Iron Tungsten Alloy Plating with Low Friction and Wear Resistance

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1. Preface

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

Especially regarding 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 chrome plating have been used for these engine components (such as piston rings, bubble lifters, 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, peeled hard film is damaging to the contacting surface, and the compatibility is extremely limited to only certain types of lubricants. Furthermore, dry coating like DLC requires 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 slightly insufficient. It requires a high bath renewal frequency and large volumes of waste water subsequently become a burden to the environment. Hard chrome plating is a functional plating that has been widely used for a long time to achieve wear resistance properties. The greatest concern with this plating is hexavalent chromium contained in the plating bath that users have to deal with to protect the environment.

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

2. Plating Overview

2.1. Plating Method

The plating equipment used in this development is shown in Figure 1. We used insoluble anodes made of titanium with platinum vapor-deposited over it. The bath was mixed with a magnetic stick stirrer during plating. The plating bath parameters used are shown in Table 1. The bath temperature was 75℃±5℃ and the pH was adjusted to 6.5 with diluted sulfuric acid. Deposition could start around 2.0A/dm^2 of the cathode current density. However, in consideration of practical plating speeds, we proceeded with 7A/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 0.20mol/L. By using the same amount of the complexing agent, the iron and tungsten became ion-complexed together.

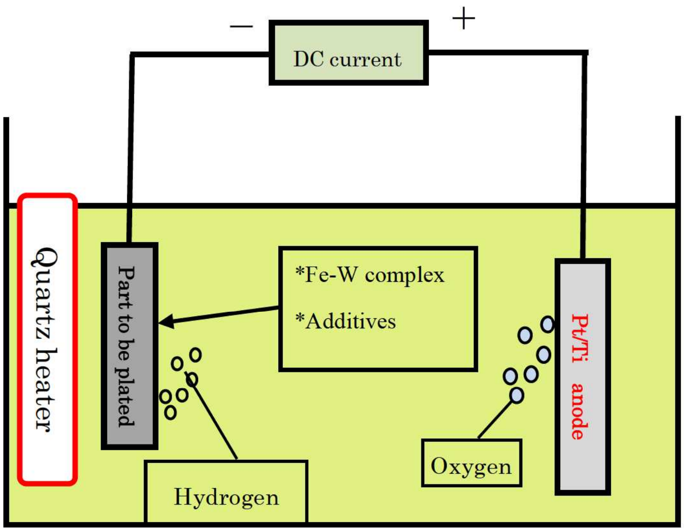


Figure 1. Plating Equipment Layout

Table 1.
Other Plating Conditions

Item	Range
Bath Temp.	75±5℃
Cathode Current Density	1～10A/dm^2
pH	6.5±1.5
Mixing	Needed

Table 2. Plating Bath Components

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

2.2. Plating Film Properties

Tungsten itself is not deposited in 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% (weight ratio) 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 those 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.

3. Plating Film Properties

3.1. Film Hardness and Behavior Against 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.

The hardness right after the plating was confirmed to be Hv800 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. The highest hardness obtained was Hv1,150 at 300℃ to 500℃, and then the hardness declined after 600℃ was exceeded. However, when 400℃ was exceeded, iron crystallization progressed, reducing the ductility of the plating film. Therefore, we determined that 300°C max was the appropriate heat treatment temperature and the condition enabling full performance of this film's heat resistance.

In addition, the same heat load was applied to the DLC and the hardness change was also recorded. In the range after 150℃ was exceeded, the bonding force started to relax, reducing the hardness. As the temperature continued to rise, the hardness decreased markedly. When 300℃ was reached, 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℃ or so was exceeded.

