

Metastable surface modification processes for corrosion and oxidation control

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This technical note discusses recent advances in the field of high energy surface alloying with particular reference to their non-stoichiometric solid state interaction and their corrosion resistance behaviour by electrochemical techniques. High energy treated surfaces undergo solid state interaction like diffusion, unconventional miscibility, solid solubility and non-stoichiometric compositions which impose a certain degree of metastability on the surface, which alters the electrode surfaces significantly. By introducing a high degree of surface metastability, it is possible to create scope for the physical and chemical properties of the electrodes. This transition of the interface from the metastable state to a stable state is normally accompanied by the formation of a stress free stable thin adherent and protective surface oxide layer. All these aspects are discussed in the present paper in the context of their corrosion resistance industrial usage, in particular to chloroalkali industrial applications. A generalised mechanism of protection of these high energy treated surfaces, is proposed based on surface metastability induced on the surface, as a result of the non-stoichiometry of solid state processing and its electrochemical interactions.

Keywords: High energy surface modification, Surface coating, Metastability and interconnected porosity structure

Introduction

The high energy surface processes¹⁻⁵ and surface modification techniques are solid state interaction aimed at metallic surfaces, revealing improved mechanical properties and resistance to oxidation and corrosion. Such surface altered substrates affect the changes of the specific and selected physicochemical properties like resistance to wear, erosion, corrosion, stress corrosion cracking (SCC) and corrosion fatigue. Surface modification processes may be either of the high energy category like ion implantation, laser irradiation and surface alloying methods or the low energy classes, for example, diffusion coating, thermal spraying and electroplating in a suitable electrolyte. Conventional thermal spraying and electroplating are non-diffusional, while chromiding and diffused salt plating come under the diffusional category. However, all the high energy processes may not necessarily form a diffusional alloy layer, for example in plasma spraying process, the barrier layer is formed from each particle accompanied with various degrees of interconnected porosity with virtually no formation of a diffusional alloy layer at the interface. On the contrary, high energy processes like laser alloying, ion implantation and surface alloying involves the

formation of a specific and a very thin layer of diffusional alloy between the interfaces of coating and the substrate. The present paper has discussed all the above aspects and compared the different high energy interfaces, in the context of their resistance to corrosion and oxidation.

Surface modification and their electrochemical interactions

It appears that surface modifications, whether the high energy or low energy category, involving diffusional or by non-diffusional techniques, possess varying degrees of surface metastability, as a result of a step change in the level of surface energy as a result of surface modification treatment. Depending on the degree of surface metastability, the modified surfaces may develop either a protective adherent film or a semiprotective marginally adherent layer, during their exposure to an industrial environment. The salient feature of some of the popular high energy surface modification processes, such as ion implantation, amorphous metallic glass and metal metalloid barrier, laser surface modification and plasma surfacing are discussed below. In all these processes, there is an active component known as surface metastability, which is responsible for the protective surface barrier in contact with an aggressive corrosive environment as in the chloroalkali industries. The root cause of the surface metastability may be connected to the surface non-stoichiometry, attained as

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a result of the application of these high energy surface modification processes. A literature investigation has revealed enormous volumes of published material on all these processes, but on the other hand there is no systematic approach to compare and categorise these high energy solid state interactions and processes, in terms of their corrosion resistant behaviour in particular environments. With the advent of sophisticated technologies, we are going to enter in a new era of surface alloying technology, where corrosion may be a major player as far as destabilisation of the metallic surfaces are concerned. Previous workers on amorphous surfaces have been mostly concerned on the surface analysis keeping aside the unique anodic interaction of the surface as a result of the surface metastability.⁶⁻¹⁵ Studies on laser treated surfaces have not dealt with the specific correlation of metastability and the formation of surface film.¹⁻³ Furthermore, earlier workers also have not discussed the role of interconnected porosity, which renders that such deposits are useless for corrosion resistance coatings unless attention has been attracted to consolidate their porous structure.^{4,5}

