Enhancement of Co-W Electrodeposits on Cast Iron And Steel Substrates by use of a Cobalt Strike

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A method of improving the deposit-substrate interface and surface properties of an electrodeposited amorphous Co-W alloy on iron based substrates, was investigated. The structural integrity of Co-53wt%W deposited onto mild steel and cast iron was examined by SEM and chemical composition analysed by XRD, EDX and XRF methods. It was concluded that application of a thin cobalt strike layer at the deposit-substrate interface results in high quality smooth deposits, with greatly improved contact between the deposit and the substrate material. The use of the strike layer allows a heat-treated Co-W coating to be produced with comparable wear resistance and significantly enhanced corrosion resistance compared to those of electroplated chromium deposits.

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Introduction

The electrodeposition of alloys of tungsten with one or more of the iron group metals has received much attention due to the interesting properties that they exhibit, i.e. high surface hardness and corrosion resistance[1]. It has also been shown[2] that the as-deposited hardness of these alloys can be increased further by suitable heat treatment. Consequently, these alloys are now being considered as a possible replacement for conventional hard chromium electrodeposits, which are commonly used for their protective properties, in particular their resistance to wear. Despite producing a coating with attractive properties, the chromium electroplating industry is coming under increasingly stringent operating controls. This well established process uses a hexavalent chromium solution, which eventually produces large volumes of chrome contaminated toxic waste. This requires special disposal methods for the toxic waste and the availability of expensive breathing apparatus and exhaust systems to deal with gaseous evolution during plating[3]. Another major problem related to hexavalent chromium in solution is that it is a recognised carcinogen and is also able to create other health problems such as skin and lung irritation. A further concern is associated with the fact that chromium-plating baths are generally only ~15% efficient and that deposits often have difficulty maintaining uniformity of coating thickness[4].

Tungsten containing alloy coatings can be produced with widely different compositions and microstructures depending on the composition of the plating bath and the deposition parameters. Amorphous, crystalline and nanocrystalline deposits of nickel-tungsten and cobalt-tungsten alloys are all quoted in the literature[5,6]. Alloys with amorphous or nanocrystalline structures are of particular interest as they often possess good corrosion resistance and attractive tribological properties.

Electrodeposited tungsten alloys have a tendency to exhibit poor adhesive and cohesive properties, and in particular have a problem adhering to hard steel substrates[7]. The quality of the deposits is further reduced when they are subjected to heat treatment in an attempt to improve the hardness of the alloy to values comparable with electrodeposited chromium. Careful selection of the plating bath ingredients and operating conditions, including pH, temperature, and current density, has led to only a degree of improvement.[8,9,10] Application of a thin cobalt strike layer onto the substrate, prior to alloy deposition, has also been suggested as a means of overcoming these problems when plating onto high carbon steels[11].

The purpose of the present investigation was to find a way of improving the integrity of the interface between electrodeposited Co-53wt%W and iron-based substrates, and to obtain corrosion and wear properties of the coating to a standard at least matching that of electrodeposited chromium. Use of an intermediate Co strike layer between mild steel and cast iron substrates and the Co-W electrodeposit was chosen as a method of achieving this. The coatings were characterised by scanning electron microscopy and the protective properties investigated by assessing the corrosion and reciprocating wear resistance of both the alloy and the dual plated specimens, in the as-deposited and heat treated conditions.

Experimental Details

Electrodeposition

Electrodeposition of Co-W was carried out in two ways, a) directly onto the substrate and b) on top of a thin cobalt strike applied to the substrate prior to alloy deposition.

The Co-W alloy plating bath composition was as follows: 15.0 g/l cobalt sulphate heptahydrate, 16.5 g/l sodium tungstate dihydrate, 40.0 g/l boric acid, 110.0 g/l sodium gluconate, 30.0 g/l sodium chloride. All chemicals were of analytical grade. The bath was maintained at pH 6.0 by the addition of either NaOH or H_2SO_4, and the volume of the bath was adjusted, during approximately six hours of plating, by additions of distilled water. Boric acid was added to the bath since it has been shown that small amounts of boron co-deposited with the Co-W alloy promotes an amorphous structure, and hence the excellent properties that are characteristic of such materials, such as high hardness[11].

