6 presents SEM micrographs of the TiN–NiMo reinforcedhardfacing. The PTA welding process does not significantly influencethe structure and composition of the cermet particles. However, it isfound that besides a high amount of TiN-based spherical precipitates(Fig. 6d), TiN diffusing from the cermet zone to the matrix during depositionthe structure of cermet particles along the interface (Fig. 6b)differs from the microstructure of the cermet particles at the core(Fig. 6c). The particles near the interface are partially dissolved showingdecrease in grain size and modification in their shape. However,partially dissolved grains are still core-rim structured TiN–(Ti,Mo)Nparticles as confirmed by the EDX analysis of spots 1 and 2 indicatedin Fig. 6b and c and shown in Table 2.Table 2 identifies the chemical composition (wt. %) of TiN–NiMoreinforced hardfacing examined with energy dispersive X-ray (EDX)analysis. Results presented in Table 2 show average values of atleast 5 spot analyses. The corresponding EDX spots are labelled withnumbers in Fig. 6. Spot 1 corresponds to the core part of the TiCbasedgrain and shows only Ti and C, i.e. a TiC phase. Spot 2 wasof Mo with a concentration varying between 4 and 12 wt.%. This distributionof elements, verified at approximately 5 spots taken at therim part, confirms the presence of the (Ti,Mo)N phase, whichaccording to the XRD results can be non-stoichiometric carbide.

3.3. Mechanical properties

3.3.1. Hardness

The measured Vickers hardness of the pure NiCrBSi matrix was 365 ± 15 HV50, which is in good agreement with the previous study [22]. The macro hardness of the TiN–NiMo reinforced hardfacing is 571 ± 25 HV50. The hardness increase is probably due to the high content of uniformly distributed cermet particles and TiC-based precipitations.

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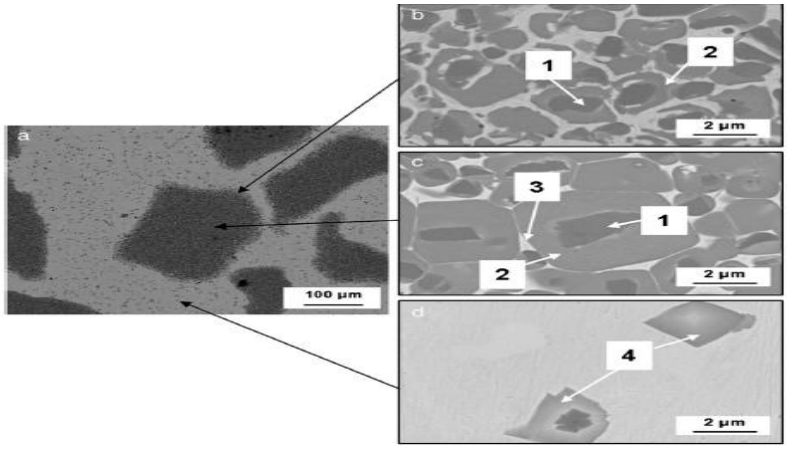

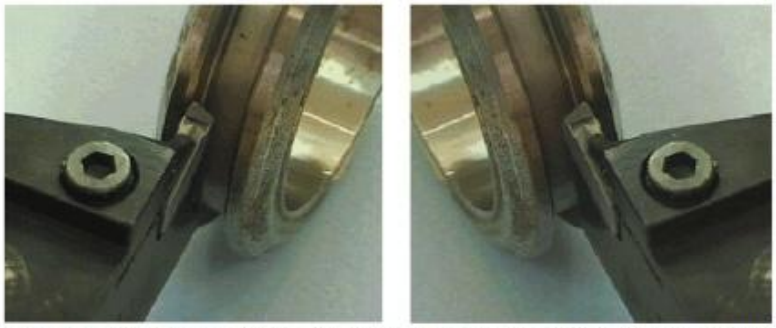

Figure 16: Machining a Synchronizing Ring with CBN CUT-GRIP Tools.

