

The remanufacturing process of a hydraulic cylinder rod becomes a challenging prospect in the industrial sector producing heavy equipment. That is because remanufactured components can have the same product quality as new components with a more economical price.

Hard chromium electrodeposition is a well-known technique to provide a protective coating for the cylinder rod so that it has favorable wear and corrosion resistance properties. Associated with remanufacturing applications, the used chromium plating covering the cylinder rod should be removed first before applying the new chromium one. Whereas the removal process often slightly consumes the base metal and fresh thicker chromium should be deposited in order to preserve its original diameter. The main problem is that the thick chromium may experience macrocrack after the baking process at 200 °C. Hence, the observation of as-plated and as-baked thick and hard chromium deposit properties is the novelty of this research.

In this work, the thick and hard chromium plating over a flat carbon steel substrate was produced by the electrodeposition method. A conventional single-layer chromium deposit with a plating current density greater than 40 A/dm² shows macrocracks after the baking process at 200 °C for an hour. For the chromium duplex plating composed of two Cr layers, the maximum thickness of the deposit was 261.0±8.5 microns, and the macrocrack was observed. Meanwhile, the as-baked duplex chromium plating composed of a polished Cr-C layer and a Cr layer has a microcrack density of 337±8 cracks/cm and hardness of 924.8±22.2 HV_{0.3} without macrocracks. EPMA characterization confirmed the presence of a carbon element in the Cr-C layer, and it is presumed due to carbon co-deposition from formic acid additives

Keywords: *hard chromium electrodeposition, remanufacturing, macrocrack, chromium duplex plating, chrome-carbon deposit*

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FABRICATION OF MACROCRACK-FREE THICK CHROMIUM DUPLEX PLATING FOR REMANUFACTURING APPLICATIONS

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1. Introduction

Remanufacturing of a component is simply defined as the process of recovering old components from a used product to become new remanufactured components. This surely minimizes waste disposal as used components are recycled and recovered. Remanufactured components are claimed to have 45 to 65 % costs with about 85 % quality compared to new manufactured components [1]. An example of a remanufactured component is a hydraulic cylinder rod.

The cylinder rod has direct contact with the fluid, rubs against the rubber seal, and is exposed to extreme weather in the outdoor environment. Thus, it should be coated with hard chromium metal to have wear and corrosion resistance properties. Generally, there are several methods to deposit chromium metal on the base metal surface, such as HVOF (High Velocity Oxygen Fuel), electrodeposition, laser and weld coating, PVD (Physical Vapor Deposition), and CVD (Chemical Vapor Deposition) [2]. However, some methods are costly and impractical for large components like the cylinder rod. So, one of the most suitable methods

to apply a hard chromium coating to cylinder rods is electrodeposition.

Hard chromium electrodeposition is performed using a hexavalent chromium solution consisting of chromic trioxide (CrO₃) and sulphuric acid (H₂SO₄) with a volume ratio of 100:1. Indeed, chromium plating industries usually add more solution such as hydrofluoric acid (HF), silicic hydrofluoric acid (H₂SiF₆), or their salts to improve cathode efficiency, coverage, and throwing power [3]. The commonly used anode material is lead-based anodes, for example, PbSb₂, PbSb₅, PbSn₆, and PbSn₂Ag₂. It has high conductivity and high efficiency in oxidizing chromium(III) to chromium(VI). Whereas platinized titanium and platinized niobium are also used as an alternative anode.

In the process of remanufacturing the used cylinder rod, the chromium layer should first be removed to obtain the base metal surface. The process of removing the chromium layer from the base metal is known as stripping. However, in some cases, the stripping process not only removes the chromium layer but also erodes the base metal materials, so that the cylinder rod experiences some dimensional loss. As a result, thicker chro-

mium deposition is needed to compensate for the dimensional loss and preserve its original diameter. After the electrodeposition process, the as-plated thick chromium deposit should be followed by the baking process at an elevated temperature commonly 200 °C for a certain baking duration, depending on the strength and size of the component. It is aimed at removing the occluded hydrogen in the chromium deposit and preventing hydrogen embrittlement [4]. A new problem appeared is that the as-baked thick chromium deposit tends to experience macrocrack, which is undesirable. It is the crack on the deposit surface that can be observed visually by the naked eye. While observed by the cross-section method, the crack tip of the macrocrack ends and «touches» the base metal surface, which reduces the corrosion resistance of the component.

Research on chromium electrodeposition using hexavalent chromium solutions has been conducted since 1848, and currently such a research topic seems irrelevant. Right now, the focus of the scientists shifted to the development of eco-friendly trivalent chromium electrodeposition. However, many industries still use hexavalent chromium methods due to their feasibility to obtain a bright surface appearance with appreciable thickness, high hardness and corrosion resistance properties. In connection with remanufacturing applications, research on macrocracks on the as-baked thick chromium deposit by using hexavalent chromium solutions has not been conducted or published yet. It is important to conduct research on this topic because the results of such research are necessary for practical application in some industries, which produce thick chromium deposited components. In industrial applications, macrocracked components will not pass the quality control by visual test and are rejected due to low corrosion resistance properties. Therefore, research devoted to the development of thick and hard chromium deposition using hexavalent chromium solutions is relevant.

2. Literature review and problem statement

Microcrack is a common feature in hard chromium deposits processed by electrodeposition. It can be functioned for lubricant oil storage to improve wear resistance properties. In [5], it is shown that low friction and minimum wear of a hard chromium deposit are achieved if the crack density is about 3 % combined with post-polishing treatment.

There are several factors affecting the microcrack density in hard chromium deposits, such as chromic acid-to-catalyst ratio, plating temperature and deposit thickness. The paper [6] shows that for a hard chromium deposit with a surface crack density between 150 and 400 cracks/cm, an increase in crack density led to an increase in the hardness, wettability, and wear resistance properties. Meanwhile, the authors of [7] show that the microcrack density increases with the thickness of the chromium deposit. Whereas, the paper [8] presents that an increase in thickness resulted in enhanced corrosion resistance properties. Therefore, it is important to maintain the microcrack density in the ideal range at an optimum deposit thickness.

