Rising to the challenge of a chrome-free world

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Harish Mistry, Senior Development Chemist, Indestructible Paint
Graham Armstrong, Sales and Technology Mentor, Indestructible Paint
John Bourke, Global Technical Sales Manager, Indestructible Paint

Introduction

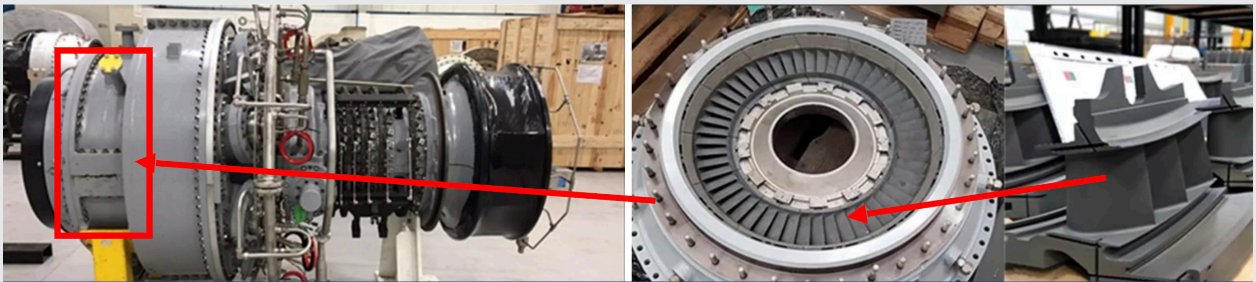
The drive towards greater environmental sustainability creates both challenges and interesting opportunities for innovative coatings manufacturers to develop new solutions for the future.

When the REACH regulations were introduced in 2007 – to protect human health and the environment from the use of chemicals – Indestructible Paint anticipated future issues for chrome (Cr^{VI}), which is a core component in one of the company's high-performance diffusion coatings, IP1041 (known commercially as Ipal).

Diffusion coatings are formulated with aluminium and silicone powders carried in an inorganic acidic binder comprising a blend of chromium trioxide (chromic acid) and phosphoric acid, with a small percentage of magnesium salts. They are used in the hot gas path of turbine engines – particularly industrial and marine engines – as their resistance to temperatures up to and above 1,000°C and to oxidation in sour gas atmospheres are essential to long-term durability. Diffusion coatings are also required to provide long-term resistance in high SOx atmospheres.

Diffusion happens during processing where components are exposed to temperatures typically greater than 865°C in an inert atmosphere. Under this treatment, the aluminium and silicone, together with metal ions within the substrate, diffuse together. Once all the aluminium and silicone from the coating are consumed, the temperature drops, and the metallic structure is 'frozen'. The carrier binder – no longer part of the coating structure, forms on the surface of the diffusion layer as a bisque – which is removed by light burnishing under a humid atmosphere.

Indestructible Paint began a challenging and extensive project to develop a resilient, chrome-free coating that would maintain the required performance. After ten years of research, development and testing, the solution – which the company named CFIpal – has been successfully developed. The chrome-free coating is now market ready and already approved by a major engine manufacturer.



Diffusion coatings are applied to both static and rotating components in the turbine section of the engine. Temperatures here are often 800-1,000°C

Developing a chrome-free diffusion coating

Phase 1: Development

During the initial development – with part funding from Innovate UK – it initially appeared simple to remove chromic acid from the binder blend, and replace this with another inorganic acid, or even utilise phosphoric acid. There seemed no reason to consider deviating from the metal powders, and the grades used. These had been successfully used within the traditional chrome-based coating, and this decision was justified when specification testing was completed during the laboratory testing phase.

However, during manufacture of the chromic acid original, there was an exothermic reduction reaction between the aluminium powder and the chromium trioxide, which effectively stabilised the blend to allow long-term storage. Without the chrome content, this exothermic reaction was much slower, and early blends (made with the aluminium and silicone powder in chrome-free acid blends) reacted, causing 'bottle explosions' usually on overnight standing on the laboratory bench.

Further research showed that storage stability could be achieved by offering the chrome-free coating as a two-component product: 1) The metal powders were stabilised in a non-acidic inorganic liquid with 2) the acidic binder as a separate part. As the metallic powders were stabilised within the first part, when mixed for application with the second part using a simple 1:1 volume mix, any reaction was very limited, giving the blended product a working life of 6-8 hours, allowing for a typical working shift.

