SPOTLIGHT

Novel nanostructured coatings by pulsed electrodeposition

Pulsed Electrodeposition (PED) has been developed by the International Advanced Research Centre for Powder Metallurgy and New Materials (ARCI), Hyderabad as an alternative to conventional electroplating – hard chrome coating – for enhanced corrosion and wear protection

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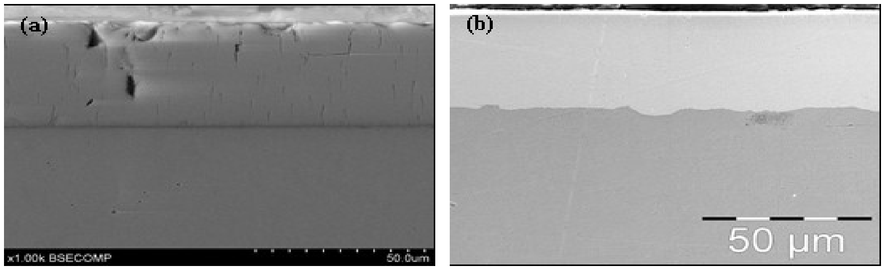
THE global quest for futuristic and advanced technologies with a potential to replace the conventional processes is often driven by the concurrently increasing need for (a) enhanced materials performance; (b) multi-functionalisation; and (c) stringent environmental regulations associated with a given process. In this context, ARCI (International Advanced Research Centre for Powder Metallurgy and New Materials, Hyderabad, India) has developed a novel environmentally benign process called Pulsed Electrodeposition (PED) as an alternative to conventional electroplating. PED is applied for depositing wear and corrosion resistant coatings by means of well-modulated currents during the electroplating process. The candidate materials discussed in the present article includes nanocrystalline Ni-W alloy and Ni-W/SiC nanocomposite coatings that can be used as an alternative for conventional hard chrome-plating. In this context, the present article deals with the properties and the performance of these novel coatings developed at ARCI in comparison to commercially successful and industrially acceptance conventional hard chrome and NIKASIL coatings.

After world war II, owing to its excellent hardness (600-1100 HV), hard chrome (Cr) coatings have been rapidly developed to cater to the needs of numerous industries and military applications demanding improved wear resistance. These coatings are deposited using conventional (direct current) electroplating techniques employing typically a sulphuric acid bath comprising desired catalysts to get required hardness and aesthetics. However, due to inherent micro cracks [**Figure1 (a)**] generated by the residual stresses present in coatings, there is an overall debit on corrosion and fatigue life. Therefore, to alleviate this problem, an inner layer of Ni coating is often provided to hinder the corrosion species easily reaching the underlying substrate, of course, adding to an extra cost of overall coating. Chrome coatings are generally used in the as deposited condition without any further thermal treatments and, therefore, not suitable to function at elevated service temperature due to significant decrease in hardness above 200°C (from 1100 HV at room temperature to 500 HV at 500°C).

Furthermore, the conventional hard chrome (Cr) electroplating process, which releases Cr6+ fumes (carcinogenic) into the atmosphere, is known to be hazardous

Figure1: Cross-sectional morphologies of (a) Conventional hard chrome coatings with numerous cracks, porosity present in it; (b) Ni-W coatings with virtually crack free structure



to the health of personnel working in the plating plant. Therefore, stringent emission standards have been imposed by the Occupational Safety and Health Administration (OSHA) to limit the maximum permissible levels of Cr to 0.0005 mg/m3 at workplace which led to the shutdown of many hard chrome plating plants across the globe, including those in many developed countries. Therefore, there has been a global search for new, alternative coating techniques to alleviate the typical problems associated with conventional Cr in terms of both health issues and concurrently improved coating performance. The new process shall, therefore, be capable of utilising the existing electroplating infrastructure and will be environmentally benign too.