Many attempts have also been conducted in the field of chromium composite coatings to enhance the mechanical properties. The paper [9] presents the research on the hexavalent chromium deposit with the addition of zirconia (ZrO_2) nanoparticles. Adding 3 g/L zirconia nanoparticles yielded an optimum surface deposit hardness of 1,185 $HV_{0.5}$. The maximum thickness of the deposit with a four-hour

electrodeposition process was 107 microns. The presence of zirconia nanoparticles in the deposit also improved the corrosion resistance properties.

The paper [10] shows similar attempts to obtain composite coatings by introducing alumina (Al_2O_3) particles to the chrome-carbon (Cr-C) deposit in a trivalent chromium solution bath. It is shown that the maximum hardness of 1,075 $HV_{0.1}$ was obtained with 21.5 vol % alumina particles contained in the Cr-C deposit. Besides, the introduction of alumina particles in the Cr-C matrix significantly improved the corrosion resistance properties of the deposit due to the particles, which reduces the crack density, thus blocking corrosive media. However, the thickness of the Cr-C/ Al_2O_3 composite coatings was less than that of the original Cr-C deposits. That is caused by inert alumina particles, which inhibit the electrodeposition process. In addition, the paper [11] explains that the thin Cr-C deposit obtained from a trivalent chromium bath containing formic acid is darker due to the presence of nanocrystal graphite, which differs from the bright hexavalent chromium deposit.

Previous studies mainly discuss how to improve the properties and performance of the as-plated chromium deposit only. However, as mentioned in [4], the as-plated chromium deposit of the technical components should be followed by a baking process at about 200 °C to remove the occluded hydrogen and prevent hydrogen embrittlement. It turns out that the baking process also affects the formation of macrocracks, especially for thick chromium deposits (200 to 500 μm). So, the issue of investigating and/or improving the properties of the as-baked chromium deposits, in which the macrocrack can occur, remained unresolved. The reason for this may be the objective necessity related to the chromium deposit thickness. Usually, manufactured hard chrome-plated components have a deposit thickness of 3060 μm , and it is quite enough for coating the substrate materials. However, in remanufacturing industries, where a thicker chromium layer (200 μm or more) is needed and followed by the baking process, this topic is important to be concerned.

A way to obtain a thick chromium deposit is the duplex plating method. This method actually has been applied in Ni/Cr duplex plating. However, the capital and production costs for nickel and chromium plating solutions are significant. Therefore, duplex chromium plating composed of two chromium layers is preferred to reduce the costs. All this suggests that it is advisable to fabricate as-baked macrocrack-free thick chromium deposits for remanufactured chrome-plated component applications.

3. The aim and objectives of the study

The aim of the study is to develop thick and hard chromium deposits with an optimum quantity of microcracks without macrocracks for remanufacturing applications. This will make it possible to obtain a minimum thickness of chromium deposits of about 150 μm with a minimum hardness of 800 $HV_{0.3}$, and a microcrack density of not more than 800 cracks/cm.

To achieve the aim, the following objectives are accomplished:

- to determine the thickness, hardness, and microcrack density of thick and hard conventional chromium and chrome-carbon deposits;
- to determine the properties of the chromium duplex plating.

4. Materials and methods

In this work, duplex chromium deposits were fabricated by using a hexavalent chromium bath via an electrodeposition process. The materials used in this work are as follows. Low-carbon steel substrate with dimensions of 20×10×60 mm. Hexavalent chromium solution obtained from Komatsu Indonesia company, Jakarta, Indonesia. The solution composed of 250 g/L CrO₃, 2.5 g/L H₂SO₄, and HEEF catalyst. Formic acid with 90 % purity obtained from CV Harum Kimia, Jakarta, Indonesia. Lead anode with dimensions of 200×50×10 mm.

The substrate was first ground and polished using a Struers Tegramin-25 polishing machine to obtain a mirror-like surface. Then, it was insulated with a duct tape leaving an area of 20×25 mm for the chrome deposition process. Before the electrodeposition process, the specimen was surface-activated using the anodic etching method operated at 5 to 10 A/dm² for two minutes and then rinsed with aquadest.

Conventional chromium deposition was performed using a hexavalent chromium solution. While chrome-carbon deposition was performed using a hexavalent chromium solution mixed with formic acid by a certain composition depending on the experiment parameter. The mixing process of the latter solution was left for about three hours before the electrodeposition process was executed. The plating temperature for chrome-carbon deposition was 35±3 °C. During the electrodeposition process, the solution was agitated using a magnetic stirrer at 200 rpm to maintain good ionic circulation in the solution. The heat treatment or baking process was done using a Yamato DX 31 drying oven at 200 °C. The experimental design used is shown in Tables 1, 2.

The mass of the chromium deposits was measured by using a Kern ABJ 220-4NM analytical balance. The hardness of the chromium deposits was measured by a Mitutoyo HM-220 micro Vickers machine with 300 gf loading and 10 seconds dwell time. The thickness of the deposits was measured by using Fischer Dualscope MPOR. The microstructure and the crack pattern of the chromium deposits were examined using a Keyence VHX-5000 stereo microscope. The elements mapping of the Cr-C/Cr deposit was examined by using Shimadzu EPMA-1720H. The images of the crack pattern were processed using ImagePro-10 software, and the crack density was calculated manually based on the formula used in [12, 13].