General Operating Characteristics of Cutting-tool Materials

Tool materials	General characteristics	Modes of tool wear or failure	Limitations
High-speed steels	High toughness, resistance to fracture, wide range of roughing and finishing cuts, good for interrupted cuts	Flank wear, crater wear	Low hot hardness, limited hardenability, and limited wear resistance
Uncoated carbides	High hardness over a wide range of temperatures, toughness, wear resistance, versatile, wide range of applications	Flank wear, crater wear	Cannot use at low speeds because of cold welding of chips and microchipping
Coated carbides	Improved wear resistance over uncoated carbides, better frictional and thermal properties	Flank wear, crater wear	Cannot use at low speeds because of cold welding of chips and microchipping
Ceramics	High hardness at elevated temperatures, high abrasive wear resistance	Depth-of-cut line notching, microchipping, gross fracture	Low strength and low thermomechanical fatigue strength
Polycrystalline cubic boron nitride (cBN)	High hot hardness, toughness, cutting-edge strength	Depth-of-cut line notching, chipping, oxidation, graphitization	Low strength, and low chemical stability at higher temperature
Diamond	High hardness and toughness, abrasive wear resistance	Chipping, oxidation, graphitization	Low strength, and low chemical stability at higher temperatures

Source: After R. Komanduri and other sources.

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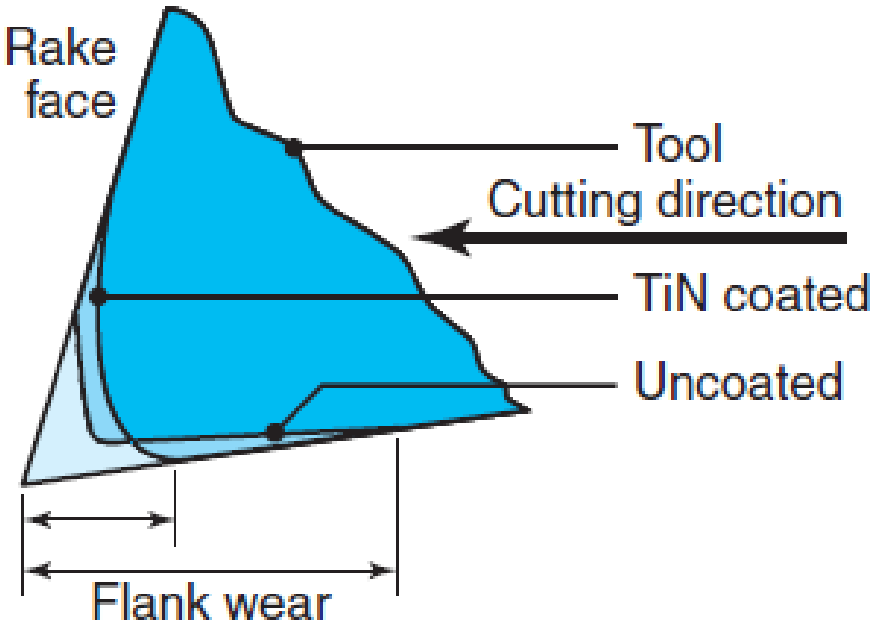

