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Iron Tungsten Alloy Plating with Low Friction and Wear Resistance

by
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ABSTRACT

An alloy plating film developed by finely crystallizing iron and tungsten demonstrates both a high level of hardness and excellent ductility. In addition, low friction can be achieved by its application under a layer of lubricant. The modern automotive industry has been striving to reduce energy loss caused by friction. Low friction and improved durability can be attained by applying this technology to the surface of parts which constantly slide in operation. This in turn contributes to better fuel efficiency. On the other hand, diamond like carbon (DLC), a typical low friction coating, causes peeling at early stages when loaded under high pressure and shows poor synergistic effects with lubricants. Therefore, the application of this coating is not recommended for sliding parts. Alternatively, the wet plating technology we developed does not have these disadvantages. It also has the merit of greater cost performance as compared with DLC produced with PVD technology.

Introduction

The largest challenge facing the automotive industry these years is CO_2 reduction (through lower fuel consumption). They need to meet fuel efficiency regulations that will take effect in various regions in the near future. In mid- to long-term policies, all of the automotive makers have been rigorously working to reduce CO_2 in exhaust to cope with global climate changes.

In particular regard to the reduction in friction loss in the internal combustion engine, the industry holds high expectations toward the development of surface treatment technologies that can both decrease friction coefficients for engine components sliding with each other and establish high wear resistance for them. Conventionally, dry plating like DLC (diamond-like carbon) and CrN (chromium nitride), and wet plating including electroless nickel plating and hard chromium plating have been used for these engine components (such as piston rings, bubble lifters and crankshaft bearings) which have metal-on-metal sliding contact.

DLC provides low friction and excellent wear resistance, but peeling is also likely to occur when the ductility is insufficient. In addition, a peeled hard film is damaging to the contacting surface, and the compatibility is extremely limited to only certain types of lubricants. Furthermore, dry coatings like DLC require a batch process which raises the cost, and so it is not widely used.

Electroless nickel plating has excellent covering power, but its friction properties and wear resistance are somewhat insufficient. Further, it requires a high bath renewal frequency and large volumes of waste water subsequently become a burden to the environment. Hard chromium plating is a functional plating process that has been widely used for a long time to achieve wear resistance properties. The greatest concern with this plating is the hexavalent chromium contained in the plating bath that users have to deal with to protect the environment.

We have developed a functional plating method which can be wet processed, thereby promoting process cost control, and which also has high wear resistance and low friction properties without nickel and chromium.

Plating overview

Plating method

The plating equipment used in this development is shown in Fig. 1. We used insoluble anodes made of platinized titanium. The bath was mixed with a magnetic stirrer during plating. The plating bath parameters used are shown in Table 1. The bath temperature was 75 ± 5°C and the pH was adjusted to 6.5 with diluted sulfuric acid. Deposition could start around 2.0 A/dm^2 of the cathode current density. However, in consideration of practical plating speeds, we proceeded with 7.0 A/dm^2 as our main focus. The bath temperature was slightly high, but overall it was a typical electroplating method.

The bath was mixed with ferrous sulfate hydrate and sodium tungstate hydrate as shown in Table 2. The total of these metallic salt concentrations was 0.20 mol/L. By using the same amount of the complexing agent, the iron and tungsten became ion-complexed together.

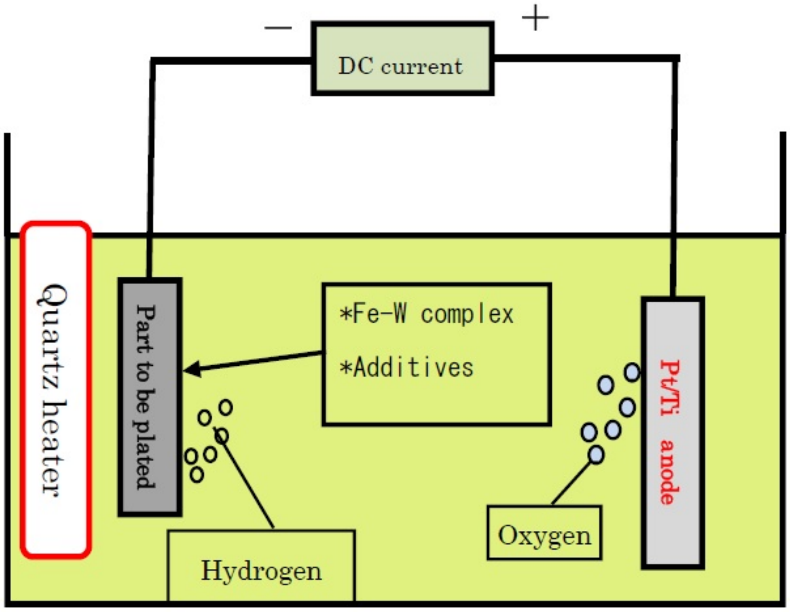


Figure 1 - Plating equipment layout.