High energy processes at glance

Ion plating differs from the ion implantation and laser treatment processes in that, unlike the other processes, a visible coating is formed on the modified surface after ion plating. It is a modern deposition technique in which high energies are imparted to the vapour atoms by means of a glow discharge, resulting in the formation of an adherent surface coating. Ion plating of lead and cobalt using conventional techniques and reactive ion plating of titanium nitride have become very popular in industry. Ion implantation, despite a high energy process, has not become very popular because of the low corrosion resistance it normally shows. Other functional applications are limited owing to the fact that the coating thickness, including the diffusional alloy layer, remains within a few angstrom range. As in the case of ion implantation, ion plating provides a means of implanting any ion into any metal substrate irrespective of the equilibrium solubility of the implanted species on the substrate. It may be recalled that such unconventional mutual solid solubility among the elements of extremely different melting points which are not covered by the conventional phase diagrams is the reason behind the high degree of metastability imposed on the high energy treated surfaces. In fact such surface metastability is a direct offshoot of the non-stoichiometric strains imposed on the matrix. The basic functional difference between ion implantation and ion plating lies in the fact that the thickness of ion plating may go up to even 100 μm

Laser surface treatment

The basic nature of alloy formation in laser treatment is more or less similar to that of electron beam melting although laser processing is characterised by its particle to particle quenching associated with the generation of a very high cooling rate ($\sim 10^6 \text{ K s}^{-1}$) being the reason behind the formation of an amorphous back up layer in the laser melted interface. Optimisation of energy and power density of the laser source, the distance between the substrate and the source, and the exposure time may

help in obtaining the right type of output accompanied with minimum loss of laser energy because of reflection. Although indiscriminate use of laser processing has been reported to be associated with the generation of surface defects and heterogeneities, parameter optimised laser treatment has been found to be useful in reducing the surface embrittlement of sensitised matrices. Laser treatment has also been useful in the consolidation and reduction of the interconnected porous structure of the plasma sprayed barrier layers; improvement of surface topography and reduction of lattice defects associated with high dose ion implantation on metallic surface and also for the improvement of the oxidation and corrosion resistance of commercial alloys. Recently pulsed lasers employing tetrasecond pulses have appeared in the industrial arena for obtaining controlled microstructure and abrasion free metallic surfaces.⁷

Plasma surfacing

Thermal spray coatings are produced by using ceramic powders and particulates to produce desirable surface properties on various metallic and non-metallic substrates. Such properties include, resistance to oxidation, abrasion, wear resistance and enhancement of lubrication retaining capacity. Recently they have been used to compensate and restore worn out engineering components. This also applies to the coatings of oxides and carbides obtained by the spray technique using plasma beams, i.e. plasma surfacing. However, as in the case of the conventional thermally sprayed layers, plasma sprayed barrier coatings also reveal a large number of interconnected porosity which allows easy substrate attack by the electrolyte. Recently there has been a tendency to use these barriers in jet engines and turbo jet environment owing to their refractory nature and high temperature stability. However, the presence of corrosive gases makes these porous coating greatly unstable in high temperature turbo jet environment. Low pressure plasma deposition (LPPD) layers reveal lower degree of porosity, compared with the air sprayed variety because of the avoidance of substrate oxide products. However, parameters optimised and cost effective consideration of these sprayed barrier coatings are absolutely necessary for their subsequent use in corroding environment. Plasma sprayed barrier coatings are formed by a particle by particle process, allowing considerable scope for the introduction of oxide debris and porosity in among these particles, particularly when the spraying is conducted in the absence of vacuum.

Experimental study

In order to experimentally study high energy surface alloying methods commercially available carbon steel substrates, metallic glass foil and carbon steel coated with amorphous barriers have been used for our present studies. Metallic glass foil specimens of the composition $\text{Fe}_{82}\text{B}_{10}\text{Si}_8$, have been obtained from allied chemicals. While $\text{Pb}_{85}\text{Sb}_{15}$, $\text{Pb}_{80}\text{Sb}_{20}$, $\text{Pb}_{80}\text{Sb}_{10}\text{Sn}_{10}$ and the surface doped ribbon of $\text{Pb}_{80}\text{Sb}_{19}\text{Cu}_{0.71}\text{Ni}_{0.13}\text{Cd}_{0.09}\text{Fe}_{0.01}\text{Al}_{0.04}\text{Si}_{0.02}$ were obtained by a rapid quenching technique using a spinning wheel route designed and fabricated at the Central Electrochemical Research Institute (CECRI). Ni-P-B clad carbon steel panels were obtained through current assisted electroless routes,