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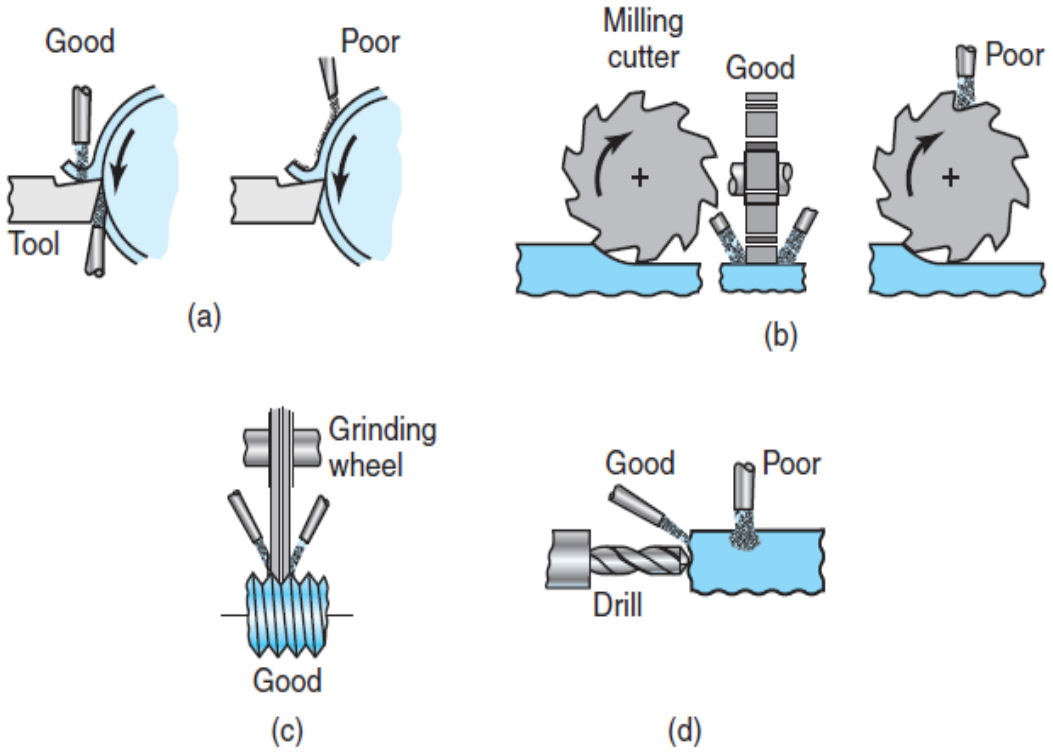
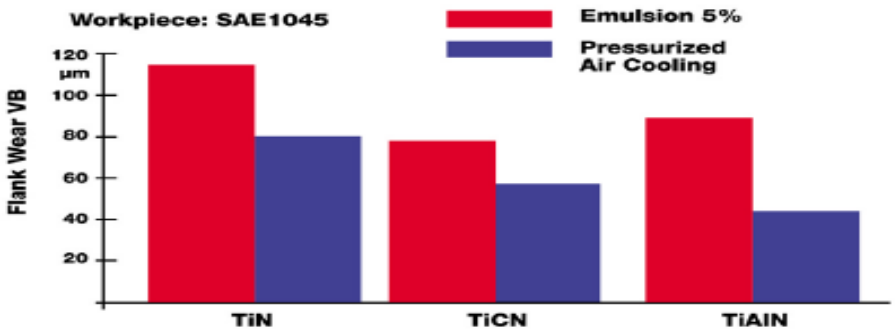


3.5. Abrasive wear behaviour

Wear tests exploiting steel and rubber wheels were carried out to reproduce three-body abrasion process. Quantitative wear analysis was performed by determination of volume loss, Fig. 12. The relative wear resistance of the TiN–NiMo reinforced hardfacing was comparedto conventionally used Ni-based reference hardfacing consisting of 40 vol.% of WC/W2C particles (Castolin Eutectic EuTroLoy PG 6503alloy). Generally, both materials under investigation indicate low wear values; however, conventionally used tungsten carbide reinforcedcoating shows approximately 40% higher wear resistance.The volumetric wear values of the materials tested with steel wheel are drawn on the abscissa. Wear of the commercially used WC/W2C reinforced alloy is significantly increased (almost by a factor Fig. 8. Calculated modulus of elasticity (E) vs. hardness (H) of different phases in the TiC–NiMo reinforced NiCrBSi hardfacing measured by nanoindentation.Fig.



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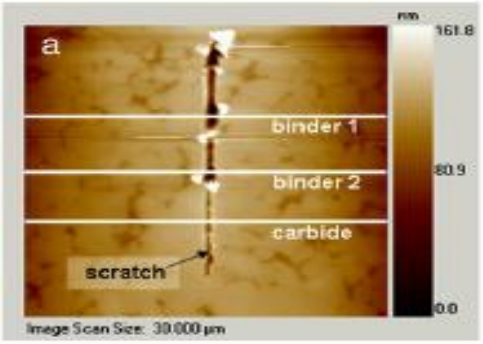
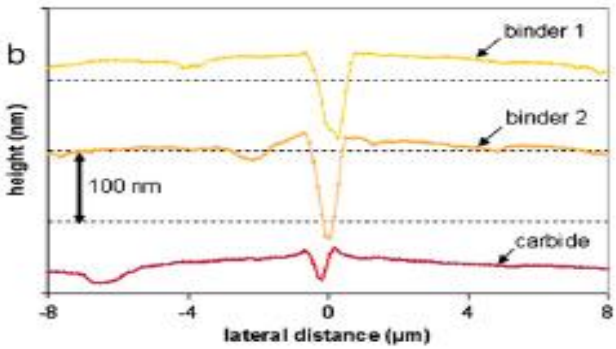
Designation	Workpiece Material	Carbide Grade	Vc (m/min)	fz mm/z	Tool Life TL
SEKR 1203 AFN-76	17-4 PH	IC 328	120	0.1	30'
SEKR 1203 AFN-42				0.1	20'
SEKR 1203 AFN-76	17-4 PH	IC 328	80	0.1	50'
SEKR 1203 AFN-76	Inconel	IC 328	25	0.1	28'
SEKR 1203 AFN-42					18'