During the last two decades, numerous research groups across the world have focused on synthesis of bulk nanocrystalline alloys using pulsed electrodeposition (PED) as a suitable alternative for conventional hard chrome plating. In the PED process, current is applied in the form of a square wave or pulse and, therefore, by modifying the pulse parameters, it is possible to obtain the deposits with desired composition, structure and porosity. Interestingly, pulse deposition also reduces the quantum of bath additives by 50-60% and simultaneously provides a uniform/fine surface finish even at significantly enhanced deposition rates. In addition, it should be noted that the PED process allows extremely low level absorption of hydrogen and, therefore, provides improved corrosion resistant properties. In view of such an interesting portfolio of properties, the PED process and resulting performance of Ni-W alloy and Ni-W/SiC nanocomposite coatings are briefly presented in the following sections.

Ni-W ELECTROPLATING PROCESS

Considering the potential advantages of pulsed electrodeposition, ARCI's research team has recently developed a novel process to deposit crack free Ni-W alloy coatings as shown in **Figure1 (b)** with high hardness in the range of 600-750 HV coupled with excellent corrosion resistance, as deposited. A novel combination of cathodic and anodic pulses during the pulsed current electroplating helped to achieve such crack-free Ni-W coatings containing significantly lower hydrogen and impurity concentration, which otherwise is difficult to achieve through conventional electroplating techniques.

Depending upon the specific application requirements, the W content of Ni-W coating can be varied from 0 to 28 at%. It is noteworthy to mention that the grain size and the corresponding hardness of the coating greatly changes with the change in W content of Ni-W alloy coatings as shown in **Figure2** following a classical Hall-Petch relation. The hardness of these coatings therefore can be varied from 200 to 800 HV (3 to 10 GPa). The hardness can further be increased up to 1200 HV upon heat treatment of these coatings at 300-500°C. Such a technological flexibility provides the window of opportunities for significantly enhancing the value addition to the industrial components working in harsher environments.

Corrosion and wear protection

The relative corrosion and wear performance evaluation of Ni-W alloy coatings in comparison with hard chrome coatings was investigated. It was observed that Ni-W alloy coatings are resistant to corrosion in highly aggressive H2SO4 environment. As illustrated in **Figure3** (**a**), the corrosion resistance of Ni-W coatings is 10 times higher than conventional hard chrome coatings. It may be noted that the increase in corrosion resistance with increase in W content of coatings suggests the synergetic effect of W for improved corrosion resistance. It was observed that W forms highly passive WO3 film on the surface of Ni-W alloy due to selective dissolution of Ni during corrosion process, thereby protecting it from further corrosion.

The tribological performance of coatings was evaluated under dry sliding wear mode as per ASTM G99. The hard WC-Co disc was used as counter body during the wear tests. The friction coefficient of Ni-W coatings falls within a window of 0.4-0.6 whereas the average friction coefficient of hard chrome coatings was about 0.6. The wear rate of Ni-W alloy coatings was only about 50% of hard chrome coatings especially at higher loads suggesting an improved load bearing capacity of Ni-W alloy coatings. The wear mechanism in Ni-W coatings was dominated by abrasive wear mode while it was mostly limited to adhesive wear mode in the case of hard chrome coatings.

Due to such an outstanding performance resisting degradation under wear and corrosion modes, Ni-W alloy coatings have attracted significant attention in various industrial components such as valves, pipes, pumps, heat exchangers in automobile, aerospace, energy, electronics, and petroleum industries. In order to further improve the properties of Ni-W alloy coatings in extreme environments as well as high temperature exposure, the submicron-sized SiC particles were introduced into the Ni-W matrix thereby forming nanocomposite coatings as detailed in following section.

Figure2: Influence of W content on the grain size and hardness of Ni-W alloy deposited through PED technique