Preliminary experiments of single-layer chromium deposition

Table 1

Conventional chromium deposits						
	Sample	<i>I</i> (A/dm ²)	<i>T</i> _{plating} (°C)	<i>t</i> _{plating} (hours)	<i>T</i> _{baking} (°C)	
1	Cr-30	30	55±3	8	200 °C for an hour	
	Cr-40	40				
	Cr-50	50				
	Cr-60	60				
	Cr-70	70				
	Cr-80	80				
Conventional chromium (Cr) and chrome-carbon (Cr-C) deposits						
	Sample	[HCOOH] (mL/L)	<i>I</i> (A/dm ²)	<i>T</i> _{plating} (C)	<i>t</i> _{plating} (hours)	<i>T</i> _{baking} (°C)
2	Cr-4H-200	0	40	40±3	4	200 °C for an hour
	Cr-6H-200				6	
	Cr-8H-200				8	
	Cr-C-4H-200	10	40	35±3	4	200 °C for an hour
	Cr-C-6H-200				6	
	Cr-C-8H-200				8	

Table 2

Experimental design of chromium duplex plating

Sample	1st layer	2nd layer	Baking process
DL Cr+Cr	Cr layer	Cr layer	Baked at 200 °C for 10, 30, 60, 90 minutes
	<i>I</i> _{plating} =30 A/dm ²	<i>I</i> _{plating} =80 A/dm ²	
	<i>T</i> _{plating} =45±3 °C	<i>T</i> _{plating} =55±3 °C	
	<i>t</i> _{plating} =6 hours	<i>t</i> _{plating} =5 hours	
DL Cr-C+Cr	Cr-C layer	Cr layer	Baked at 200 °C for an hour
	<i>I</i> _{plating} =40 A/dm ²	<i>I</i> _{plating} =80 A/dm ²	
	<i>T</i> _{plating} =30±3 °C	<i>T</i> _{plating} =55±3 °C	
	<i>t</i> _{plating} =4 hours	<i>t</i> _{plating} =6 hours	
DLP Cr-C+Cr	Cr-C layer (Polished before applying the 2 nd layer)	Cr layer	Baked at 200 °C for 10, 30, 60, 90 minutes
	<i>I</i> _{plating} =40 A/dm ²	<i>I</i> _{plating} =80 A/dm ²	
	<i>T</i> _{plating} =30±3 °C	<i>T</i> _{plating} =55±3 °C	
	<i>t</i> _{plating} =5 hours	<i>t</i> _{plating} =6 hours	

5. Results of research on thick and hard hexavalent chromium electrodeposition

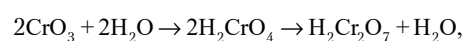
5.1. Properties of single-layer conventional chromium and chrome-carbon deposits

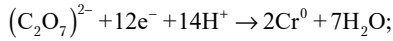
Table 3 summarizes the obtained properties of conventional chromium deposits. The figures attached in the table represent the as-baked chromium deposits condition. They have a bright and smooth visual appearance.

It can be seen that the thickness of the deposits increases periodically along with increasing current density. This makes sense because the higher the current density used, the higher the electron supply transported to the cathode, and thus the faster the electrochemical reaction, resulting in thicker chromium deposits.

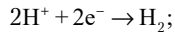
Viewed from an electrochemistry standpoint, during the electrodeposition process there are three possible electrochemical reactions at the cathode surface in which they compete with each other, according to [14, 15]. The reactions are described as follows:

1) the main reaction is the deposition of solid metallic chromium (Cr⁰) through the reduction of hexavalent chromium from chromic acid (CrO₃):

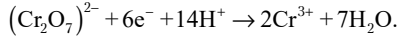




2) hydrogen evolution, which is the most dominant reaction:



3) reduction of hexavalent chromium into trivalent chromium ion (Cr^{3+}):



The table shows that the thickness of the deposits increases slightly when the current density is about 60 to 80 A/dm². That may be caused by the dominant hydrogen evolution reaction, which consumes more electrons, thereby lowering the cathode current efficiency.

The trends in the as-plated microcrack density did not directly correlate with the increasing current density. However, the microcrack density increases after the baking process. As mentioned in [16], dissolved hydrogen in chromium deposits is combined with chromium atoms to become the metastable chromium hydride (CrH) phase. When heating at an elevated temperature, that metastable CrH phase will tend to go back into its stable α -chromium phase, and hydrogen is released. This is accompanied by the unit cell reduction from hexagonal or face-centered cubic CrH into body-centered cubic α -chromium, resulting in cracks. Another explanation in the literature [3, 17] showed that hydrogen combined with chromium leads to an increase in the residual tensile stress. As the tensile stress reaches the maximum point, it suddenly drops producing cracks in the chromium deposits. It also can be seen that the as-baked chromium deposits show macrocracks at a plating current density of 50 A/dm² or more.

There is also no correlation between as-plated hardness and increasing current density. However, on the other hand, the hardness of the deposits decreases after the baking process. In connection with the metastable CrH phase, the works [16, 17] believed that the high hardness of the as-plated chromium deposits comes from the contribution of metal hydrides in which the interstitial hydrogen atom blocks the slip.

The second pre-trial experiment was conducted because we want to observe the influence of some variables, e.g. plat-

ing duration and baking temperature, on the properties of thick conventional chromium and chrome-carbon deposits. Fig. 1 shows the amount of the chromium deposit in grams along with the extended plating duration. Generally, the obtained chromium deposits increase along with the plating duration, and this corresponds to Faraday's law of electrochemistry, as well as the plating thickness shown in Fig. 2. It can be seen that chrome-carbon (Cr-C) deposits have lower mass and lower thickness than that of conventional chromium (Cr). From these trends, we formulate two hypotheses.