of three), while wear of TiN–NiMo reinforced coating remains at almost the same low level.It is well known that abrasive wear behaviour is stronglyinfluenced by material hardness and microstructural features [33].Under conditions of three-body abrasion several wear mechanismscan dominate depending on material of a testing wheel. Exploitation of a rubber wheel simulates low stress abrasion, while application of asteel wheel results in a high stress mode of abrasion characterised by other mechanisms of material removal as compared to mechanismsoperating at low stress wear mode. To study the wear mechanisms,SEM surface sectional images of the worn areas were examined asshown in Fig. 13. High performance of WC/W2C reinforced alloy under testing with a rubber wheel is in a good correlation with previousstudies [6,7], where the high matrix hardness and dense distribution of coarse primary carbides ensure excellent wear resistance(Fig. 13a). Moreover, the secondary precipitations in matrix do not negatively influence the low-stress abrasion resistance and no crackswere detected by scanning electron microscopy. For the TiC–NiMo reinforced alloy the increase in wear rate can be attributed to lowhardness of the matrix material. The titanium Nitride based precipitates are small enough for successful protection of the matrix againstcoarse silica abrasive particles (Fig. 13c). The dominant wear mechanisms in this case are ploughing and cutting of ductile Ni-basedmatrix. Additionally, the inter-particle distances between cermet reinforcements are large that leads to the formation of hills in cermetsupported areas of the matrix.The behaviour of a material in a rotating wheel abrasion test depends not only on the intrinsic properties of the test piece itself, butalso on the conditions of the test [34]. Application of a steel wheel can cause a significant fragmentation of abrasive particles or theirembedment into the surface of base material [35]. Certain ductility





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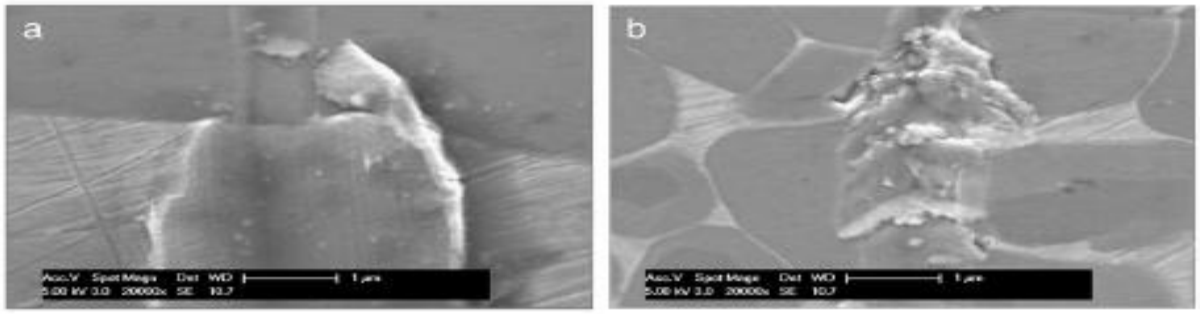

and specific microstructural arrangement are required to increase the abrasive wear resistance of multiphase materials. For the WC/W2C reinforced hardfacing (Fig. 13b) the brittle fracture of both primary carbides and matrix precipitates was observed; extensive crackingand subsequent chip removal explain a significant increase in wear rate by a factor of three. Compared to the brittle fracture behaviour ofthe Ni-based reference hardfacing consisting of 40 vol.% of WC/W2C particles, the TiN–NiMo reinforced alloy performs in a more ductileway (Fig. 13d), where no well pronounced brittle fracture of hard particles was detected: neither matrix precipitates nor cermet particlesindicate extensive crack formation. These results can be also correlated with the data obtained during nano-scratching, where no cracking ofhard particles was detected.