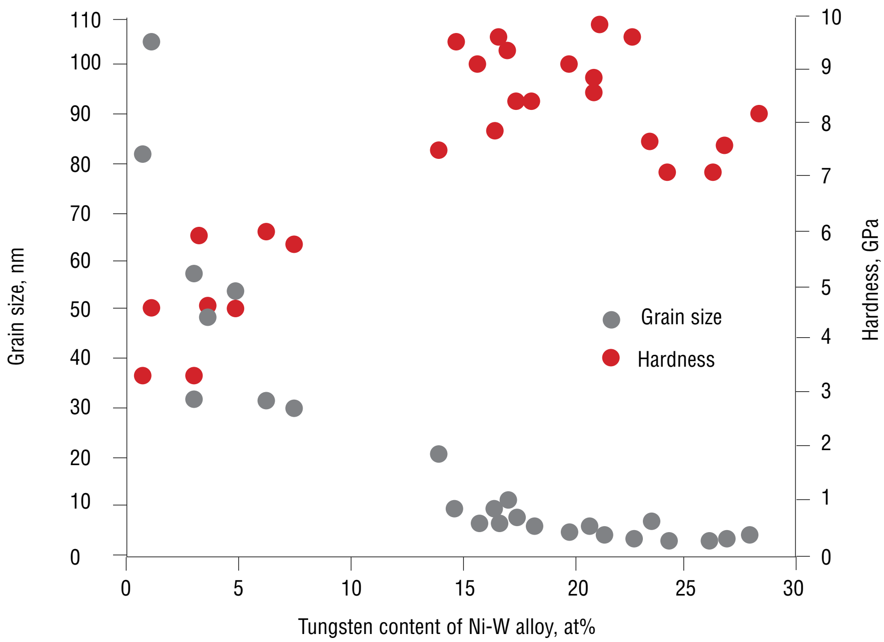
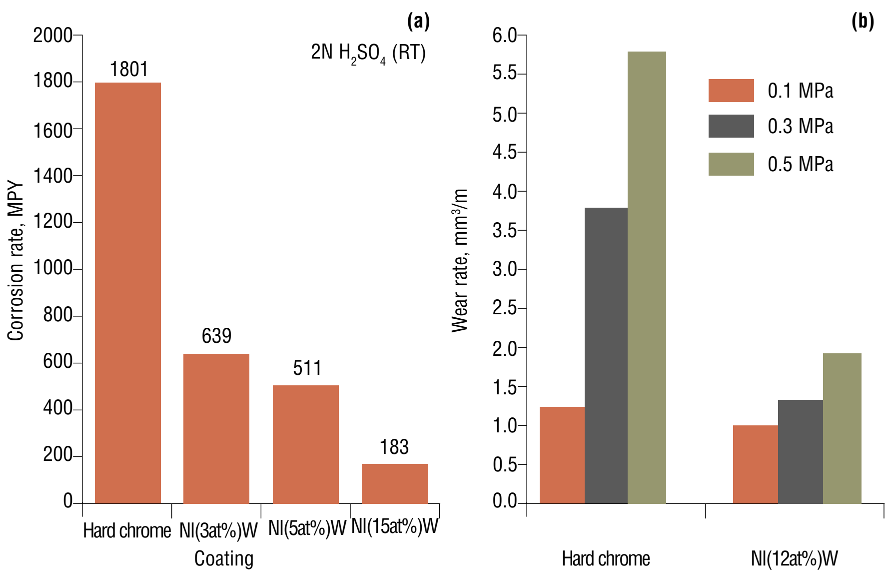


Figure3 (a) Corrosion and (b) wear performance of Ni-W alloy coatings in comparison to hard chrome



Ni-W/SiC NANOCOMPOSITE ELECTROPLATING PROCESS

The electroplating of Ni-W/SiC nanocomposite involves deposition of nickel and tungsten in the presence of SiC (hard) particles dispersed in electrolyte using carefully optimised pulsed current parameters thereby the co-deposition of SiC in Ni-W alloy matrix is achieved. The optimised pulsed current ensures the uniform deposition of SiC particles within the Ni-W matrix without any adverse agglomeration. The process is presented schematically in **Figure4** (**a**).

The resultant coating consists of a tough Ni-W alloy matrix and hard SiC particles uniformly distributed within the matrix as shown in **Figure4** (**b**). The surface morphology shows less globular Ni-W matrix in the presence of SiC particles thereby restricting the surface roughness to minimal level. Accordingly, the coating cross section [**Figure5** (**a**)] indicates uniform distribution of SiC particles throughout the coating thickness and good interface bonding between the particles and surrounding matrix as can be inferred from the transmission electron micrograph presented in **Figure5** (**b**). The Ni-W alloy is seen as a single phase material with a face centred cubic (FCC) structure as indicated by selected area diffraction pattern. The grain size of Ni-W matrix is estimated to be 7 nm which is much less than the SiC particle size. This indicates that the hardness is simply not due to dispersion effect but due to the composite effect.