Table 1 Electrochemical characterisation of Pb-Sb rapidly quenched alloy ribbons, using galvanostatic current potential relationship*

Sl. No.	Materials studied	Treatment conducted on the materials		Galvanostatic current potential values	
		Pretreatment	Post-treatment	Potential, mV	Current, mA
1	Pb ₈₅ Sb ₁₅	As cast alloy, cast at 523°K using graphite mould	Nil	-300 ± 5	1000 ± 10
2	Pb ₈₅ Sb ₁₅ rapidly quenched	Cast at 523°K and remelted within 423–473°K for rapid quenching	Nil	-300 ± 5	800 ± 10
3	Pb ₈₅ Sb ₁₅ rapidly quenched ribbon	Cast at 523°K and remelted within 423–473°K for rapid quenching	The rapidly quenched ribbons aged at 323 K for 1/2 h	-300 ± 5	500 ± 5
4	Pb ₈₅ Sb ₁₅ rapidly quenched ribbon	Cast at 523°K and remelted within 423–473°K for rapid quenching	The rapidly quenched ribbons aged at 323 K for 1 h	-300 ± 5	400 ± 5

Electrolyte: 3%NaCl solution with respect to SCE.

using bath formulations developed at CECRI. A CO₂⁻ continuous laser of 2 kW capacity was used to obtain laser alloyed interfaces of Cr-Fe and Ni-Cr-Fe. Initially Cr and Ni-Cr layers were sprayed on the carbon steel substrates by a conventional plasma spraying unit, followed by laser chromiding. The TiO₂-Al₂O₃ and Ni-Al coated panels were obtained by using a plasma-tron machine, employing a mixture of plasma grade powders of TiO₂-Al₂O₃ (95:5) and Ni-Al (95:5) using argon as carrier gas after sand blasting of the substrate with 5 Kg cm⁻² blast pressure. Then the specimens were heat treated at an appropriate temperature.

Results and discussion

Table 1 shows the electrochemical characterisation of Pb₈₅Sb₁₅ as cast, rapidly quenched alloy ribbons with and without aging using galvanostatic current potential relationships. It can be seen that although the potential values remain constant at -300 mV rapid quenching of the cast Pb₈₅Sb₁₅ alloy and subsequent aging at 323°K for periods ranging from 1/2 to 1 h, the current value reduces in a progressive manner, which indicates that the kinetic factor, namely the galvanostatic induced leaching of the ribbon surface is considerably reduced as a result of consolidation of the ribbon surface owing to heating and pressing. It further appears that there is a thermally activated homogenisation of the matrix, along with the sealing porosity during the aging process. Table 2 reveals the corrosion resistance properties of the rapidly quenched Pb₈₀Sb₂₀ alloy ribbons in the as quenched and heat treated state. It seems that the proportional corrosion rates are of a much lower magnitude than in the case of as quenched, heat treated and cold pressed state, which indicates that alternate heating and cold pressing tends to consolidate the porous structure of the

as quenched ribbons resulting in a decrease of surface corrosion and leaching owing to reduction of the galvanically induced dissolution. This is a result of the reduction of the stress raiser sites around the pores on the surface of the ribbons. It is further observed that impurity doping of the Pb₈₀Sb₂₀ rapidly quenched ribbons was not very effective as far as the reduction of the corrosion rates of the ribbons caused by the post consolidation treatments are concerned. From an overall consideration of all the data presented in Tables 1 and 2, it appears that alternate cold pressing and heating of the Pb-Sb based ribbons result in better homogenisation of the matrix microconstituents along with the sealing of the surface pores and neutralisation of other surface defects as reflected in their lower proportional corrosion rate values.