Polished mild steel sheet (plating area 30 cm^2) and sections of spheroidal graphite cast iron piston rings (13 cm^2) were used as the substrate materials. These substrates were initially cleaned using acetone and left to soak in an alkaline cleaning solution for at least half an hour. A final intensive clean was carried out by making the substrate the cathode in an electrolytic cleaning bath (15.0 g/l sodium gluconate, 20 g/l Activax and 30 g/l sodium hydroxide in deionised water). Cathodic cleaning was carried out at a current density of 2 A/dm^2 for 2 minutes. The substrates were carefully rinsed in distilled water between each preparation stage and finally dipped in 10% H_2SO_4 for 30 seconds to neutralise any remaining alkali and to activate the surface ready for plating.

An iridium oxide coated platinised titanium mesh (7 cm x 10 cm) formed the anode. Electrodeposition of the Co-W alloy was carried out under galvanostatic controlled conditions at an applied current density of 5 A/dm^2 and constant bath temperature of 80°C. The plating time was 1 hour to achieve a 20 μm thick deposit or 2 hours to produce a thickness of 40 μm.

The plating bath ingredients used for the deposition of the cobalt strike were based upon those outlined in previous work[6] (25 g/l cobalt sulphate in distilled water, with the pH adjusted to 0.5 by additions of sulphuric acid). Co-deposition of the strike was carried out using a current density of 5 A/dm^2 with the temperature maintained at 80°C.

Electrodeposited chromium was supplied by a commercial electroplating company. It was produced to a thickness of 20 μm on to a similar substrate to that used for the Co-W deposits.

Heat Treatment

Heat treatment of the Co-W alloy samples deposited onto mild steel was conducted in a tube furnace, evacuated and back filled with argon, at 600°C for 2 hours. A titanium getter was placed in the furnace to capture any residual oxygen. These conditions were chosen as previous work[12] conducted by the authors had shown that deposits of optimum surface hardness were produced, whilst also preventing oxidation of the Co-W alloy.

Characterisation

The structure and morphology of the coatings were observed using scanning electron microscopy (SEM), working at an accelerating voltage of 20 kV. The SEM was also fitted with an energy dispersive x-ray (EDX) analyser, used for chemical composition analysis of the deposited coatings. X-ray fluorescence (XRF) measurements were also made to determine chemical composition of the alloy, including its boron content. X-ray diffraction (XRD) for structural and compositional analysis was conducted using CuKα radiation, scanning a 2θ range of 10° to 100°. Hardness measurements were conducted on a microhardness indenter under a load of 25 g. The breakdown in corrosion resistance was measured as the time taken until the first spots of red rust appeared on the surface of samples placed in a neutral salt spray cabinet working to ASTM B117. The resistance to wear of all samples was measured using a reciprocating sliding wear machine. The pin was in the form of a 1" diameter sphere of 440-C stainless steel, whilst the plate comprised of the coated specimens. The system was operated at 160 cycles per minute at room temperature, under an applied load of between ~60 and 64 N.

Results & Discussion

As-deposited Co-W alloy

The Co-W deposits as produced on both mild steel and cast iron substrates were semi-bright and light grey in colour. The deposits had an average thickness of 20 µm.

EDX and XRF measurements revealed an average alloy composition of Co-53wt%W (Co-27at%W), which was constant throughout the thickness of all deposits, both with and without the intermediate cobalt layer. A small amount of boron was detected in the deposits (0.05wt%). XRD confirmed that the as-deposited Co-W alloy was amorphous.

SEM micrographs of as-deposited Co-W on mild steel and cast iron, without an underlying cobalt strike layer, are shown in Figures 1 and 2 respectively. Examination of the structure and surface morphology of the as-deposited alloy revealed that nodular growth of the deposit on both substrates has occurred. Cracks running down to the substrate-deposit interface are present in numerous places and deposits are often very poorly bonded to the substrate surface (Fig. 1). It is evident in the case of the cast iron substrates that at points where graphite particles are present at the substrate-deposit interface, nodular growth of the alloy is exaggerated (Fig. 2) and in some cases, no deposition occurred at all.