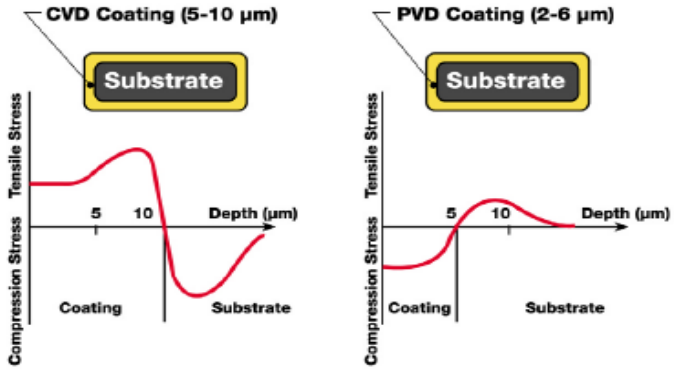

Figure 10: Stress Distribution in PVD and CVD Coated Layers.

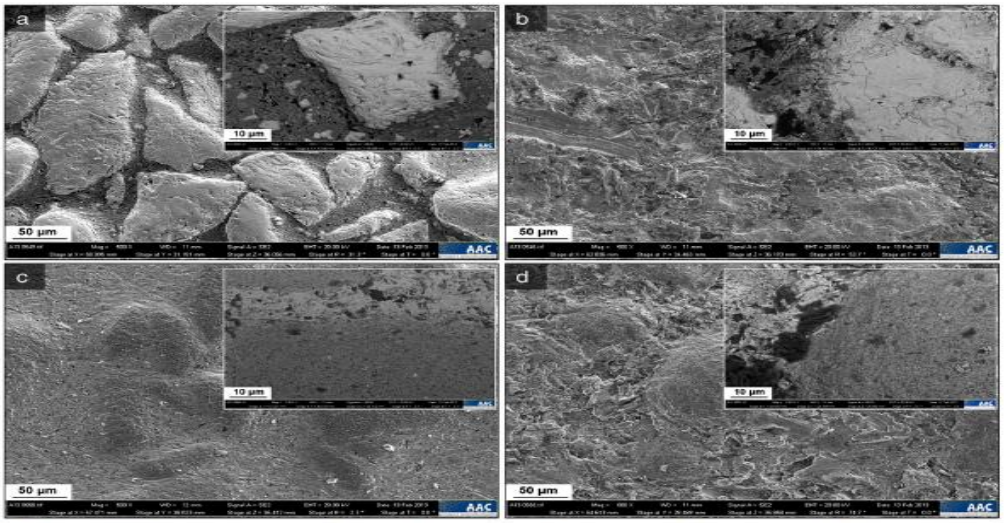

Fig. 13. SEM micrographs of worn hardfacing surfaces after three-body abrasion tests: a) and b) WC/W2C reinforced coating – rubber and steel wheel; c) and d) TiC–NiMo reinforced coating – rubber and steel wheel.

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IV. CONCLUSIONS

Based on the study within this work, the following conclusions canbe drawn:

- The titanium carbide based cermet particles recycled from TiNMo2C-Ni composites' scrap and applied for hardfacings deposition using the PTA technology can be successfully used for deposition of thick coatings characterised by uniform distribution of constituents and low level porosity.
- The mechanical properties of the TiN and (Ti,Mo)Ni phases measured by nanoindentation are very similar exhibiting a narrow distributionof the hardness and Young'smodulus values. Both carbide and precipitate phases indicate similar high hardness values, whereas the precipitatephase has significantly lower Young' modulus.
- The nano-scratching test reveals excellent bonding between the matrix and cermets in the hardfacing. No extensive cracking was detected in the interface matrix/hard phase region.
- The performance of the TiN–NiMo reinforced hardfacings under low stress three-body abrasion is lower as compared to the commercially used WC/W2C reinforced coatings. Wear mechanisms operating in TiN–NiMo reinforced alloy are matrix material ploughing and cutting. Fine structured TiN-based precipitates do not provide sufficient protection against coarse abrasive particles.
- Under high-stress three-body abrasion TiN–NiMo reinforced hardfacings show significantly higher wear resistance as comparedto commercially used WC/W2C reinforced coatings. The tungsten carbide reinforced coating shows brittle fracture of the coarseprimary carbides and secondary precipitates, while fine-grained structure of TiN–NiMo reinforcements is not subjected to extensivecracking during the test.

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