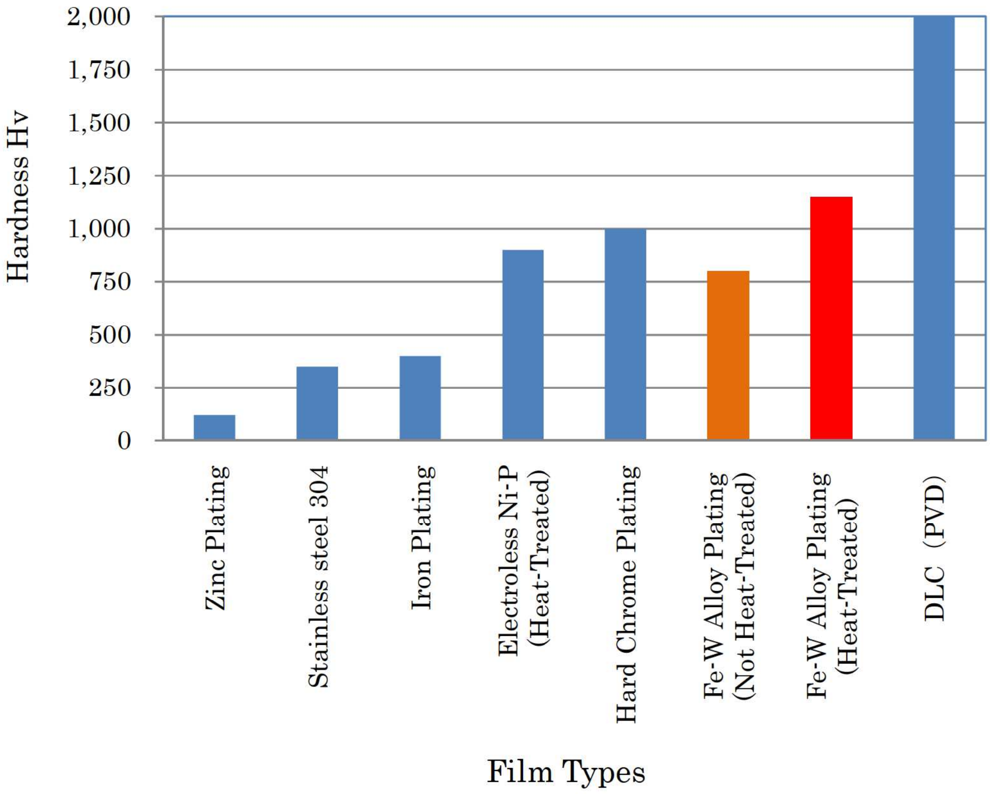


Figure 2 Comparison of Each Plating Hardness

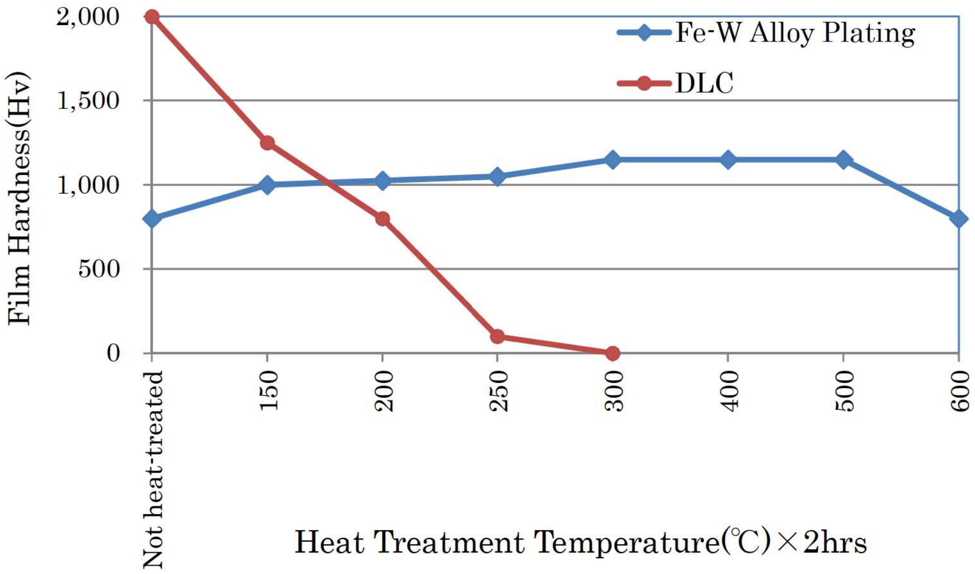


Figure 3. Hardness Changes in Fe-W Plating and in DLC through Heat Treatment

3.2. Wear Resistance

A ball-on-disk type friction/wear tester was used in this evaluation. The equipment diagram is shown in Figure 4 while the measurement conditions are indicated in Table 3. A high speed tool steel with hardness of HRC62 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 Rz0.1μm. 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 the round shape, the ball had a point contact with the plating test sample, and that local load was 1.57GPa.