Table 1 - Operating conditions.

Item	Range
Bath temperature	75 ± 5°C
Cathode current density	1 ~ 10 A/dm^2
pH	6.5 ± 1.5
Mixing	Required

Table 2 - Plating bath components.

Chemical formula	Chemical name
$Na_2WO_4 \cdot 2H_2O$	Sodium tungstate dihydrate
$FeSO_4 \cdot 7H_2O$	Ferrous sulfate heptahydrate
Additive A	Complexing agent
Additive B	Electrolyte, etc.

Plating film properties

Tungsten itself is not deposited via a normal wet plating method. However, when a ferrous type transition metal like iron is also present, it can be co-deposited as an alloy. In this development where the tungsten ratio in the film was controlled to be 50 to 60 wt% under the conditions previously described, we were able to obtain an Fe-W alloy film with excellent hardness and ductility.

In addition, as this alloy plating contains much iron like the steel materials used for mechanically sliding parts, we verified that there were good synergistic effects and compatibility with lubricants and that low friction results were readily obtained when a lubricant was used during friction coefficient measurements.

Plating film properties

Film hardness and behavior versus heat load

Figure 2 shows the results of a test done to identify the film hardness, a crucial factor for wear resistance. Measurements were performed with a nanoindenter (Nanoindenter G200 manufactured by MTS), and the results were converted to the Vickers hardness scale.

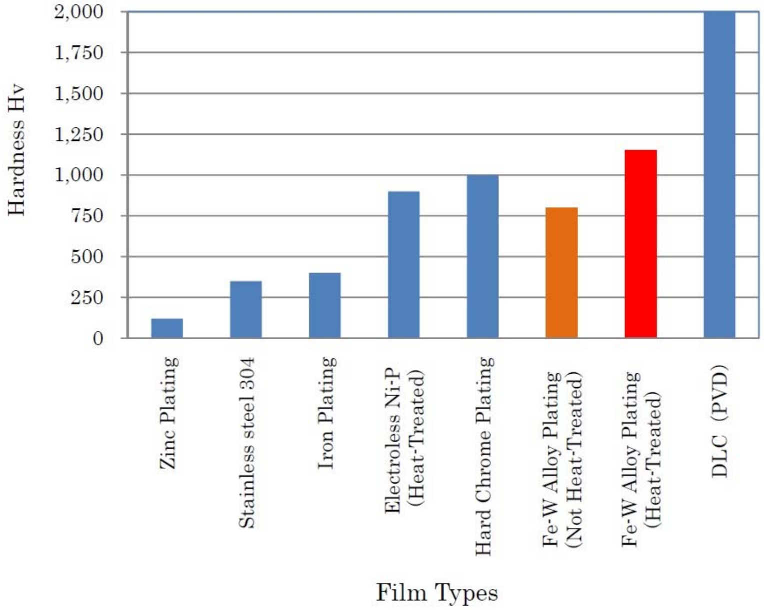


Figure 2 - Comparison of plating hardness.

The hardness immediately after plating was confirmed to be HVN 800 by controlling the iron and tungsten ratio in the film. The hardness of this film gradually improved during heat treatment for the film under atmospheric pressure, as shown in Fig. 3. The highest hardness obtained was HVN 1150 at 300 to 500°C. The hardness was reduced after the temperature exceeded 600°C. However, above 400°C, iron crystallization progressed, reducing the ductility of the plating film. Therefore, we determined that 300°C was the appropriate heat treatment temperature and the condition enabling full performance of the heat resistance of the film.

Further, the same heat load regimen was applied to the DLC coating and the hardness change was also recorded. In the range above 150°C, the bonding force started to relax, reducing the hardness. As the temperature continued to rise, the hardness decreased markedly. At 300°C, the DLC quickly turned to carbon dioxide and disappeared within a short period of time.

