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Novel composite coating technology in primary and conversion industry applications

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Monitor Coatings

Abstract

Historically, electroplated coatings have always represented the most cost-effective method for applying deposits of metals and alloys that were pure and dense, mirroring in general the properties of the parent metal. For engineering purposes, particularly in conversion industries, such as steel manufacturing, and primary industries, such as oil extraction, coating specifications and expectations far exceed conventional coating capabilities. In response to these requirements, a composite coating technology has been developed, which consists of a hard metal component from the tungsten carbide family of coatings and a hard refractory oxide layer produced from a slurry coating. Capable of functioning in extreme environments where temperature, corrosion, abrasion, fatigue, friction and erosion are merely starting blocks in the design of a coating system, this composite coating technology shows significant technical and commercial advantage. In the oil exploration and extraction industry, field studies have shown the composite coating to exceed by two orders of magnitude the life expectancy of conventional coatings in high-temperature, heavy particulate-laden fluids, which are therefore very abrasive, with salinity in excess of 360 000 ppm of chloride ions. In the steel industry, continuous casting mould plates have shown an increase in life expectancy of between four- and eight-fold. With virtually unmeasurable low wear rates, there are marked improvements in the downstream surface quality of the billets and slabs, while at the same time the integrity of the original copper asset is maintained.

Keywords: Steel manufacturing; Steel industry; Slab casting; Billet casting; Moult mastings; Oil industry; Oil exploration drilling; Directional mud rotor coating; Composite coating; Slurry coating; Hard metal coating; Refractory oxide coating; High velocity oxy fuel (HVOF); Tungsten carbide coating

1. Introduction

Conventional materials used in hostile tribological applications, such as offshore oil-drilling, mining equipment and conversion industry applications, such as steel manufacturing, are at the limit of established technologies. Traditional technologies include electroplated coatings with an emphasis on hard chromium with a nickel undercoat to give a combination of wear and corrosion resistance. New coatings applied by the high-velocity oxy fuel (HVOF) process can meet all the requirements for corrosion resistance of hard chromium, for instance in a seawater environment, and provide as much as 10-fold the abrasion resistance [1].

Hard-metal composite coatings produced using HVOF techniques can be manipulated in terms of composition to give an optimum microstructure design. This goes beyond the simple dual-phase alloys of tungsten carbide and cobalt to composite architectures [2]. Tungsten carbide hard metals and their analogues are now considered to be a mature technology; however, recently there has been a considerable amount of stimulating research in which the concepts of microstructure design have been used to produce alternatives to the conventional two-phase structure [2]. Significant performance improvements in coating properties have been achieved by changes in size, shape and distribution of the phases to produce ultra fine-grained materials.

Despite very dense corrosion- and abrasion-resistant coatings, even tungsten-based hard-metal coatings do not ultimately meet the requirements of specific oil and steel industry applications. Microporosity in the coatings [3] can lead to crack initiation sites or corrosion paths

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Table 1
Range of coating systems and their corresponding characteristics

Treatment	Typical thickness or case depth (μm)	Hardness Vickers (Hv)	Corrosion resistance (hours)[a]	Friction value[b]	Erosive wear factor[c]	High stress abrasive wear factor	Adhesive dry rubbing wear factor (M^3/Nm)[d]
Carburise steel	1000–3000	700–900	2	0.35	–	4000	10^{-14}
Nitride steel	5–10	400–600	2–20	0.25	800	5000	10^{-15}
PVD TiN	1–5	2000–3000	2	0.50	2000	–	10^{-16}
PVD CrN	2–20	1800–2500	–	-	–	400	–
CVD CrN	10–15	1100–1300	–	0.50	–	300	10^{-16}
CVD CrC	10–15	1500–2000	–	0.50	200	200	–
Chromium Plate	5–25	800–1000	<10	0.50	700	500	10^{-15}
Nickel Plate	10–1000	250–650	>1000	0.70		8000	10^{-11}
Plasma CrO	20–100	1200–1600	10	0.50	200	1000	10^{-16}
HVOF (Hard-metal)	20–100	1000–1600	1000	0.50	300	100	10^{-16}
Slurry coating	5–250	1000–2000	>2000	0.20	1500	4000	10^{-15}

[a] Tested to ASTM B177, comparative only, not indicative of in-service performance.

[b] Friction force divided by the applied load, result is dimension less.

[c] Indicative erosive wear factors 1000 PPM of silica sand in water with impact velocity of 25 ms^{-1}.

[d] As determined from a pin-on-plate sliding test using a polished, hardened steel pin rubbing against the treated plate surface at a loading of 10 Nm^{-2}.

for the corrosive species found in the operating environment [4].

To combat this phenomenon, slurry coatings [5] are used to hermetically seal the underlying coating, forming a physical barrier between the component and the working environment. Thermochemically formed ceramic coatings from slurries are unique, in that a metal oxide bond is established not only between the particulate materials, grains or powders used to form the coating, but also between the coating and the substrate.