Depending upon the SiC content (0-6 vol%) of Ni-W matrix, the hardness of composite coatings can be varied between 800-900 HV in the as-deposited condition. The hardness can further be increased to 1200-1550 HV after heat treatment at 300-500°C, which can be used for realising protective coatings on critical components. However, it may also be noted that the heat treatment does not lead to any phase change in matrix alloy or the interaction between

Figure4: (a) Schematic of composite coating deposition process; and (b) surface morphology of typical Ni-W/SiC nanocomposite coating

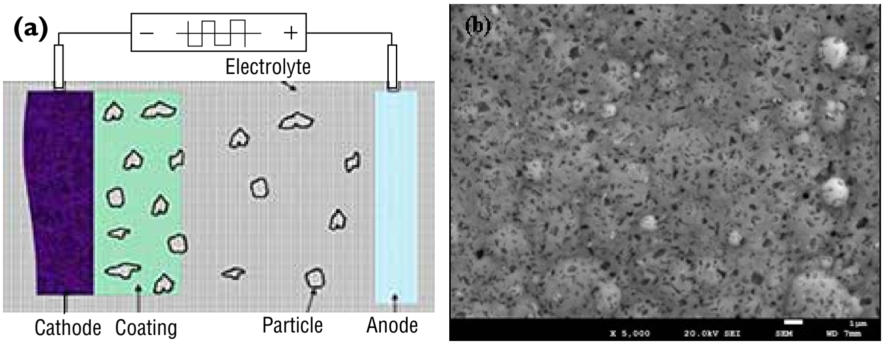
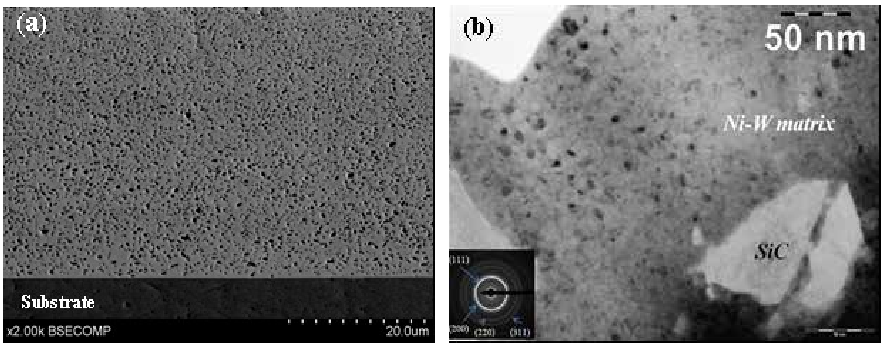


Figure5: (a) The cross-sectional view of Ni-W/SiC nanocomposite coating; and (b) TEM micrograph indicating excellent interface bonding between Ni-W matrix and SiC particle (selected are diffraction pattern is presented inset)



Ni-W and SiC particles as established through the detailed X-ray diffraction studies. In support of this argument, the Differential Scanning Calorimetry (DSC) analysis as shown in **Figure6** indicate an excellent high temperature thermal stability of nanocomposite coatings up to 600°C unlike traditional Ni-P, Ni-P/SiC, Ni-SiC, NIKASIL coatings. Therefore, the higher hardness of heat treated composite coatings is due to the grain boundary relaxation phenomena and composite hardness effect as well. For enabling quicker understanding, the process of PED compared with the traditional hard chrome plating is presented in **Table1**.

Corrosion and wear protection

The as deposited Ni-W and Ni-W/SiC nanocomposite coatings along with traditional hard chrome coatings (50 µm thick) were subjected to salt fog environment up to 1200 hours of exposure as per ASTM B117. Subsequent to such tests, these coatings were ranked as per ASTM B537-70. ASTM rating of 10 implies the best protection capability of