Based on the above test results, the hardness of the Fe-W film is considered to be hard among wet plating types. During the normal temperature range, the hardness of the Fe-W film was not as strong as that of the DLC, but this was reversed when 200°C or so was exceeded.

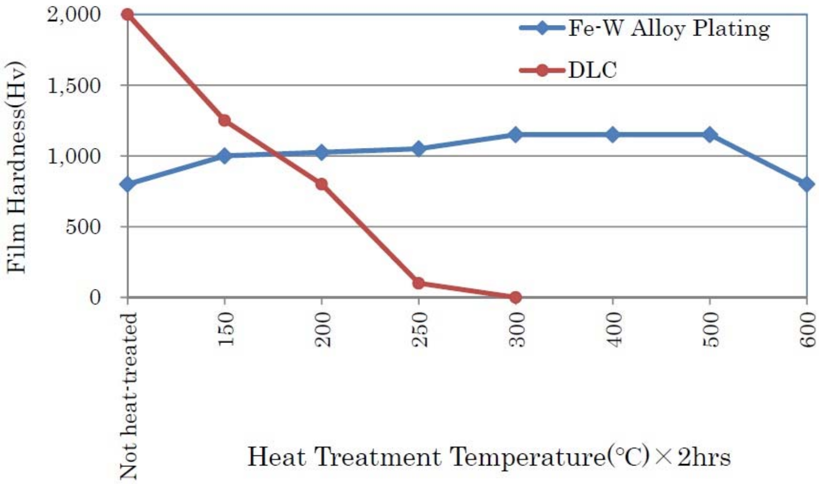


Figure 3 - Hardness changes in Fe-W and DLC coatings through heat treatment.

Wear resistance

A ball-on-disk friction/wear tester was used in this evaluation. The equipment diagram is shown in Fig. 4 while the measurement conditions are indicated in Table 3. High speed tool steel with a hardness of HRC 62 was used for the plating-side disk test samples. The surface roughness was adjusted in such a way that all the plating film test samples showed a post-plating roughness of R_a 0.1 µm. The contacting material was a mirror-finished Φ6mm ball made of high carbon chromium bearing steel. The load to the entire contacting material was 10N. However, because of its round shape, the ball had a point contact with the plating test sample, and that local load was 1.57 GPa.

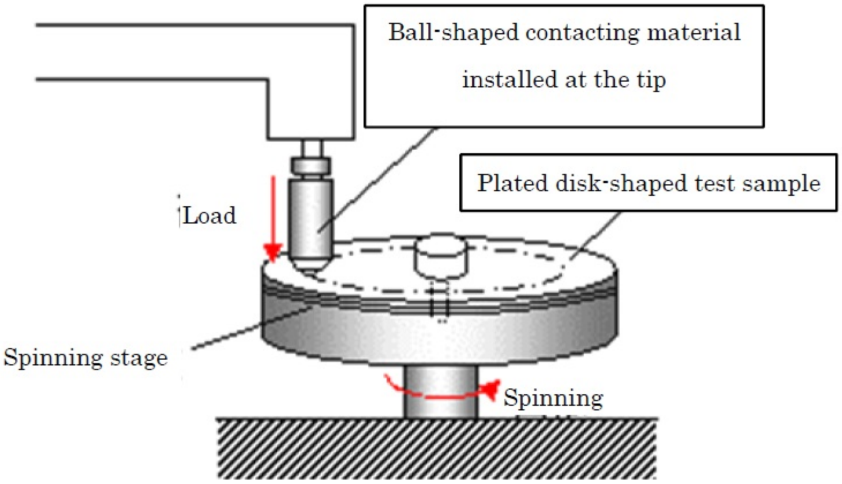


Figure 4 - Schematic diagram of a ball-on-disk friction wear tester.

Table 3 - Ball-on-disk friction/wear measurement conditions.