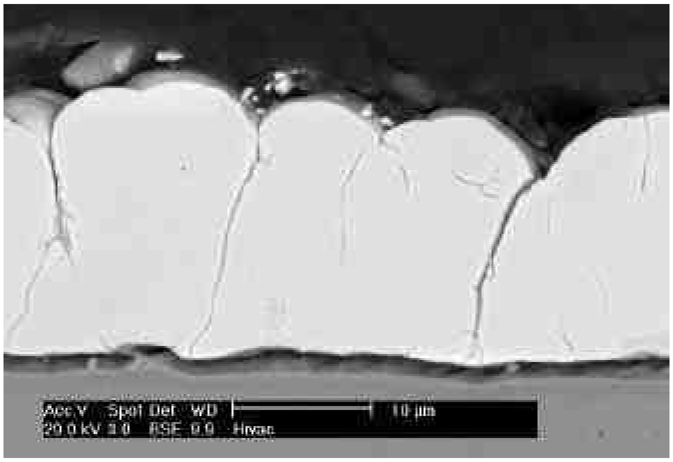

Fig. 1-As-deposited Co-W on a mild steel substrate.

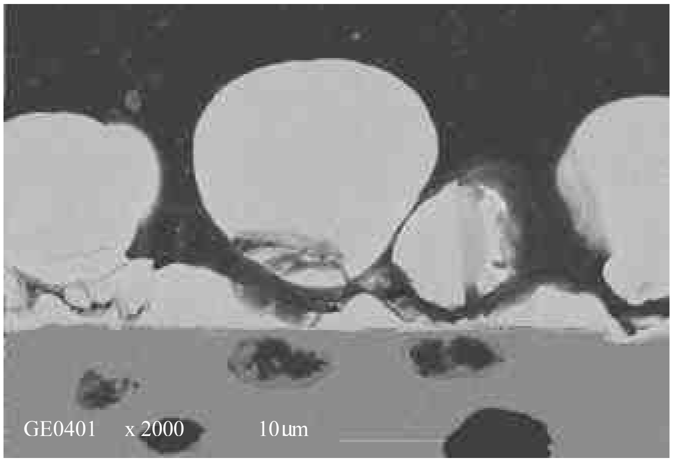

Fig. 2-As-deposited Co-W on a cast iron substrate.

Figures 3 and 4 show SEM micrographs of the Co-W alloy deposited onto mild steel and cast iron respectively, with a cobalt strike layer between the alloy and the substrate, approximately 2 µm thick. The strike layer is smooth and continuous on both substrates, the graphite particles in the cast iron also being totally covered (Fig. 4). The Co-W alloy layer subsequently plated on top of the strike layer is much smoother, the nodular morphology of the deposit being much less pronounced. Continuous contact between the alloy and the strike has also been achieved in both cases. A small number of cracks are still present in the deposits where the boundaries of the individual nodules or cells meet. However, these cracks all appear to terminate at the deposit-strike interface and do not reach down to the substrate surface.

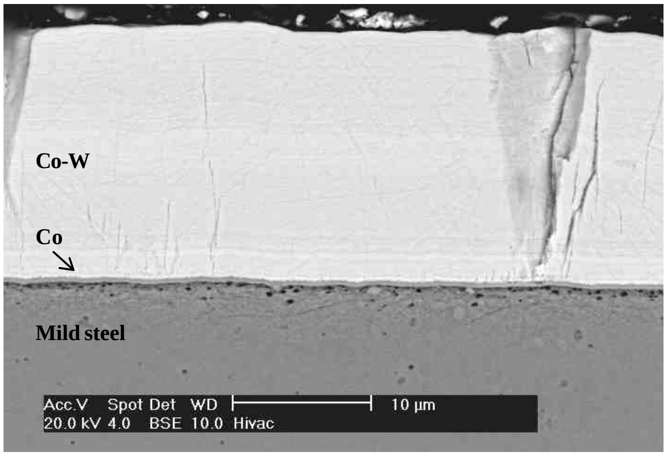

Fig. 3-As-deposited Co-W on mild steel substrate with underlying cobalt strike .

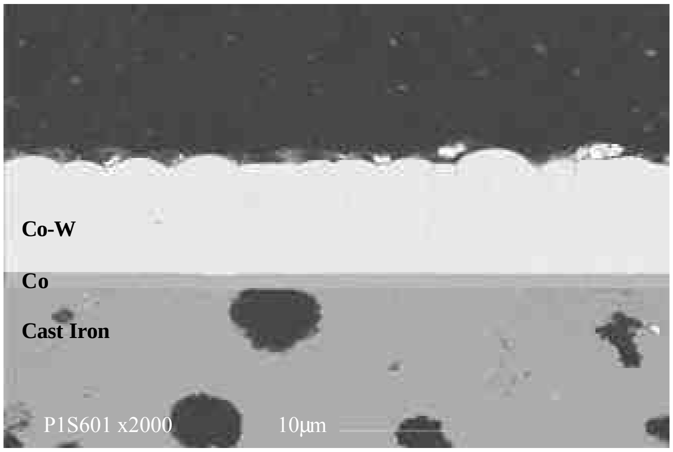

Fig. 4-Asdeposited Co-W on cast iron substrate with underlying cobalt strike.