Figure6: Differential scanning calorimetry of different coatings

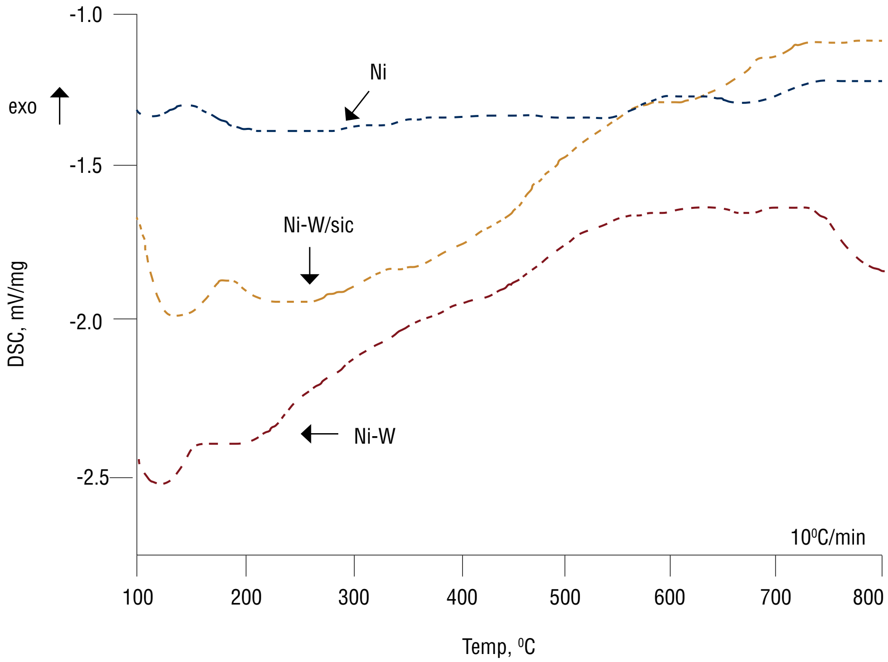


Table1: Process comparison between PED-nanocomposite and hard chrome plating

	PED-nanocomposite	Hard chrome
Process	Pulsed electrodeposition	Direct current deposition
Deposition rate (μm/hr)	35-50	15-20
Structure	Nanocrystalline free of cracks	Micro cracked
Environmental hazard	Below OSHA	Carcinogenic
Hardness	700-900 HV as-deposited 1200-1550 HV heat treated	600-1100 HV as-deposited 300-400 HV heat treated

electroplated coating whereas rating of 1 indicates poor performance. Based on the results presented in **Figure7 (a-b)**, it is clear that both Ni-W and Ni-W/SiC coatings can withstand (700 hours, 10 rating) 1200 hours of salt fog (9 rating) whereas hard chrome coatings are rated as 0 (no protection) after 48 hours of exposure, leading to an eventual conclusion that overall corrosion resistance of PED nanocrystalline Ni-W and Ni-W/SiC nanocomposite coatings is significantly superior to that of conventional hard chrome coatings.

The wear performance of nanocomposite coating is presented in **Figure8** and the relevant data is summarised in **Table2**. The friction coefficient vs. sliding distance (against WC-Co disc) of nanocomposite coatings in comparison to traditional hard-chrome, NIKASIL and Ni-W coatings is illustrated in Figure8 (b). The lower coefficient of friction is demonstrated by Ni-W/SiC nanocomposite in the as-deposited as well as heat treated conditions. Although the Ni-W/SiC nanocomposites have lower volume fraction (6 vol%) of SiC, the wear rate as well as friction coefficient is only half of the NIKASIL (16 vol% SiC) and hard chrome coatings. Such a behavior is attributed to the finer and uniform distribution of SiC particles inside Ni-W matrix.

Figure7: (a) ASTM B537-70 salt fog rating: and (b) photographs of coatings after 1200 hours of salt fog test as per ASTM B117