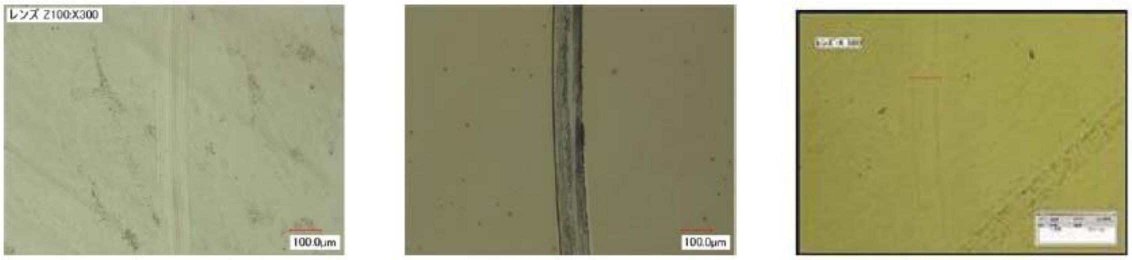
Item	Detail
Contacting material & shape	φ6mm ball made of high carbon chrome bearing steel
Load, spin speed	10N, 50mm/sec
Sliding distance	50m
Load at ball contact point	1.57GPa
Temp. humidity	25°C, 30%
Lubricant, viscosity	Liquid paraffin, v:67mm²/s
Tester	TRIBOMETER manufactured by CSEM

Test samples were cleaned with acetone to remove any surface dust and stains before measurements. Liquid paraffin was used as a lubricant so that the impact of the extreme pressure agent did not have to be considered. After a minute volume was applied to the film surface to make a mixed lubrication range, measurements were performed. Air conditioning was used so that the room temperature and relative humidity were maintained at 25°C and 30%, respectively. However, the temperature of the test sample surface was not measured during the test.

Generally speaking, wear resistance does not solely depend on the hardness of the film. If the friction resistance is large, or the affinity with other materials is strong, adhesive wear that progresses through adhesion to the contacting material becomes intense. On the other hand, if the friction coefficient and affinity with the contacting material are small but the film is soft, the film will disappear due to simple wear at an early stage. If the film ductility is low, cracks or chipping will occur soon, leading to friction resistance and subsequent adhesive wear. Wear resistance requires a balance of low friction, low affinity with the contacting material and ductility in addition to the hardness of the film.

Figure 5 shows post-test wear mark comparison photos. Even though the film hardness of the electroless nickel plating was stronger than the Fe-W plating (without heat treatment) by HVN 100, the film loss volume due to wear was the greatest among all the films and the basis metal was slightly exposed. This is because adhesive wear with the contacting material occurred more easily on the electroless nickel in addition to its higher friction coefficient.

On the other hand, the Fe-W plating not only displayed hardness and low friction properties but also had a low affinity with the contacting material. The maximum film wear depth was 0.1 μm. The DLC coating had neither film peeling at early stage nor did it exhibit local heat load. Furthermore, the film hardness was doubled and low affinity was observed. Due to these factors, the DLC coating showed the highest wear resistance.



Fe-W Plating (not heat treated)

Electroless Ni Plating (heat treated)

DLC

Figure 5 - Ball-on-disk wear mark comparison (Magnification: 300×)

Friction coefficient

A friction coefficient measurement was performed under the same conditions as that for the ball-on-disk type friction wear test. Figure 6 shows the results for each coating. The friction coefficients for the electroless nickel and hard chromium plates were at least 0.15 in most cases. The Fe-W deposit, regardless of whether there was heat treatment or not, showed values of 0.06 to 0.10. The readings for the DLC ranged from 0.09 to 0.1. According to these results, it was concluded that the Fe-W plating showed low friction as compared to the other plating films in this relative evaluation.

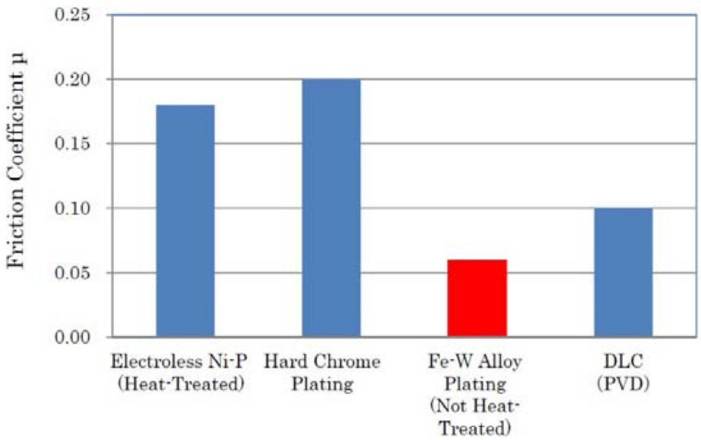


Figure 6 - Comparison of the friction coefficient for each type of coating (Same test conditions as those used in the friction coefficient measurements).