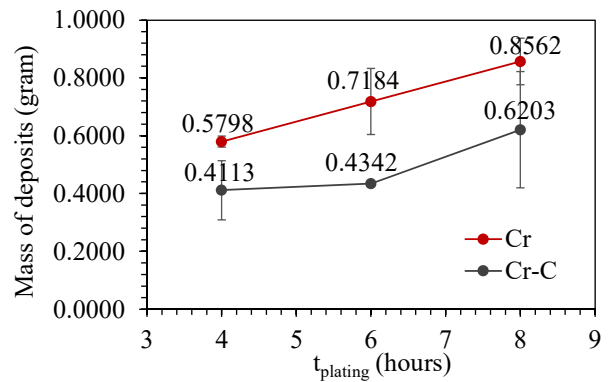


Fig. 1. Gained mass vs plating duration of as-plated chromium deposits

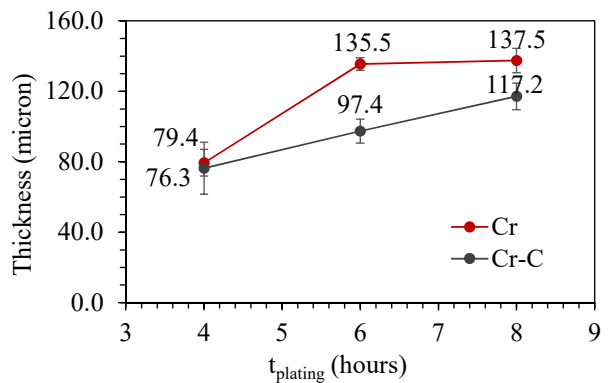


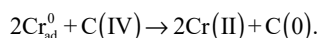
Fig. 2. Thickness vs plating duration of as-plated chromium deposits

Table 3

Properties of pre-trial conventional chromium deposits

Sample	Thickness (μm)	Microcrack density (cracks/cm)		Hardness (HV _{0.3})	
		As-plated	As-baked	As-plated	As-baked
Cr-30	104.3±2.4	153±15	250±5	1033.8±14.5	878.1±12.3
Cr-40	127.1±5.5	161±24	223±1	984.5±24.3	861.6±19.5
Cr-50	135.4±3.7	124±32	226±10	998.2±10.4	870.2±13.6
Cr-60	155.0±1.8	136±7	235±2	986.4±17.3	868.7±24.7
Cr-70	163.6±3.5	137±11	230±10	997.1±13.9	879.9±10.8
Cr-80	167.3±3.5	166±12	273±5	1001.6±20.8	872.7±17.9
As-baked microstructures					
Cr-30	Cr-40	Cr-50	Cr-60	Cr-70	Cr-80

First, according to the research papers [18, 19], the addition of formic acid to the hexavalent chromium solution will produce chrome-carbon structure deposits by a mechanism called carbon co-deposition. From a surface study conducted in [20], there is a small amount of formic acid that is incorporated into the chromium deposit. The carbon atom contained in formic acid will insert into the deposits through the so-called «unusual chemical reaction» [18]:



In addition, the deposited carbon atom will also slow down the chromium deposition rate due to the re-dissolving process of adsorbed chromium (Cr_{ad}^0) into divalent chromium ions ($Cr(II)$). Therefore, it yields thinner chromium deposits compared to conventional chromium deposits.

Second, according to [19, 21], formic acid will react with the hexavalent chromium solution producing Cr^{3+} ions, which decrease the solution conductivity and lowers the throwing power:

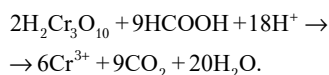


Fig. 3 shows the microcrack density of the thick chromium deposits versus plating duration for as-plated and as-baked conditions. For as-plated condition, it can be seen that the microcrack density of both Cr and Cr-C deposits is not linear with increasing plating duration. This result contradicts the research papers [3, 7], which show that the microcrack density of chromium deposits increases with increasing deposit thickness. However, [17] states that crack formation during the electro-deposition process involves the crack healing and re-cracking cyclic processes. As mentioned before, the hydrogen evolution reaction contributes to the residual tensile stress development, and cracks form when the tensile stress reaches its maximum limit and suddenly falls. Thus, for as-plated thick chromium deposits, the microcrack density will depend on the condition of the plating solutions.

Comparing the as-plated microcrack density between Cr and Cr-C deposits, it can be seen that the latter has a lower microcrack density than that of the former. A carbon atom has an empirical atomic radius of 70 pm, which is smaller than that of chromium of 140 pm. The percentage difference between both atomic radii is $(140 - 70) / 140 = 50\%$. Based on [22], it is expected that the carbon incorporation in the Cr-C deposit acts as an interstitial atom for chromium host atoms. From [16, 14], hydrogen loss from the chromium deposit during electroplating is accompanied by a 15% volume reduction and cracking. Hence, the carbon atom reduces the effect of this reduction.

Comparing the as-baked microcrack density between Cr and Cr-C deposits, it can be seen that after an hour of baking, the microcrack density increases. According to [14], this is attributed to the liberation of hydrogen atoms, which have been dissolved into the chromium deposits. When ex-

posed to high temperatures, hydrogen diffuses out followed by volume reduction, then the crack increases extensively.

Fig. 4 shows the hardness of the thick chromium deposits versus plating duration for as-plated and after HT conditions. For as-plated Cr and Cr-C deposits, the hardness behaves inconsistently as the plating duration increases, which may be influenced by the condition of the plating solutions during the electrodeposition process. Nevertheless, the hardness values of the deposits are in the range of 8001,200 $HV_{0.3}$, and this corresponds to the «hard» properties of chromium deposits.

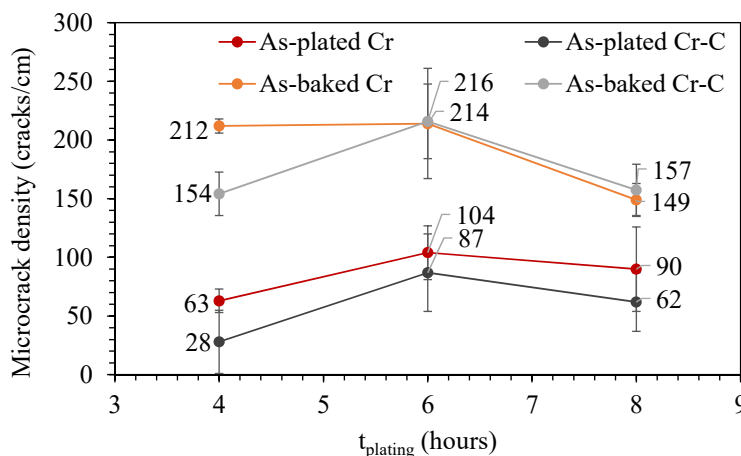


Fig. 3. Microcrack density vs plating duration of conventional chromium and chrome-carbon deposits