Phase 2: Laboratory testing

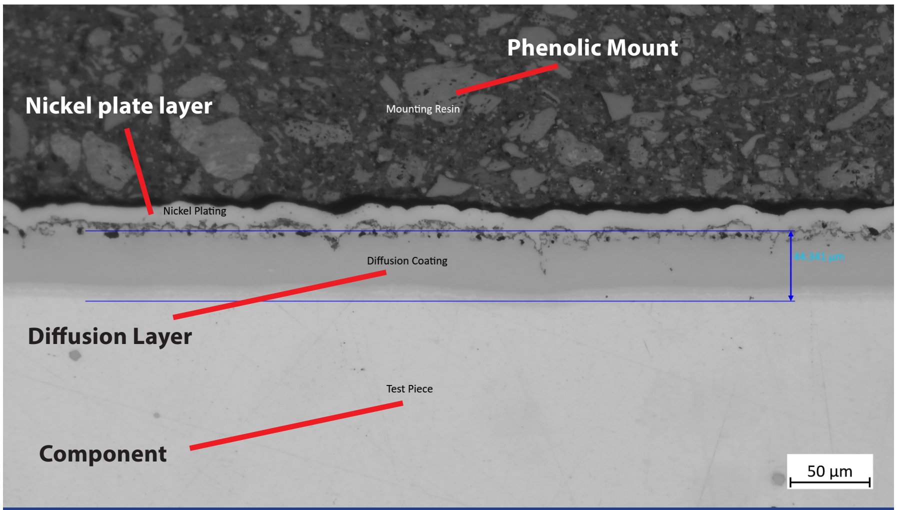
Using the original chrome-based coating (Ipal) as the control, a series of performance and durability tests were carried out, including both type I and type II hot corrosion testing, where both grades were still protective after 500 hours.

On type I testing, both products showed higher rates of attack at 900°C compared to 700°C, but again, minimal difference could be observed between the new and original versions.

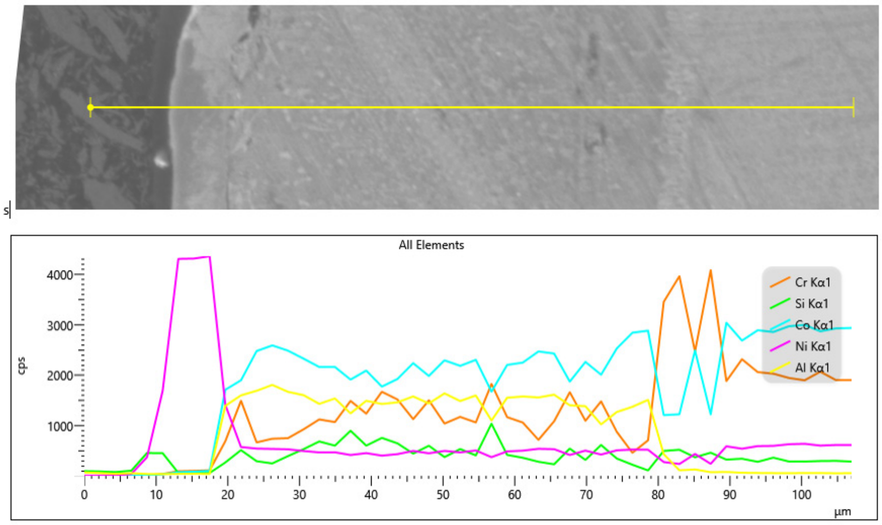
In addition, Accelerated Fatigue Corrosion Testing (AFCT) could not distinguish between the chrome and chrome-free coatings, across a range of alloys to include CMSX-4 and IN738.

At this stage, samples were submitted to a leading UK engine manufacturer for testing and feedback. The chrome-free product met the requirements of the company's specification, with a comment that – in some areas – the chrome-free coating actually outperformed the original. Therefore, the company classed the development product as achieving Technical Development Level (TRL) 4.

Further analysis was also carried out on test panels, using 'cut throughs' of applied panels, with the cut section being mounted into a phenolic holder, and then analysis under a microscope to view the integrity of the diffused film. It became evident that the chrome-free material provided a more even, integral coating than both of the original chrome-containing versions. This would substantiate the test performance on both hot corrosion testing and SOx resistance.



Cut through of turbine blade illustrating evenness and completeness of CFIpal diffusion coating.



Graphical analysis showing metallic content within the diffusion layer.