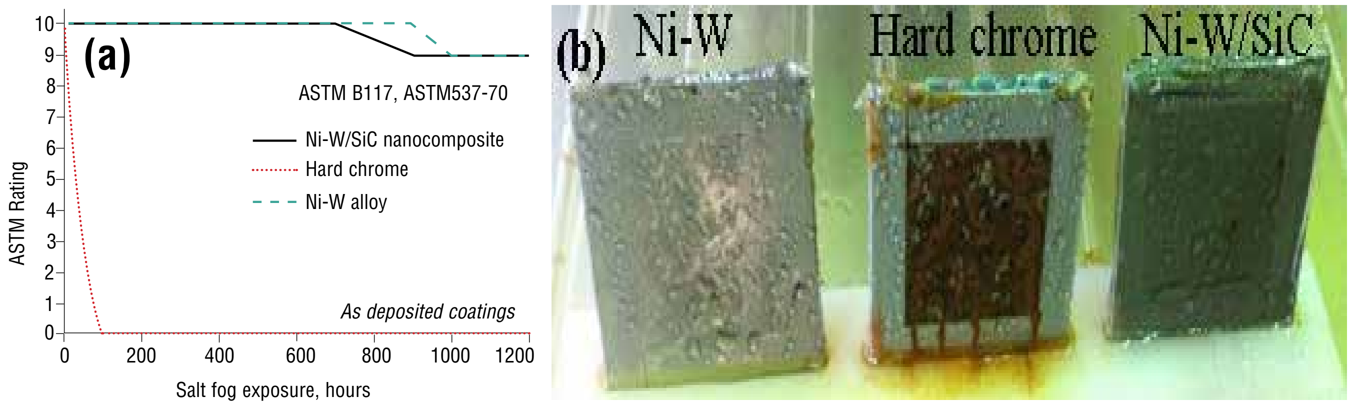


Figure8: (a) Dry sliding wear rate; and (b) friction coefficient Ni-W/SiC in comparison to NIKASIL and hard chrome

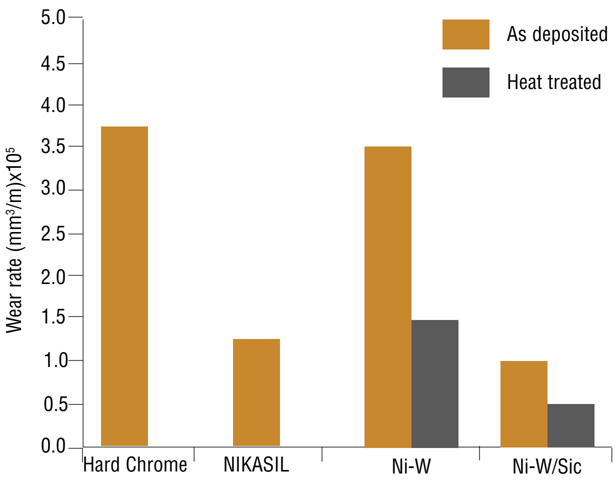


Figure8: (a) Dry sliding wear rate; and (b) friction coefficient Ni-W/SiC in comparison to NIKASIL and hard chrome

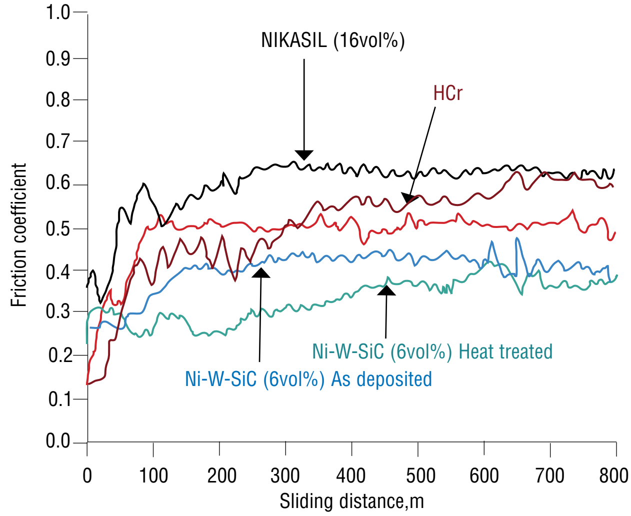


Table2: The properties and performance comparison of PED: Ni-W/SiC nanocomposite, commercial NIKASIL coatings and hard chrome plating