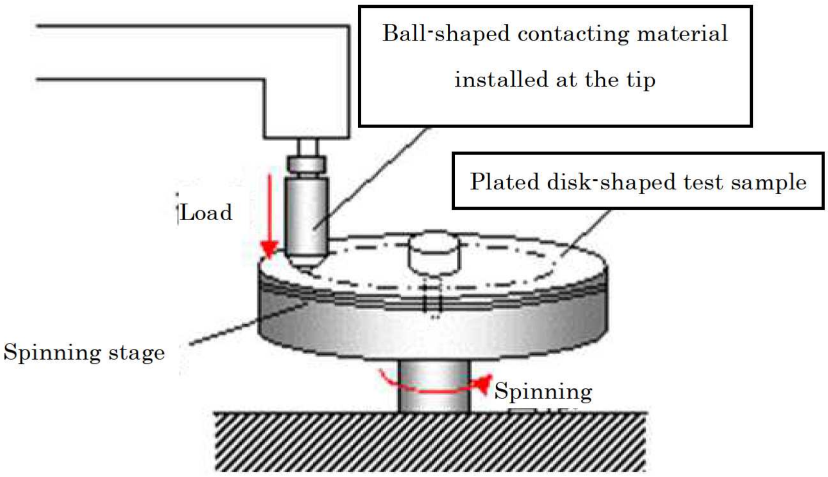


Figure 4. Image of a Ball-On-Disk Type Friction Wear Tester

Table 3. Ball-On-Disk Friction Wear Measurement Condition

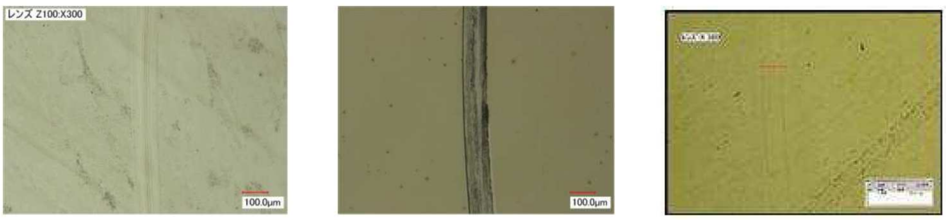
Item	Detail
Contacting material & shape	φ6mm ball made of high carbon chrome bearing steel
Load, spin speed	10N, 50mm/sec
Sliding distance	50m
Load at ball contact point	1.57GPa
Temp. humidity	25°C, 30%
Lubricant, viscosity	Liquid paraffin, v : 67mm²/s
Tester	TRIBOMETER manufactured by CSEM

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 moisture were at 25°C and 30%. 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 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 Hv100, that film's loss volume due to wear was the greatest among all the films and the base metal was slightly exposed. This is because adhesive wear with the contacting material occurred more easily to 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 film wear depth was 0.1μm at the most. The DLC in this test neither had film peeling at early stage nor caused local heat load. Furthermore, the film hardness was twice as strong with low affinity. Probably due to these factors, the DLC 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: 300x)

3-3. 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 friction coefficient results comparing each plating. The friction coefficients of the electroless nickel plating and hard chrome plating were at least μ0.15 in most cases. The Fe-W plating, regardless of whether there was heat treatment or not, showed μ0.06 to 0.1. The readings for the DLC were around μ0.09 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.

In Figure 7, friction coefficient trends of the electroless nickel plating and the Fe-W plating are shown for comparison. In many cases of the electroless nickel plating measurements, the friction coefficient temporarily went up to around μ0.25 from the beginning of the measurement for a time. After that, it gradually decreased and stayed around 0.17 until the end of the test in many cases. On the other hand, the Fe-W plating had readings of μ0.06 to 0.10 right after the start and all the way through the end of the test.

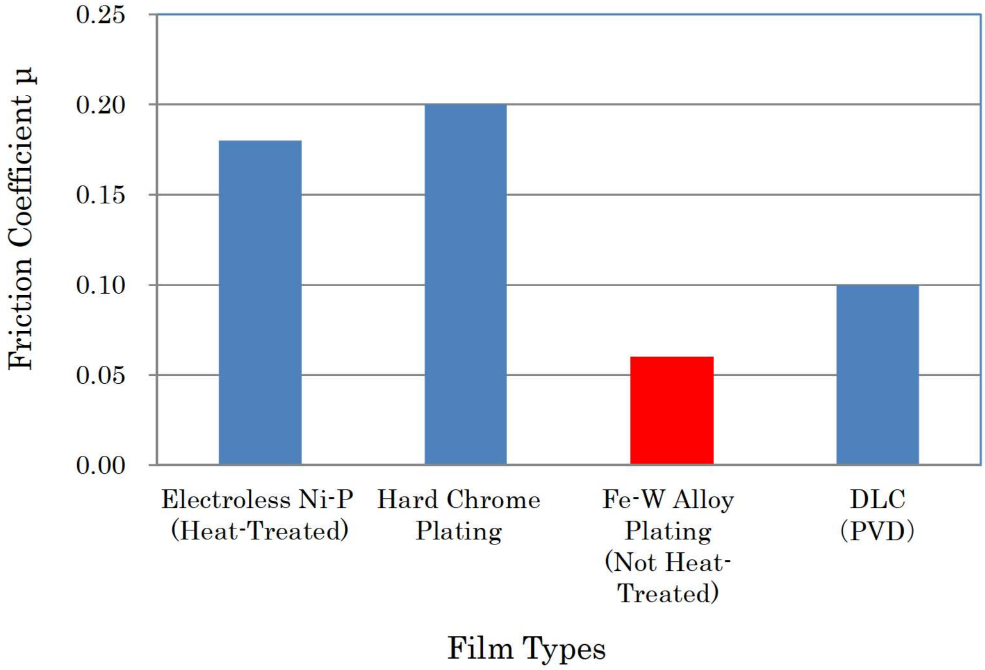


Figure 6. Each Plating Type and Friction Coefficient Comparison

(Same test condition as that for the friction coefficient measurements)