Suitable substrates for the coating include all ferrous metals, nickel alloys and titanium alloys. Components are prepared for coating by solvent cleaning and grit blasting to generate a matt surface capable of retaining a liquid film. The slurry coating is water-based and contains sub-micron-sized particles of chromium-, silicon- and aluminium-based compounds and can be applied in a similar manner to paint. Reinforcing particles of materials such as boron carbide and silicon carbide can also be added to the coating formulation.

Deposition techniques include pressure spraying for most external surfaces, dipping for complex geometry shapes and draining for internal surfaces, such as cylinder liners. The thickness of the slurry deposit can be within the range of 5–250 μm, depending on the geometry or application criteria. Once the slurry deposition is complete, the coating is dried to remove all moisture and the component is then heated to the process temperature. The resulting coating consists of a refractory oxide layer with a significant increase in surface hardness, corrosion resistance and frictional properties. If the process is vacuum-assisted, then penetration of the slurry can be complete, thus totally filling all porosity through the underlying coating, and improving hardness and strength.

Table 1 shows a range of coating systems and their corresponding characteristics in terms of hardness, corrosion resistance to standard salt spray tests and a range of values for various dynamic stress conditions. Nickel and chrome electro-deposits have been discussed in terms of their historical application as a solution to wearing corrosive environments. Physical and chemical vapour deposition techniques have been deemed to show favourable characteristics in the past; however, recent work has shown the need for generally thicker coatings to support high stress loads in the applications described here [6–8].

2. Case 1: steel manufacturing

One aspect of steel manufacturing involves the use of a copper mould as part of a continuous casting process [4]. The water-cooled copper mould is the most vital and critical part of continuous casting in terms of process reliability and quality of the cast product. Its primary function is to extract sufficient heat from the liquid steel to form a sound solid shell that is strong enough to contain the liquid core as the steel exits the mould. The mould also defines the cast product size and shape in cross-section.

The copper mould plates have to withstand substantial thermal and mechanical stresses and strains [4]. The mould plate surface faces a harsh environment, and suffers from wear, thermal fatigue and mechanical damage. Usually, continuous wear of the mould plate as the solidifying strand moves through the mould means

Table 2
Field data for steel manufacture

Plant identification	Normalised end of plate life	
	No coating	Monitor composite coating
UK 1[a]	5.5	11
UK 2	1.2	3
UK 3	1	1.5
UK 4	3	14
UK 5[b]	5	23
USA 1	5	20
CAN 1	1.6	13

All plants listed above now use ceramic composite coating as standard. Coating marketed as Castcoat™ under licence to Corus plc.

[a] Wear reduced from 3.5 to less than 1 mm.

[b] Company broke the world record for continuous casting of steel slab using Monitor ceramic composite coating on narrow faces.

regular re-machining of the plates, which eventually reach a minimum thickness and require replacement. This is a well-known problem and many approaches have been tried, such as chrome or nickel plating. The main purpose of a mould coating is to reduce the wear rate on the copper mould plates, and thus increase mould life, and extend the casting campaign, thus saving on production time and costs per ton.

The mould plate material must give a high heat transfer rate, and a copper alloy is commonly used because of the good heat extraction obtained. It is at the exit end of the mould that severe friction exists during withdrawing, between the casting mould and the hardening steel shell. The cause can be anything from the mould plate taper not being compatible with the shrinkage characteristics of the steel, unsuitable casting speed for the mould design, to poor machine alignment.

Copper alloys are not very resistant to this continuous abrasive wear, which causes severe wearing out of the copper plates. In addition, entrapment of abrasive material, such as slag and mould powder nodules, can occur, which can lead to scoring or other mechanical damage to the copper plate surface.

3. Case 2: oil exploratory drilling

The use of mud rotors in directional drilling places tough physical- mechanical- and chemical-resistant requirements on the hardware. The rotor and stator assembly lies back from the drill head and is primarily used to power the drill bit to extract mud, debris and cutting fluids from the drill head. The operating environment is influenced by changes in formation characteristics due to stringers or faults present in the geological strata.

There are considerable down-hole-formation temperature changes, and the circulating fluid characteristics change due to fluid/solid and gas influxes or additions. Various types of water-based mud are used in the drilling process, including saturated potassium chloride mud to inhibit swelling of bentonite shale. In addition to these, there are oil- and polymer-based muds, and more recently, ester, ether and alternative invert emulsion systems. There are various agents found in circulating fluids, which promote different forms of component corrosive attack. Acid gas influx into the mud system can occur at any time. These gases, notably carbon dioxide and hydrogen sulfide, reduce the mud pH and greatly accelerate corrosion, especially in water-based muds. Acid gases can cause sudden and severe motor-component corrosion attack. High corrosion levels can occur when the motors used are inactive at the rig site or during transit. Increased down-hole temperature raises corrosion rates, while down-hole pressure increases can cause entrapped corrosive gases to dissolve in the circulating fluid, increasing corrosiveness.