Phase 3: Application Trials

In any development, taking a new product from TRL 4 into a production-viable system can be the hardest to achieve, with some promising projects failing at TRL 5 or 6. Indestructible Paint was determined for this not to be the case for CFIpal and established a task force of exceptional chemists, technical service personnel, and an industry expert who had used the chrome-containing coating extensively. The team carried out multiple trials involving increasingly complex applications.

In line with the laboratory tests, the first trial continued to use test panels; however, the team looked at varying the application weight of the coating to view what effects thin or heavy application would give. Building upon this, the second trial looked at working to achieve the typical 'weight gains' that would ensure correct diffusion coating thickness.

Further trials repeated these initial applications, to give a basic instruction process, and to introduce a new team member with no previous experience to ensure the devised process was practical. This presented an opportunity for skills

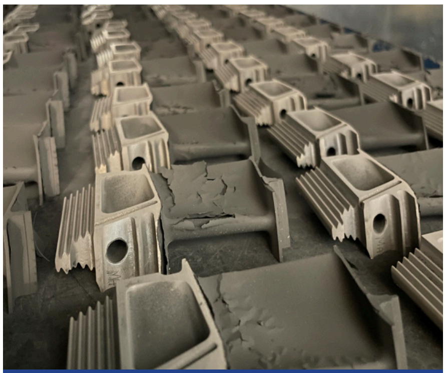
Harish Mistry from the laboratory development team applying CFIpal onto a five-blade array.

development and to prove that the application process could be adopted by new personnel, as would be required upon entering the market.

Trials then moved onto scrap 'real gas turbine parts'. Metallurgical analysis including scanning electron microscopy (SEM) was undertaken, and components manufactured from different alloys were evaluated. Throughout this process, the team was plagued by a series of heavily-varied results from the very poor – with film bubbling and cracking – to the excellent, affecting each applicator involved.

Turbine blades showing the applied wet film of CFIpal.

One day in the laboratory, the team had been looking to apply CFIpal onto a fairly complex blade array. The results of one set of tests in the morning were poor. However, when another team member sprayed the same batch of coating onto the same complex component in the afternoon, excellent results were achieved. Initially skill levels were assumed to be the reason. However, upon deeper investigation, the true cause turned out to be humidity, which had dropped from 56% to around 48%. This revealed the criticality



Blades after diffusion treatment illustrating the formation of the 'bisque'

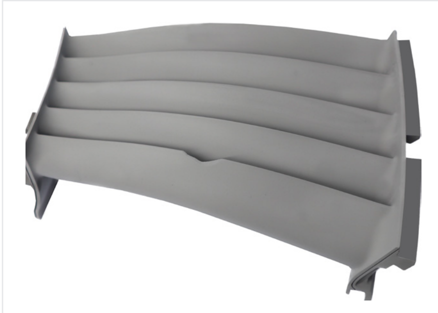
of humidity and temperature control during the CFIpal application process.

Working closely with one of the applicator companies – which has a humidity/temperature-controlled spray booth – Indestructible Paint subsequently demonstrated that, if the parameters are set correctly, then the application is consistent and straightforward. The company has since run multiple trials on a range of turbine components and is now achieving consistently reproducible results.

Results

As a result of extensive testing of many formulation modifications – all still giving the necessary storage stability – a chrome-free coating was achieved that provided equivalent, if not superior, technical performance to the original chrome version.

On the basis of these results, the product is set to be listed initially as approved for overhaul and be recognised as having achieved TRL 8 and 9. Application trials continue in partnership with customers with an emphasis on analysis of the



Five-blade array coated with CFIpal after 350°C cure but before diffusion treatment.

coating by cut throughs, SEM analysis and chemical analysis of the metal content of the diffusion coating. Further customer approvals are then subsequently expected as trials are successfully run on their individual products.

Conclusion

The increasing regulation of chemicals and pressure to solve environmental sustainability challenges is driving the restriction and removal of a growing number of chemicals from use, making projects designed to bring ground-breaking solutions such as CFIpal to market essential.

The process can become surprisingly complex and at times feel insurmountable. However, as Indestructible Paint has demonstrated, by having a clear vision and bringing together a strong team from the experts in the laboratory to those who specialise in application and to the sales team that know the market well, interesting results and excellent solutions can emerge.

Now is an important time for innovation and perseverance in the chemical industry so that less sustainable solutions can be reimagined and reformulated for a safer and greener future.

Indestructible Paint Ltd is a UK-based coatings manufacturer, with over 45 years' experience supplying coatings to the Aerospace and Defence Industries worldwide.

For further information, contact John Bourke
+44(0)121 702 2485 | sales@indestructible.co.uk