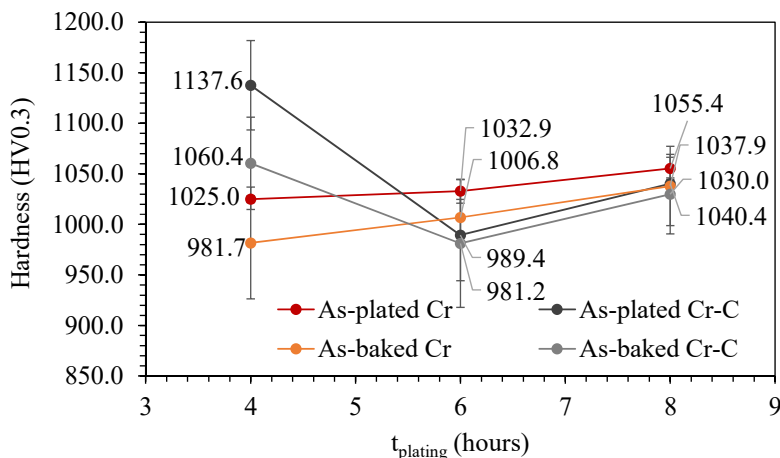


Fig. 4. Hardness vs plating duration of conventional chromium and chrome-carbon deposits

Comparing the hardness after HT for both Cr and CrC deposits, it can be seen that the hardness of both deposits decreases. This can be explained by the theory from Snavely [16] that the decrease in hardness is due to the phase transformation of the metastable HCP or FCC chromium hydride phase to the stable BCC alpha chromium phase. The interstitial hydrogen atom is liberated out from the deposits, thus the chromium deposit lost its strengthening mechanism.

5. 2. Properties of thick chromium duplex plating

Table 4 recaps the thickness, hardness, and microcrack density of the chromium duplex plating. The table shows that all the samples achieved thick chromium deposits with about 200 microns. Besides, the microcrack density changes of each sample from as-plated to as-baked conditions are as

follows. In sample DL Cr+Cr, the microcrack density increased by $(218-171)/218=21.6\%$. In sample DL Cr-C+Cr, the microcrack density increased by $(224-174)/224=22.3\%$. In sample DLP Cr-C+Cr, the microcrack density increased by $(337-131)/337=61.1\%$.

The hardness after baking of the deposits was also not less than $800\text{ HV}_{0.3}$. In sample DL Cr+Cr, the hardness drops by $(1076.1-946.8)/1076.1=12.0\%$. In sample DL Cr-C+Cr, the hardness drops by $(1032.5-998.1)/1032.5=3.3\%$. In sample DLP Cr-C+Cr, the hardness drops by $(1030.5-924.8)/1030.5=10.3\%$.

Fig. 5 summarizes the microstructure of each chromium layer before and after the baking process. The terms DL and DLP respectively mean «Double Layer» and «Double Layer with the 1st layer polished prior».

The as-plated first layer of sample DL Cr+Cr had a bright and smooth surface, being one of the characteristics of hard hexavalent chromium deposits. Without the polishing process, the as-plated second layer of sample DL Cr+Cr resulted in a satin surface. The as-plated first layer of sample DL Cr-C+Cr and sample DLP Cr-C+Cr had a satin surface. With the polishing process, the as-plated second layer of sample DLP Cr-C+Cr had a satin surface, as well as sample DL Cr-C+Cr without the polishing process. After the baking process, sample DL Cr+Cr showed macrocrack. Whereas sample DL Cr-C+Cr and sample DLP Cr-C+Cr showed major and minor microcracks.

Fig. 6 shows the cross-section and microcrack density examination of sample DLP Cr-C+Cr. It can be seen that in Fig. 6, *a*, sample DLP Cr-C+Cr has two layers of chromium deposit. The two-layer boundary can be observed after rubbing the polished crosscut sample by electric etching using 3% nital solutions. While in sample DL Cr+Cr and DL Cr-C+Cr, the two-layer

boundary cannot be observed due to the unpolished 1st layer before applying the second layer. Fig. 6, *b* shows a defect caused by poor adhesion surface during the electrodeposition process.

The crack development of chromium deposits towards baking duration was observed as shown in Fig. 7. By increasing baking durations, the microcrack in sample DL Cr+Cr develops into a macrocrack. This is attributed to hydrogen liberation. On the other hand, the microcrack in sample DLP Cr-C+Cr did not develop to macrocrack at all even if the baking duration is extended to 190 minutes. It is presumed that the Cr-C first layer minimizes the volume reduction side effect from hydrogen liberation.