Table 3 reveals the response of the metastable rapidly quenched Pb-Sb binary and ternary foils, amorphous Ni-P-B coated and codeposited thin carbon steel substrate and Fe based metglas alloy ribbons in 3%NaCl environments. There is reduction in the level of corrosion rate along with an increase in the level of melting point and surface hardness values as a result of reinforcement of composite particulates such as tungsten carbide, boron carbide, silicon carbide and alumina within the current assisted amorphous Ni-P-B deposits. On the other hand addition of Sn in the Pb₈₅Sb₁₅ ribbons results in an increase of the level of the melting point and that of the corrosion rate values, while the change of the surface hardness value is only marginal. However, aging of Fe-B-Si metallic glass foils at a temperature of 873°K appears to increase the surface leaching of the foils with an attendant decrease in surface hardness value compared with that at 673°K aging treatment. This may be explained by considering

Table 2 Corrosion resistance properties of rapidly quenched Pb-Sb alloy ribbons in quenched and heat treated static*

Sl. No.	Ribbon material composition	Proportional corrosion rate value (Relative evaluation) [†]	
		As quenched foils	As quenched foil cold present and heat treated
1	Pb ₈₀ Sb ₂₀	2.500 ± 0.001	1.000 ± 0.01
2	Pb ₈₀ Sb ₁₉ Cu _{0.19}	2.502 ± 0.01	1.001 ± 0.01
3	Ni _{0.13} Cd _{0.09} Fe _{0.01} Al _{0.004} Si _{0.02}	3.750 ± 0.01	1.080 ± 0.01

*Electrolyte: 3%NaCl solution.

[†]Based on weight loss corrosion rate values.

the fact that at 673°K there is the possibility of precipitation of submicroscopic second phase particulates resulting in an increase in surface hardness owing to matrix reinforcement. Heating at 873°K, coagulates these submicroscopic particulates into bigger ones, resulting in lowering of the surface hardness values. The larger coagulated particulates become galvanically active, resulting in a substantial increase in corrosion rate values compared with the ribbon treated at 673°K. Submicroscopic precipitation at 673°K also increases the level of surface metastability resulting in the formation of a protective surface film in contact with 3%NaCl electrolyte.

Table 4 reveals the uses of ion plated and laser chromided carbon steel substrates. It can be seen that ion plating may be conducted using metals like Pb, Al and hard materials like titanium nitride and boron nitride on mild steel, therefore generating different types of ion specific surface activities such as resistance to wear corrosion and friction. Aluminium ion plated specimens reveal superior properties compared with

those of cadmium plated. Moreover, ion plated nitride barrier layers have become very popular in industry owing to their superior wear resistance. It appears that the overall lower porosity level together with better substrate to coating bonding, as well as a decreased impurity level are all responsible for the superior performance of the ion plated barriers in comparison with their conventionally coated counterparts, such as electroplated and spray coated specimens. It is also observed that laser chromiding involving chromium plating on a carbon steel substrate followed by laser torching modifies the surface composition from 0.2 to 10%Cr, which may be employed as corrosion resistant surface for a variety of aggressive environments. This is owing to its lower corrosion rate values.

Table 5 reveals the corrosion rate values of the ceramic metal and ceramic oxide coated carbon steel substrates obtained through the plasma spraying route. Ni₉₅Al₅ and TiO₂-Al₂O₃ (95:5) layers have been sprayed after sand blasting of the carbon steel substrate. It can be seen that in a low pH chloride and sulphide

Table 3 Response of metastable rapidly quenched Pb-Sb foils, amorphous Ni-P-B deposited this carbon steel substrate and quenched aged Fe based metglas alloy ribbons to thermal stress, mechanical abuse and chemical environment