Type of process-coating combination			
	PED: Nanocomposite Ni-W/SiC	**Commercial NIKASIL (Ni-SiC)**	**Hard Chrome**
SiC volume fraction	0-6 %	16 %	-
Hardness, (HV)	700-800 1400 (heat treated)	610 200 (heat treated)	600-1000 (300 heat treated)
Wear rate, (mm3/m x105)	1 (as-deposited)	1.25 (as-deposited)	3.75 (as-deposited)
Coefficient of friction	0.4 (as-deposited) 0.3 (heat treated)	0.65	0.6
Salt spray rating	10 For >700 hrs		7 for 12 hrs 1 by 48 hrs
Deposition mode	Pulsed current	Direct current	Direct current

SCALE-UP, APPLICATION DEMONSTRATION, AND TRANSFER OF PED TECHNOLOGY

Since Ni-W and Ni-W/SiC nanocomposite coatings established at ARCI were found to exhibit the exciting combination of hardness, wear and corrosion resistances coupled with outstanding thermal stability, it is envisaged that any industrial component that is being traditionally provided with conventional hard chrome or NIKASIL coatings can make use of these novel coatings. In line with this concept, the applications related to automotive engine components such as exhaust valves, internal coatings on cylinder liners, piston rings and others as depicted in **Figure9** were pursued and comprehensive functional capabilities were established at ARCI. In recognition of other potential applications in the other sectors such as oil and gas, agriculture and aerospace, the PED technology has been scaled up to make it suitable for industrial mass production application. Utilising the extended scale of operations, various sizes and geometries of components including the internal coating on larger parts are being currently provided with a variety of alloys and nanocomposite coatings to meet the functional requirements. The PED technology developed at ARCI is readily available for industry in India and abroad for commercial exploitation in terms of application development and technology transfer.

Figure9: Various industrial components coated with PED technology at ARCI

References

1 Nitin P Wasekar, G Sundararajan: An improved method for preparing nickel electrodeposite having predetermined hardness gradient. Indian Patent No: 285178 (Granted on 14/07/2017)

2 Nitin P Wasekar, D Srinivasa Rao, G Sundararajan: A method and an apparatus for preparing nickel tungsten based nanocomposite coating deposition. Indian Patent (Application No. 201611001190, dated 13/01/2016)

3 NP Wasekar, L Bathini, G Sundararajan: 'Tribological behavior of pulsed electrodeposited Ni-W/SiC nanocomposites,' Journal of Materials Engineering and Performance, 27 (2018) pp 5236-5245

4 MVN Vamsi, NP Wasekar, G Sundararajan: 'Sliding wear of as-deposited and heat-treated nanocrystalline nickel-tungsten alloy coatings,' Wear, 412 (2018) pp. 136-143.

5 MVM Vamsi, Nitin P Wasekar, G Sundararajan: 'Influence of heat treatment on microstructure and mechanical properties of pulsed electrodeposited Ni-W alloy coatings,' Surface and Coatings Technology, 319 (2017) pp.403-14.

6 M Sribalaji, OSA Asiq Rahman, P Arun Kumar, K Suresh Babu, Nitin P Wasekar, G Sundararajan, AK Keshri: 'Role of silicon carbide in phase-evolution and oxidation behaviors of pulse electrodeposited Nickel-Tungsten coatings,' Metallurgical and Materials Transactions A, 48(1) (2017) pp.501-12.

7 Nitin P Wasekar, S Madhavi Latha, M Ramakrishna, DS Rao and G Sundararajan: 'Pulsed electrodeposition and mechanical properties of Ni-W/SiC nanocomposite coatings,' Materials and Design, 112 (2016) pp.140-50.

8 Rahman, OSA, NP Wasekar, G Sundararajan, AK Keshri: 'Experimental investigation of grain boundaries misorientations and nano twinning induced strengthening on addition of silicon carbide in pulse electrodeposited nickel tungsten composite coating,' Materials Characterization, 116 (2016) pp.1-7.

9 Singh, S, M Sribalaji, NP Wasekar, S Joshi, G Sundararajan, R Singh, AK Keshri: Microstructural, phase evolution and corrosion properties of silicon carbide reinforced pulse electrodeposited nickel-tungsten composite coatings, Applied Surface Science, 364 (2016), pp.264-72.

10 Nitin P Wasekar, G Sundararajan, 'Sliding wear behavior of electrodeposited Ni-W alloy and hard chrome coatings,' Wear 342 (2015) pp.340-8.

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