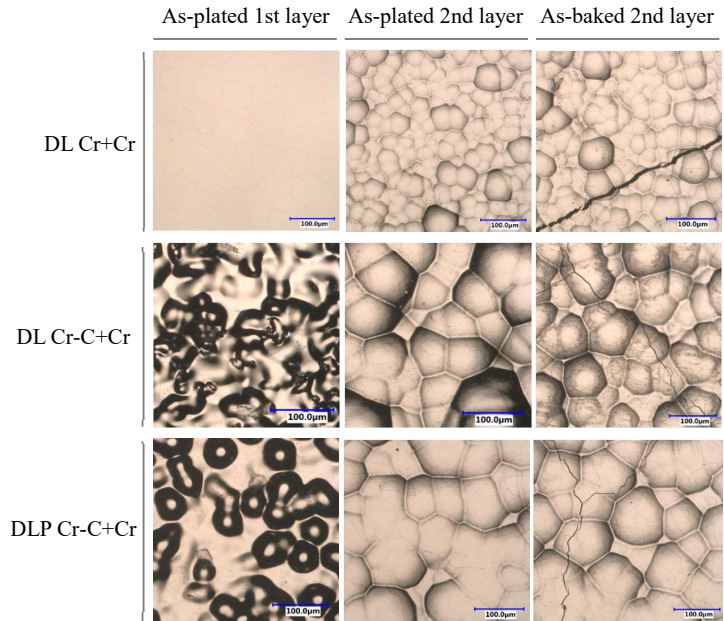


Fig. 5. Microstructure examination of duplex chromium deposits

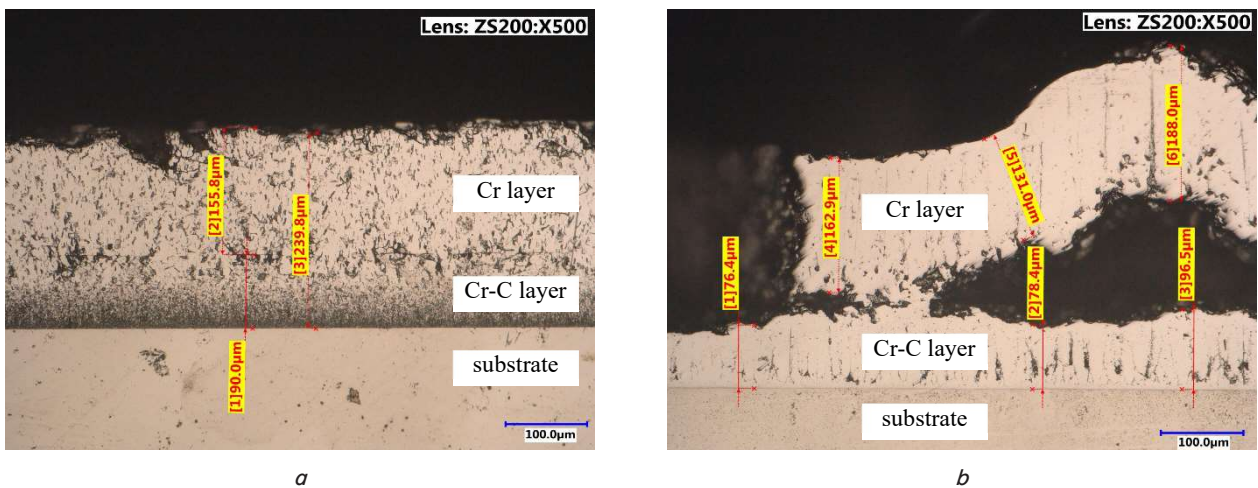


Fig. 6. Stereo microscope examination of sample DLP Cr-C+Cr: *a* – all layer thickness; *b* – plating defect

Table 4

Properties of chromium duplex plating

Sample	Thickness (μm)		Microcrack density (cracks/cm)		Hardness ($\text{HV}_{0.3}$)	
	1st layer	2nd layer (overall)	As-plated	As-baked	As-plated	As-baked
DL Cr+Cr	90.1 ± 3.4	261.0 ± 8.5	171 ± 49	218 ± 8	1076.1 ± 14.5	946.8 ± 12.6
DL Cr-C+Cr	92.0 ± 3.9	226.4 ± 5.6	174 ± 28	224 ± 7	1032.5 ± 59.4	998.1 ± 8.9
DLP Cr-C+Cr	93.8 ± 3.8	219.4 ± 4.6	131 ± 36	337 ± 8	1030.5 ± 13.8	924.8 ± 22.2

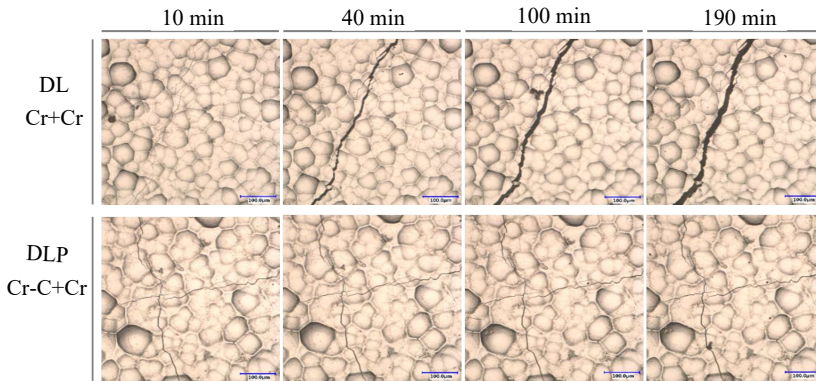


Fig. 7. Crack development of sample DL Cr+Cr and sample DLP Cr-C+Cr after baked at 200 °C for 10, 40, 100, and 190 min

Fig. 8 shows the hardness development of sample DL Cr+Cr and sample DLP Cr-C+Cr by varying baking temperature. It is shown that the hardness of sample DLP Cr-C+Cr falls significantly compared to that of sample DL Cr+Cr. The authors take a closer look to confirm this result by taking 78 micro indentations in three regions for each sample.

Fig. 9 shows the indentation results of both samples after baked at 200 °C for cumulative 190 min. Generally, sample DL Cr+Cr has a higher hardness than sample DLP Cr-C+Cr, as confirmed by the result in Fig. 8. Interestingly, for sample DL Cr+Cr, the hardness values in the region without macro-crack are similar to that in the around macro-crack region.