Heat-treated Co-W alloy

Heat treatment of Co-W coated mild steel, both with and without the cobalt strike layer, was carried out in an attempt to improve the mechanical properties of the alloy deposit. A hardness increase from 540 Hv to almost 1200 Hv was observed at the optimum heat treatment conditions of 600°C for 2 hours in argon. This increase in hardness is accompanied by a phase change in the alloy; i.e. the amorphous deposit was replaced by a very fine Co_3W phase.

Whilst heat treatment improves the hardness of the alloy, the quality of the deposit and its potential to protect the substrate are considerably reduced. Figure 5 shows a cross section of the Co-W alloy deposited onto mild steel without a Co strike and after heat treatment. It can be seen that the alloy is heavily cracked and in some areas whole nodules or cells have become detached from the substrate greatly exaggerating the poor integrity of the as-deposited alloy. This is most likely caused by the differences in thermal expansion between the substrate and the Co-W alloy, introducing additional stress into the alloy during heat treatment. This leads to the easy detachment of the deposit from the substrate to which it is already poorly bonded. Figure 6 is an SEM micrograph of Co-W deposited onto a steel substrate with a Co strike that has been heat-treated at 600°C. These deposits were continuous and contain fewer and smaller cracks, which terminate at the strike-alloy interface. It can also be seen that the Co strike has remained in full contact with the steel. The smoother morphology of these deposits provides fewer nucleation points for cracks to form and grow at nodule boundaries and the greatly improved contact between the alloy and the substrate prevents the deposit becoming detached during heat treatment. It is clear that application of a Co strike layer between the Co-W deposit and the steel substrate allows significant improvement in the hardness of the alloy by heat-treatment to occur, whilst preventing degradation of the integrity of the deposit by this treatment. Similar behaviour was also found when the treatment was applied to cast iron substrates.

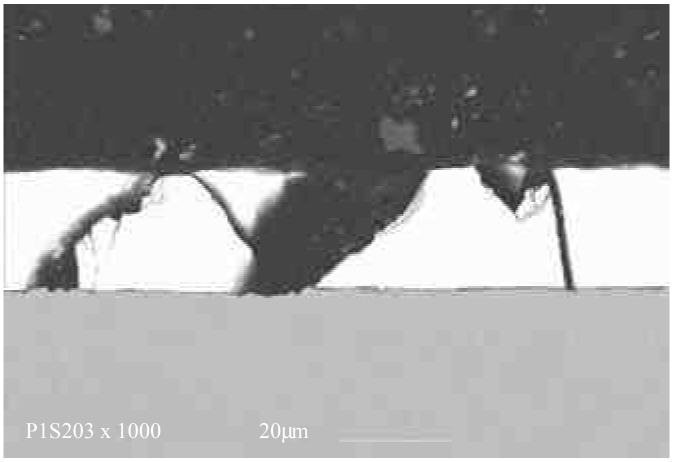

Fig. 5-Heat-treated Co-W on a mild steel substrate.

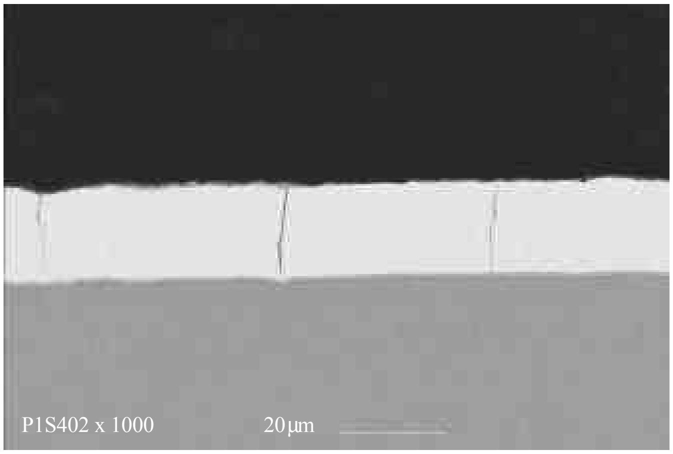

Fig. 6-Heat treated Co-W on a mild steel substrate with underlying cobalt strike.