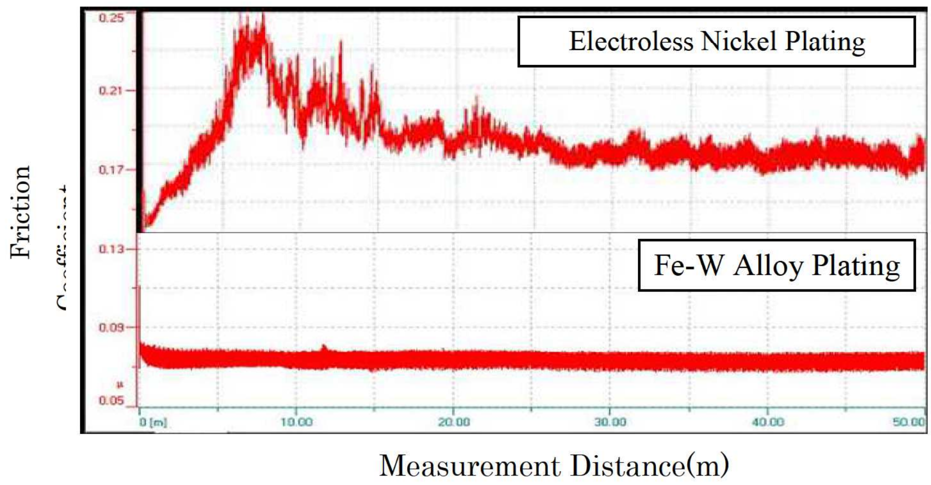


Figure 7. Friction Coefficient Trend Comparison of

Electroless Nickel Plating and Fe-W Alloy Plating

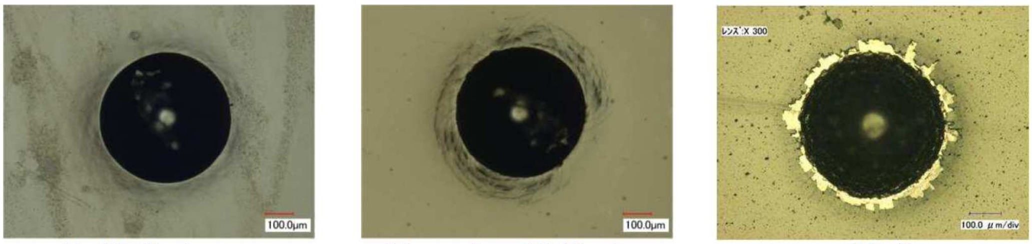
In the mixed lubrication range where the measurements were made this time, the lubricant was there but the oil was so sparse that the plating surface and the contacting ball did directly contact each other in some cases. When this happened, the electroless nickel plating was likely to show an increase in the friction coefficient at the beginning of the measurement. As time went by, the contact ball and the plating surface degraded a bit, enlarging the contact surface. Once the contact point load decreased, the friction coefficient probably 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.

3.4 Adhesion

The Rockwell Indentation Method was used in our adhesion test. The conditions are shown in Table 4. Figure 7 shows enlarged photos of film damaged around the indentation in the Rockwell Indentation Method. They were taken for enlarged observations using a video microscope.

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

(300x)



Fe-W Plating (Not Heat Treated) | Electroless Ni Plating (Heat Treated) | DLC

Figure 7. Adhesion Comparison –

Indented Area Observations in Rockwell Indentation Method

Table 4. Rockwell Indentation Method Condition

Item	Description
Indenter Type	Diamond, Scale C
Load	150kg
Load Time	10 Seconds
Sample Material & Hardness	HSS : HRC62.0
Observation Equip.	Video Microscope

4. 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 go up regarding surface finishes providing appropriate measures. However, the use of electroless nickel plating and hard chrome plating are not easy choices when the impacts on humans and environment are considered. Facing this situation, we developed Fe-W plating using iron and tungsten because they are not subject to environmental regulations. The following lists the properties of the Fe-W plating as evaluated:

(1) It was important that the film had 50 -60% tungsten (weight ratio) to achieve sufficient film hardness and ductility. The hardness 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 plating 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 cracks observed in the electroless nickel nor peeling that occurred in the DLC.

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

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.

5. Future Direction

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 become materialized, 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 a lot of 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 fuel efficiency. Aluminum is a typical material for that purpose, and we have received many requests to plate 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 μ to 0.01.

6. References

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