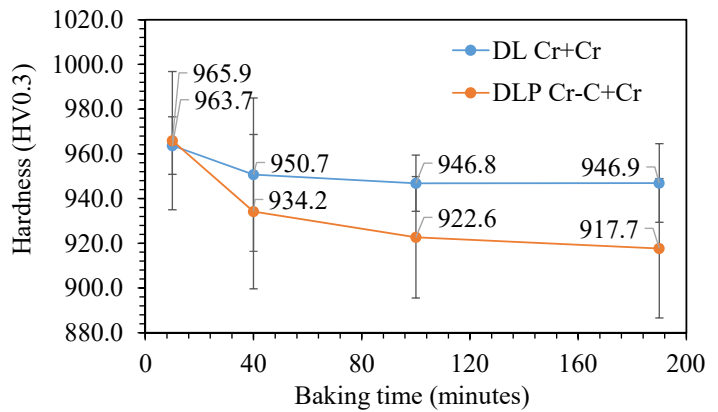


Fig. 8. Hardness development vs baking time of sample DLP Cr-C + Cr after baked at a constant temperature of 200 °C

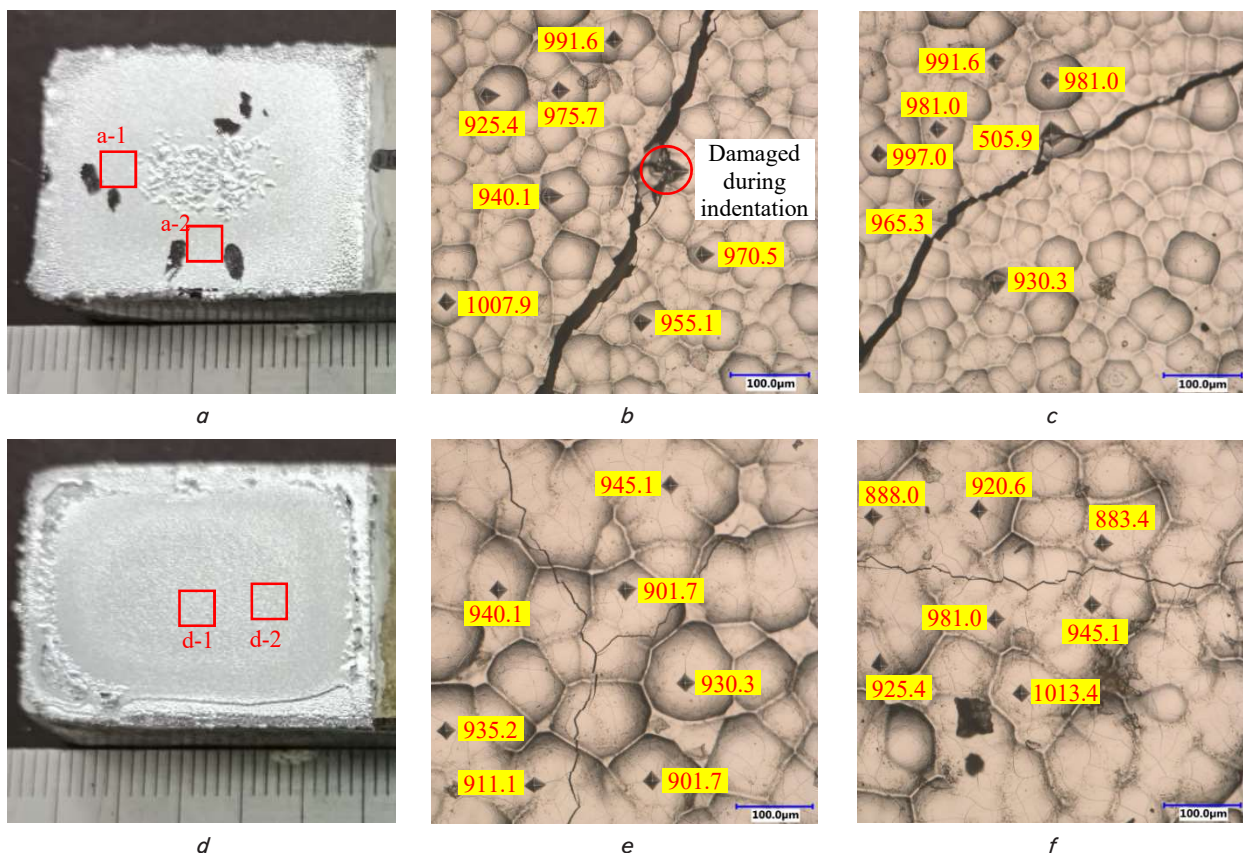


Fig. 9. Hardness (in HV_{0.3}) of chromium deposits of: a – DL Cr+Cr; b, c – microscopic view of a-1 and a-2, respectively; d – DLP Cr-C+Cr; e, f – microscopic view of d-1 and d-2, respectively

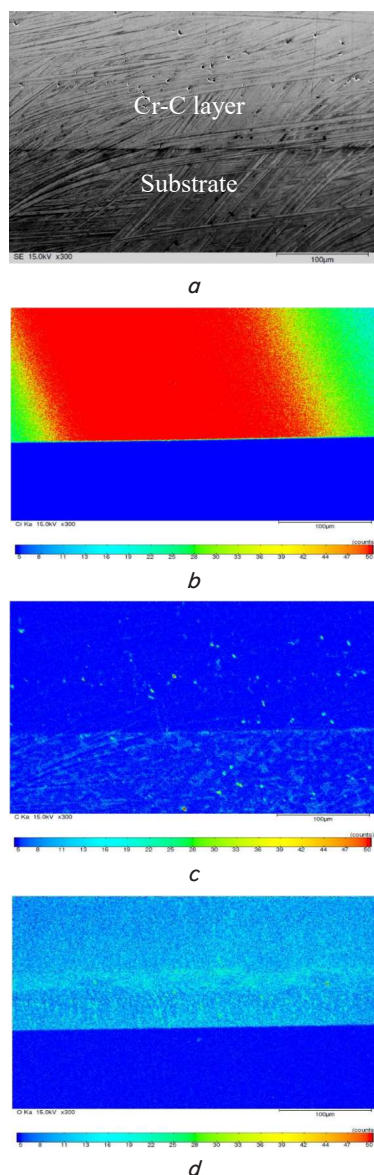


Fig. 10. EPMA elements mapping of sample: *a* – DLP Cr-C+Cr; *b* – Cr; *c* – C; *d* – O

6. Discussion of the results of thick and hard hexavalent chromium electrodeposition

It is interesting to discuss that the chromium metal obtained by the electrodeposition process has a different strengthening mechanism compared to pure chromium metal. The authors tested the hardness of pure chromium. Our result showed that pure chromium has a hardness of about 150 HV_{0.3}. In addition, from materials database on Matweb.com, the hardness of as-swaged chromium and annealed chromium is 131 HV and 91 HV, respectively. This means that there might be such kind of strengthening mechanisms that the chromium electrodeposit can gain its «hard» properties. Scientists have proposed their hypothesis in order to explain how the chromium electrodeposit can obtain the «hard» properties up to 1,200 HV with brittle properties. The most familiar hypotheses are due to (1) the formation of the chromium hydride (CrH) phase as a result of hydrogen combined with chromium atoms, and (2) the finer grain size of chromium [16].