Corrosion Resistance

The results of the corrosion tests, carried out for as-deposited and heat treated Co-W alloy, both with and without a cobalt strike layer, as well as the electrodeposited chromium samples, are given in Table 1.

As-deposited Co-W directly onto mild steel has shown very promising corrosion protection. No substrate corrosion was observed for the Co-W alloy (20 µm thick) for at least 1200 hours exposure to the neutral salt spray despite the exaggerated nodular morphology of the deposit and its poor contact with the substrate surface. It would appear that the numerous cracks in these deposits, formed at the contacting nodules or cells and running down to the strike layer (Fig. 1), do not allow corrosion to initiate.

Table 1
Salt Spray Corrosion Test Results

	Strike Layer Thickness / µm	Alloy Layer Thickness / µm	Time to onset of substrate corrosion / hrs
As-deposited Co-W Alloy	0	20	>1200
	2	20	>1200
Heat treated Co-W Alloy	0	20	21
	2	20	100
	5	20	100
	2	40	> 1200
	5	40	>1200
Chromium	0	20	<20
	0	20	<20

As-deposited Co-W with an underlying Co strike has shown a similar level of corrosion protection with no sign of substrate corrosion after 1200 hours of testing. The existence of fewer and even smaller cracks in the deposits, a consequence of the much smoother alloy layer achieved on top of the strike (Fig. 3), would be expected to lead to such behaviour.

A yellow/gold surface layer formed on top of all the as-deposited Co-W samples after approximately 20 hours exposure to the salt spray; this layer was too thin to be identified by XRD. Some as-deposited samples, both with and without the strike layer, have also displayed evidence of a small amount of localised attack. This took the form of pitting on the surface the Co-W deposits, which appeared after 100 hours exposure. These small pits were filled with a black corrosion product again in quantities too small to be detected by XRD.

The benefits of using a Co strike were even more evident when the corrosion resistance of heat-treated Co-W alloy was investigated. Samples heat-treated at 600°C for 2 hours with no underlying Co strike provided protection of the steel substrate for less than 20 hours. After this time the whole sample was completely covered with red rust. This is not unexpected since cracking and spalling of the Co-W deposits after heat treatment were frequently observed (Fig. 5), leaving parts of the substrate exposed and open to attack.

In contrast, heat-treated Co-W (20 µm thick) with an underlying Co strike, 2 µm and 5 µm thick, showed no sign of substrate corrosion for 100 hours. It is clear that this improvement in corrosion protection is a consequence of the greatly enhanced Co-W deposit integrity, achieved when an intermediate Co strike is used (Fig. 6). There was no advantage in using a thicker Co strike layer.

Deposition of a thicker (40 µm) Co-W alloy layer, over 2 µm and 5 µm thick cobalt strikes, was carried out. These samples were subsequently heat-treated and their corrosion resistance investigated. Figures 7 and 8 are SEM micrographs of the top surface of the 20 µm and 40 µm thick alloy layers respectively. The nodular morphology is evident in both cases; the structure however appears much coarser in the case of the thicker deposit, where individual nodules are on average more than twice the size of those observed for the 20 µm thick deposit.

Deposition of the thicker 40 µm Co-W alloy layer considerably improved the corrosion resistance of the heat-treated system even further, with no evidence of substrate corrosion after over 1200 hours. Since the individual nodules at the surface of the deposit were much larger in diameter for the 40 µm deposit compared to the 20 µm deposit, the density of nodule-nodule interfaces was reduced, providing fewer pathways where corrosive media can easily travel down to the strike-substrate interface. At this stage of corrosion testing a thicker Co strike did not prove beneficial.

Fig. 7-Surface topography of 20 µm thick Co-W.

Fig. 8- Surface topography of 40 µm thick Co-W.

The as yet unidentified gold/yellow surface layer was observed on some deposits after corrosion testing the heat-treated samples for 100 hours. However, no surface pitting was observed on any of the heat-treated samples. It is thought that the as-deposited alloy, in its non-equilibrium, amorphous state, contained a great deal of internal stress. As a result, localised or pitting corrosion may have occurred on the deposit surface, at points where this stress was concentrated. On heat-treatment however, much of this internal stress may be released, as the phase transformation from the amorphous to the fine-grained Co_3W equilibrium phase occurred. With the stress in the surface of the deposit reduced no pitting is observed.