4. Results

Tables 2 and 3 show field data accumulated during trials of the composite coating system incorporating the slurry refractory oxide coating. In the case of the steel industry, results from five UK ConCast™ sites, one American and one Canadian steel plant show that on average there is a four-fold increase in the yield of steel

Table 3
Field data for oil exploration and extraction

Treatment	Chloride concentration in mud in parts per million					Increased life of rotor factor[a]
	<30 000	30 000–75 000	75 000–150 000	150 000–200 000	200 000–325 000	
Hard chrome plate	●	○	∇	∇	∇	1
Hard chrome with nickel underlay	●	●	○	∇	∇	3
Densified hard chrome plate	●	●	○	○	∇	5
Monitor's composite coating	●	●	●	●	●	10–100

● Optimum performance; ○ Reduced performance; ∇ Unacceptable performance.

[a] Compared to hard chrome in 75 000 to 150 000 PPM chloride.

product from the same mould using the ceramic composite coating, with one site reporting an eight-fold increase in productivity from the same mould. The actual increase in life of the mould plates is dependent on the mode of operation and the nature of the product. Some plants produce thin slab castings, which tend to be faster and may incorporate stainless steel production, which demands different coating requirements to the slower thick-slab casters.

In addition to increased yield, participating steel plants have identified a number of other improvements. These generally include:

- Longer campaign life;
- Integrity of original asset maintained;
- Quality improvements in down-stream rolling; and
- Break-out security.

It was also reported that coatings other than chrome and nickel had undergone trials, with none of them, except for this composite coating, proving successful. In all these cases, the coating had reacted with the mould powder to produce a 'dam' at the periphery of the melt pool. This had prevented the mould powder from cascading down the sides of the solidifying slab or billet in the desired manner, and all of these casting campaigns had to be terminated. The composite coating was the only coating (other than chrome- or nickel-based coatings) that did not adversely affect the required mould powder mechanisms and allowed a considerable increase in the extent of the casting campaign, even though the casting machine was operating at high speed [4].

Table 3 shows field data accumulated from oil industry applications. Traditional hard chrome coatings have been commonplace in mud rotor drilling for some years now. Advances have been made through incorporation of hard, dense nickel deposits prior to chrome plating; however, this only increased the life span by a factor of three for a subsequent rise in coating cost of 50%. Technological advancements using the slurry coating to densify the hard chrome have yielded a five-fold increase in life expectancy of rotors compared to basic chrome plate. This is achieved for double the cost of chrome plating. However, evidence has now started to accumulate showing that, even where the corrosion conditions are relatively mild, the composite coating combats abrasive wear so successively that use of the composite coating is being considered as a direct replacement for hard chromium.

Use of the composite coating incorporating the slurry-formed refractory oxide coating has led to an increase in life expectancy of between one and two orders of magnitude, although the cost implications of such a coating system are typically four-fold that of chrome. Even when the elevated costs are shadowed by the benefits, there is a compromise between cost and severity of the operating environment, and existing drilling procedures and practices. The composite coating system is generally limited to drilling conditions where mud chloride contents are in excess of 75 000 ppm [9].

5. Conclusions

Both steel manufacturing and oil exploratory drilling exhibit extreme environmental operating conditions. The key elements to contend with include a complex mix of dynamic stress vectors, elevated temperatures and highly corrosive chemical species. The bulk properties of the coating system have to be sufficiently robust to withstand high levels of thermal shock, impact resistance and low-frequency fatigue. Near-surface characteristics of the coating have to contend with frictional problems, abrasion and erosion. At the surface there is a requirement for barrier properties to contend with corrosive species, reduced wettability and good thermal conductivity.

Due to the potential for point impact damage from small particulates in the case of oil extraction or corner impact from start-up in steel manufacturing, where the mould is loaded with scrap metal and then pulled through the casting machine, the coating system should be sufficiently thick to withstand these abnormal loads. This concept is analogous to ice on mud. The brittle but hard ice, if sufficiently thick and defect-free, will withstand higher loads than the underlying soft mud (substrate). If the ice is too thin, it will shatter and collapse.

Despite innovations in thermal spray technology, which have led to almost negligible porosity within the coating microstructure, the reliability of thermal spray coatings can be compromised by the presence of tiny flaws, such as micro-cracks within the coating microstructure. This problem of flaws, surface imperfections and micro-cracks can be overcome with a supplementary slurry coating, which densifies and seals the bulk coating. The slurry coating forms a thin refractory-oxide layer bonded both internally and to the substrate with metal–oxide bonds.

A composite coating system consisting of a substantial layer of hard metal from the tungsten carbide family of coatings, which is subsequently treated with a slurry coating forming a pore-free refractory oxide layer, has been developed.

The thick, dense coating contends with a complex array of tribological facets, including corrosion, adverse thermal changes within the operating environment, and static and dynamic stress vectors, such as fatigue, impact, directional loads, friction, erosion and abrasion. The slurry coating strengthens the interface between the hard metal coating and operating environment, providing a robust physical barrier to highly corrosive constituents in the environment.

Field studies have shown typical increases in continuous casting mould life to be approximately four-fold. In the oil industry, the composite coating has shown an increase by up to two orders of magnitude in the life expectancy of mud rotors operating in environments with salt concentrations exceeding 300 000 ppm chloride and high concentrations of abrasive particulates.

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