The CrH phase was believed for the cause of high hardness in the as-plated chromium electrodeposits. Meanwhile, [4, 14] state that the presence of hydrogen in the chromium deposited component also promotes hydrogen embrittlement. That is why the as-plated chromium electrodeposits should be followed by the baking process in order to remove dissolved hydrogen. The work [24] summarizes and explains ten mechanisms of hydrogen embrittlement. One of the mechanisms that is suitably applied in chromium electrodeposition is through the hydride formation.

The works [25, 26] elaborate the main types of hydrogen that reside in metal, i.e. easily mobile hydrogen (EMH), progressively mobile hydrogen (PMH), and totally trapped hydrogen (TTH). Several techniques have been developed to quantify the hydrogen amounts in metals. Eudiometer, vacuum decay, Bernacle cell, and Devanathan cell are the techniques used to quantify EMH. Furnace control is one of the techniques to quantify PMH. Whereas vacuum fusion, inert fusion, and tin fusion methods are used to quantify TTH. Associated with CrH, it is difficult to characterize this phase because CrH is a metastable phase that the hydrogen atom can be released easily by heat exposure to become a more stable alpha-chromium phase.

In this experiment, the single-layer chromium plating showed an optimum plating current density of 40 A/dm² to prevent the occurrence of macrocrack during the baking process. It is presumed that a current density higher than 40 A/dm² will cause an intense hydrogen evolution reaction on the cathode surface. It resulted in a large quantity of hydrogen absorbed in the chromium deposit. As a consequence, the baking process will massively diffuse out the hydrogen followed by a significant volume reduction of HCP-to-BCC chromium transition unit cells, and finally a macrocrack occurred.

Theoretically, as mentioned before, a hydrogen atom can act as an interstitial atom, which blocks the dislocation motion thus enhancing the hardness properties. Considering the result in Fig. 9 of the duplex plating, the baking process up to 200 °C for cumulative 190 mins is expected that almost all of the interstitial hydrogen is diffused out of the deposits. However, the chromium deposit still retains its hardness in the range of about 900 HV_{0.3} even though it was baked at an elevated temperature. So, there might be another strengthening mechanism in hard chromium electrodeposits, e.g. finer chromium grain or crystallite size.

The thick chromium duplex plating (Cr-C plus Cr) can yield a deposit with the desired thickness, hardness, and no macrocrack formed after the baking process. Besides, the hardness still exceeded 800 HV, and the microcrack density was in the ideal range of 200 to 800 cracks/cm. It is suspected that the presence of a carbon element co-deposited in the Cr-C deposit minimizes the volume reduction of the HCP-to-BCC chromium transition unit cell, preventing the macrocrack occurrence during the baking process.

There are some limitations in this study. First, up to now, the structure of metastable hexagonal close-packed or face-centered cubic CrH still cannot be obtained easily through general characterization methods. Thus, more elaboration of the crack formation mechanism by dissolved-hydrogen liberation is required. Second, the properties of thick chromium electrodeposition may differ from the thin one. The thick one needs more extended plating durations, which leads to changes in the chromic acid-to-sulphuric acid ratio, thus the properties of the chromium deposit may change.

However, increasing the current density to shorten plating durations can also be a good idea, but this will lead to greater absorption of hydrogen in the deposit and cause the risk of hydrogen embrittlement during the baking process.

At present, scientists focus on developing the research of eco-friendly trivalent hard chromium electrodeposition. The paper [27] presents the results of trivalent chromium electrodeposition by using ternary complexing agents consisting of oxalic acid, tartaric acid, and urea. It has a bright and uniform coating surface with a thickness of about 30 microns. Another research on inventing new materials was performed in [28] using the traditional powder metallurgy method to produce materials in Fe-Cr, Fe-Cr-Zr, and Fe-Cr-B-Zr model alloy systems. It is shown that the obtained microstructures of those alloys have the potential in coating applications to enhance the hardness and wear resistance properties. More advanced research in surface engineering was conducted in [29] to form a functional protective layer in stainless steel using the laser alloying method. The results show that the coatings have a thickness of 220–320 microns with complex microstructures. The high hardness up to 16 GPa and wear resistance of the coating were caused by the contribution of martensite and some retained austenite phases.

Further research should be undertaken in the scope of optimum yield and properties of thick and hard chromium duplex plating.

7. Conclusions

1. Thick and hard chrome-carbon (Cr-C) deposits have a smaller thickness compared to the conventional (Cr) one due to the carbon co-deposition mechanism. The hardness of both chromium deposits still exceeds 800 HV_{0.3} after baking at 200 °C for an hour. The as-plated Cr-C deposit has a lower microcrack density than that of the Cr one. After the baking process, both chromium deposits have almost similar microcrack density.

2. The duplex chromium deposition showed a distinguishable two-layer system. The duplex plating DLP Cr-C+Cr composed of polished Cr-C and Cr exhibits a plating thickness of 219.4 microns. After the baking process, the deposit did not show any macrocrack since the carbon co-deposited in the deposit minimizes the effect of unit cell volume reduction. The microcrack density and hardness were 337 cracks/cm and 924.8 HV_{0.3}, respectively. It is expected that this two-layer thick chromium duplex plating can be used in remanufacturing applications.

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