Sl. No.	Materials	Physical properties response		Chemical properties response
		Thermal stress	Mechanical stress/hardness, kg m ⁻²	Weight loss corrosion rate values (3%NaCl versus SCE), gm cm ⁻² h ⁻¹
1	Metastable rapidly quenched Pb ₈₅ Sb ₁₅ ribbons	Ribbons become brittle at 673°K	12 ± 1	0.8 × 10 ⁻³
2	Metastable rapidly quenched Pb ₈₀ Sb ₁₀ Sn ₁₀	Ribbons resist at 673°K	11 ± 1	1.8 × 10 ⁻³
3	Amorphous Ni-Pb bulk deposit (150 µm) on carbon steel substrate	Resist up to 473°K without colouration	1200 ± 10	4.0 × 10 ⁻³
4	Amorphous Ni-Pb bulk deposit with codeposited WC, BC, SiC and Al ₂ O ₃ (200 µm)	Resist up to 873°K	1400 ± 10	4.0 × 10 ⁻³
5	Quench aged Fe based metglas alloy ribbon Fe ₈₂ B ₁₀ Si ₈ , aged at 673 K for 1 h	Ribbons affected at 673°K	381 ± 5	4.0 × 10 ⁻³
6	Quench aged Fe based metglas alloy ribbon Fe ₈₂ B ₁₀ Si ₈ wet glass, alloy ribbon	Ribbons aged at 873°K	354 ± 2	23.0 × 10 ⁻³

Table 4 Ion plating and laser chromiding of carbon steel substrates and their terminal application and features

Sl. No.	Base metal substrate	Metal deposited by ion plating laser alloying	Uses and applications
1	Carbon steel (0.2%C)	Lead and cobalt	Antifriction coating in vacuum and space applications
2	Carbon steel (0.2%C)	Titanium nitride and boron nitride	Wear resistance, machine tool applications
3	Carbon steel (0.2%C)	Aluminium	Aluminium ion plated fasteners are used in aircraft industries in preference to Cd ion plated fasteners
4	Carbon steel (0.2%C)	Chromium metal deposited by electroplating (10 µm) followed by laser alloying treatment	An alloy of composition 86%Fe, 10%Si, 2% air and 2% others is obtained up to a depth of 1 mm from the surface. Such 10% alloyed substrate may find applications in a variety of aggressive environments and also in high temperature oxidation.

Table 5 Corrosion rate values of plasma sprayed ceramic metal and ceramic oxide coated carbon steel substrate*

Sl. No.	Substrate	Details of coating composition	Corrosion rate, × 10 ⁻³ mg cm ⁻² h ⁻¹
1	Carbon steel (0.3%C)	Nil	a 4.70; b 4.72; average=4.71
2	Carbon steel (0.3%C)	TiO ₂ /Al ₂ O ₃ =95:5 + Na/Al=95:5	a 6.10; b 5.9; average=6.95
3	Carbon steel (0.3%C)	Ni/Al=95:5 + TiO ₂ /Al ₂ O ₃ =95:5	a 0.33; b 0.25; average=0.29

*Electrolyte: 3NaCl-0.1HCl-2Na₂S (10:1:0.1); duration: 2 h.

Table 6 Spalling characterisation of plasma sprayed ceramic metal coated and ceramic metal oxide coated carbon steel substrate

Sl. No.	Substrate	Coating composition	Coating layer	Coating hardness (BHN)	Spalling loss, $\times 10^{-5} \text{ G cm}^{-2} \text{ h}^{-1}$	
					623 K	773 K
1	Carbon steel (0.3%C)	TiO ₂ /Al ₂ O ₃ =95:5	Single layer	124-145	6.10-6.12	17.40-17.42
2	Carbon steel (0.3%C)	TiO ₂ /Al ₂ O ₃ =95:5	Double layer	124-121	3.10-3.19	29.0-29.1
					Spalling temperature 973 K	
3	Carbon steel (0.3%C)	Ni/Al=95:5	Single layer	700	0.0114	
4	Carbon steel (0.3%C)	Ni/Al=95:5 + TiO ₂ /Al ₂ O ₃ =95:5	Double layer	710	0.0052	