In Fig. 7, friction coefficient trends of the electroless nickel and the Fe-W deposits are compared. In many of the electroless nickel samples, the friction coefficient temporarily increased to around 0.25, then gradually decreased and stayed around 0.17 until the end of the test in many cases. On the other hand, the Fe-W deposits had readings of 0.06 to 0.10 throughout the time of the test.

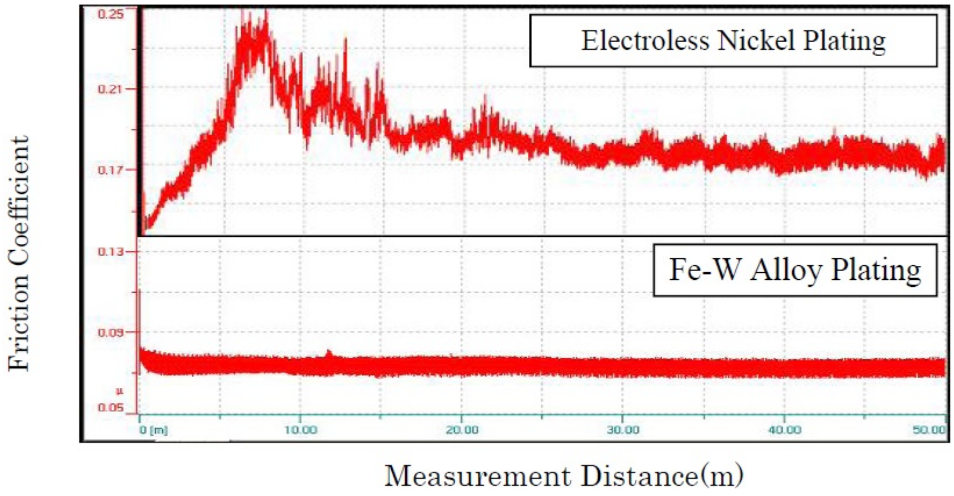


Figure 7 - Comparison of the friction coefficient trends for electroless nickel and Fe-W alloy plating.

In the mixed lubrication range where the measurements were made in this work, the lubricant was present, but the oil was so sparse that the plating surface and the contacting ball directly contacted each other in some cases. When this happened, the electroless nickel plating was likely to show an increase in the friction coefficient at the beginning of the measurement. Over time, the contact ball and the plating surface degraded somewhat, enlarging the contact surface. Once the contact point load decreased, the friction coefficient stabilized. On the other hand, in a small contact like the one in the mixed lubrication range, the friction coefficient of the Fe-W plating was hardly affected.

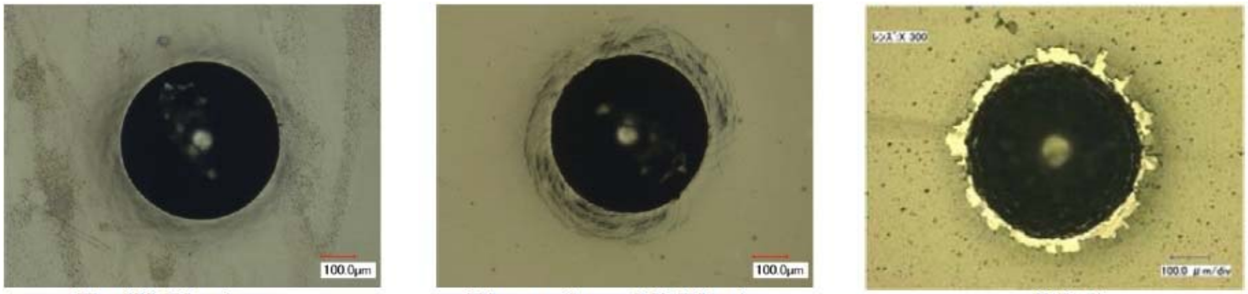
Adhesion

The Rockwell indentation method was used in our adhesion test. The conditions are shown in Table 4. Figure 8 shows enlarged photos of the film damaged around the indentation

Regarding the Fe-W deposits, although plastic deformation occurred due to the indentation, no peeling was noted around the indentation, demonstrating that the adhesion with the substrate was good. In addition, there were very few cracks in the film indicating high ductility. Peeling also did not occur on the electroless nickel plating, thus showing good adhesion. However, cracks formed in various directions in that film, and the ductility was not as good as that of Fe-W plating. On the other hand, peeling was very obvious around the indentation on the DLC, exposing the metallic intermediate layer (chromium layer) made to ensure adhesion. Improvements in DLC have recently progressed, but there remain some concerns about its adhesion.