Electrodeposited chromium, 20 µm thick, consistently failed to provide substrate protection after less than 20 hours in the salt spray test. This is comparable with the poor corrosion protection seen for the heat-treated Co-W without the presence of a cobalt strike, where a proportion of the substrate surface was left completely unprotected. It is clear that Co-W electrodeposits can be produced with corrosion resistance properties far exceeding those attainable with electrodeposited chromium. As-deposited Co-W has shown to protect steel substrates from corrosion for over 60 times as long as chromium, under the aggressive corrosive environment in the salt spray test. It has been shown that heat-treated Co-W deposits, of equal thickness to the electrodeposited chromium, provided substrate protection for over 5 times longer when an underlying Co strike layer was used to secure the alloy to the steel. Much better corrosion protection properties of the heat-treated alloy were achieved when 40 µm Co-W deposits were put down onto a Co strike layer, providing protection against substrate corrosion for over 60 times longer than the chromium.

Wear Resistance

The resistance to reciprocating wear of the as-deposited and heat-treated Co-W alloy, as well as the chromium electrodeposit, was measured by the depth of the wear track after a given number of testing cycles. The results of these tests are shown in Table 2. It can be seen that after 4000 cycles, substantial wear of the as-deposited Co-W with no underlying cobalt strike layer has occurred, the track depth equalling the thickness of the deposit itself. A slight improvement in the wear resistance was seen for this material when a strike layer was present between the substrate material and the alloy. However, the wear resistance of the as-deposited Co-W alloy still does not approach that of the chromium electrodeposit, which produced a wear scar of only 1 µm after 4000 cycles.

A significant improvement in the wear resistance of the Co-W alloy was observed when samples were heat treated at 600°C prior to wear testing. For heat-treated Co-W deposited directly onto the steel substrate the wear scar after 4000 cycles is now consistently only 1.4 µm, a result that now more closely approaches that of the chromium sample after an equal length of testing. The resistance to wear of Co-W electrodeposits with an underlying cobalt strike layer are also greatly improved compared to their as-deposited counterparts. However, the wear resistance of the heat-treated alloy plated on top of the strike layer did not show an improved resistance to wear compared to samples without this intermediate layer as might have been expected. Nevertheless, the use of the strike layer does allow a heat-treated Co-W coating to be produced with comparable wear resistance and significantly enhanced corrosion resistance compared to those of electroplated chromium deposits.

Table 2
Reciprocating Wear Test Results

Sample	Load / N	Cycles	Track Depth / µm
As-deposited Co-W, No strike	62.8	4000	20
As-deposited Co-W, No strike	59.8	4000	20
As-deposited Co-W, Cobalt strike	60.8	4000	17
As-deposited Co-W, Cobalt strike	63.7	4000	18
Heat-treated Co-W, No strike	62.8	4000	1.4
Heat-treated Co-W, No strike	59.8	4000	1.4
Heat-treated Co-W, Cobalt strike	60.8	4000	2.4
Heat-treated Co-W, Cobalt strike	59.8	4000	1.8
Chromium	63.7	4000	1.0

Conclusions

Good quality Co-W electrodeposits have been successfully deposited onto iron based substrates with greatly improved integrity of the substrate-deposit interface, by the application of an intermediate cobalt strike layer between the Co-W alloy deposit and the substrate material.

Application of a Co strike layer between the Co-W coating and the substrate allows significant improvement in the hardness of the alloy by heat-treatment to occur, whilst preventing degradation of the integrity of the deposit by this treatment.

As-deposited Co-W alloy has shown protection against substrate corrosion for over 1200 hours under salt spray conditions. The corrosion protection conferred by the heat-treated Co-W deposits has been improved to a level comparable with that of the as-deposited alloy by use of the cobalt strike layer.

The corrosion protection properties of both the as-deposited and the heat-treated Co-W alloy have proved superior to that of electrodeposited chromium, providing protection against substrate corrosion for up to 60 times longer under salt spray conditions.

The wear resistance of Co-W electrodeposits is greatly improved from that of the as-deposited alloy by heat treatment at 600°C. The performance of the heat-treated alloy under reciprocating wear conditions has proved comparable with that of electrodeposited chromium.

As such, Co-53wt%W electrodeposited coatings with an underlying cobalt strike provide a potential replacement for electrodeposited chromium.

Acknowledgements

This work was supported by the EPSRC. The authors would like to thank Dr Sally Garner for her contribution to this research and Dr Richard Nixon of the London & Scandinavian Metallurgical Co Ltd. for conducting the XRF experiments.

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