environment, the corrosion rate values are considerably lowered as a result of the application of an initial layer of Ni-Al. However, when starting with a TiO₂-Al₂O₃ layer it appears that this aggravates pitting corrosion, which can be explained by considering the fact that in the first case Ni-Al provides better metal to metal bonding while in the second case the TiO₂-Al₂O₃ being the first layer generates a lot of porosity and unbound voids at the substrate coating interface, because of metal to metal oxide bonding. The metal to metal bonding is evidently nobler than that of an unbounded metal to oxide interface since the former behaves more or less like a diffusionally alloyed layer than that of the latter which contains a large number of galvanically active stress raisers. Table 6 reveals the spalling loss characteristics of the ceramic metal Ni-Al coated and ceramic oxide (TiO₂-Al₂O₃) coated carbon steel substrates. It is shown that for both single and double layered TiO₂-Al₂O₃ class ceramic barrier layer the spalling loss value is considerably higher at 773°K compared with 673°K. However, changing the chemistry of the ceramic barrier layer by using metal powder Ni-Al, in place of metal oxide powder TiO₂-Al₂O₃ results in a drastic alteration of the coating characteristics in terms of spalling loss values. Such a drastic reduction can only be explained on the basis of the enhanced ductility of the nickel in Ni-Al layer and the superior metal to metal bonding between the carbon steel substrate and the Ni-Al barrier which leads to lower stress mismatches between the substrate and the coating. Lower spalling loss value of the composite double layer, namely Ni-Al + TiO₂-Al₂O₃, compared with the single layer Ni-Al is attributed to the combined effect of superior interfacial bonding of Ni-Al with the substrate and the ceramic top layer TiO₂-Al₂O₃.

Table 7 shows the anodic polarisation data for Pb-Sb-Sn alloy ribbons for No. 1 as cast and No. 2 rapidly quenched state as obtained in an 18% sulphuric acid electrolyte. It can be clearly seen that the as cast

curve reveals continuously increasing current values with passivation occurring at 350 mA at a potential of 0.4 V. The rapidly quenched ribbon on the other hand reveals an initial activation followed by passivation at ~0.01 V with a passivation current of 0.2 mA. At this stage, the surface film undergoes some spalling, followed by reactivation at ~0.7 mA current and associated oscillation in the current potential curve. All these data indicates the possibility that rapid quenching results in an initial activation followed by an intensive passivation owing to the formation of an adherent passive film. Such behaviour can be attributed to the inbuilt metastability of ribbons by virtue of their microcrystallinity owing to the rapid quenching operation. Although Kguchukova *et al.*¹¹ have performed some studies on the anodic oxidation of amorphous deposits, they have not been able to ascertain the initial activation steps, resulting in the formation of an adherent passive film owing to the non-stoichiometric strain, denoted as the surface metastability. The anodically activated surface passivation appears as such to be a function of the degree of microcrystallinity of the matrix.

Conclusions

Most of the processes investigated have an inhibiting metastable process component, which makes these processed materials resistant to corrosion and oxidation owing to the formation of an adherent and passive corrosion product film while in contact with an aggressive environment. However this does not strictly apply to the case of conventional plasma sprayed barriers where the level of porosities within the coating substrate interface exceeds all tolerable limits. It has been observed that rapidly quenched Pb-Sb-Sn foils initially undergo a rapid activation process. This is followed by subsequent formation of an adherent surface film, which takes the potential to more positive direction and the current to almost low values. Laser

Table 7 Anodic polarisation data for Pb-Sb-Sn both for untreated material and rapidly quenched ribbons in dilute sulphuric acid

Sl. No.	Untreated		Rapidly quenched	
	Current, mA	Potential, V	Current, mA	Potential, V
1	10	-0.1	10	-0.5
2	350	-0.4	350	-0.4
3	300	-0.4	0.2	-0.01
4	300	-0.4	0.2	+3.0
5	300	-0.5	0.7	+7.0
6	300	-0.6	-	-

surfacing and alloying has been found to have superior properties. Although plasma spraying appears to be one of the most innovative of the high energy surface processes, the presence of interconnected porosity reduces the corrosion resistance of these barrier coatings. Consolidation of this interconnected porosity structure by pore oxidation, metal cementation and subsequent post heat treatment, appears to enhance the corrosion resistance of these layers. An initial metal powder layer like Ni–Al followed by a top ceramic layer of TiO₂–Al₂O₃, appears to increase the resistance to spalling, oxidation and corrosion resistance owing to the formation of metal–metal bonding between the coating and the substrate.

Acknowledgement

The authors acknowledge the help obtained from various sections of Central Electrochemical Research Institute, Karaikudi, India during the research work and also the preparation of this manuscript. The authors also acknowledge Dr M. Raghavan, Director, CECRI, India for his interest in the present work.

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