Table 4 - Rockwell indenter conditions.

Item	Description
Indenter type	Diamond, Scale C
Load	150 kg
Load time	10 sec
Sample Material & Hardness	HSS: HRC 62.0
Observation Equipment	Video microscope



Fe-W Plating (Not Heat Treated)

Electroless Ni Plating (Heat Treated)

DLC

Figure 8 - Adhesion comparison: Indented area observations in the Rockwell test indentations.

Summary

In the future, automotive engines will continuously progress toward better fuel efficiency and higher output. As the environment where sliding components are used becomes ever harsher, expectations will go up regarding surface finishes providing appropriate measures. However, the use of electroless nickel plating and hard chromium plating are not easy choices when the impacts on humans and environment are considered. Facing this situation, we developed an Fe-W plating process using iron and tungsten because they are not subject to environmental regulation. The following lists the properties of the Fe-W plating as evaluated:

1. It was important that the film had 50 to 60 wt% tungsten to achieve sufficient film hardness and ductility. The hardness was improved further by applying a heat treatment.

2. In the wear resistance test with the mixed lubrication range, it was verified that the wear amount was less than that of the electroless nickel.

3. In the friction coefficient comparison with the mixed lubrication range, the readings were 1/2 to 2/3 lower than those of conventional plated films, and low friction properties were confirmed.

4. In the adhesion evaluation with the Rockwell indentation method, the Fe-W plating demonstrated good ductility and adhesion because it exhibited neither the cracks observed in the electroless nickel nor the peeling that occurred in the DLC coating.

Based on the above results, Fe-W alloy plating can be applied to reduce energy loss due to friction in engine sliding parts and to ensure wear resistance for those sliding components. Furthermore, this process enables a cheaper surface treatment than DLC coating for mass production as it uses the advantages of wet plating.

Engine friction loss accounts for 20% of the fuel consumed by a normal passenger car produced in 2010. However, it is expected to be reduced to 10% by 2020. It is essential to further develop materials, configurations, surface roughness improvements, lubricants and surface treatments, and to use the right materials appropriately, depending on the lubrication condition. It is our strong hope to continue our developments in this area so that Fe-W plating can be selected for these applications.

Future directions

Going forward, we will focus on the following items for our research and development for practical applications.

1. Evaluation on mass production parts and building of a track record.

   - Perform evaluations using mass production equipment with OEM support and identify issues against practical applications for modification. Through these efforts, product commercialization can be scheduled.

2. Plating bath scale-up from lab level to mass production floor.

   - As soon as the commercialization efforts are realized, mass production trials will be performed using large tanks with cooperation from plating shops to identify issues and implement countermeasures.

3. Establishment of waste water treatment method and tungsten recovery technology.

   - There are many complexed metals in this plating bath, and sedimentation is expected to be a challenging issue. Along with mass production trials, a reliable sedimentation removal method will be established.

   - It is widely known that tungsten is an extremely expensive raw material. Therefore, it is necessary to establish a tungsten recovery and reuse method instead of removing it so that costs can be lowered.

4. Consideration of Fe-W plating conditions for aluminum .

   - Lighter part weights need to be realized for better vehicle fuel efficiency. Aluminum is a typical material for that purpose, and we have received many requests to plate on aluminum.

5. Development of lower friction plating.

   - There have been requests to reduce friction resistance in the engine sliding areas to 1/10 of the current level or lower by 2030. Therefore, our focus will be the development of a plating film that can decrease the current friction coefficient to 0.01.

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About the author

Kiyohiko Watabe has joined the Technical Department at a maker of chemicals for surface treatment and processing by commissioning, Yuken Industry Co., Ltd. in Japan since 1995, and has spent his time developing wear-resistant coatings for twenty years. He was first involved with developing ceramic films by PVD methods, and commercialized wear-resistant films (TiCN, VCN, CrAlN, etc.) primarily for forging dies. Since 2010, using wet process plating methods, he has developed wear-resistant and low friction coatings for auto parts and for those chemicals. The Fe-W alloy plating introduced in this paper is a part of this work. Mr. Watabe holds an M.S. degree in Materials Chemistry from the Aichi Institute of Technology.