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Characterization of a laser-discrete quenched steel substrate/chromium system by dissolving coatings

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Abstract

A laser-discrete quenched steel (LDQS) substrate/as-deposited chromium (top high-contraction (HC) and underlying low-contraction (LC) chromium) system was investigated by dissolving coatings in order to reveal the mechanism that the service life of the coated parts is largely improved using the hybrid technique of laser pre-quenching plus chromium post-depositing. It was found that the surface characteristics of the substrate, LC and HC chromium layer can be simultaneously revealed owing to the dissolution edge effect of chromium coatings. Moreover, the periodical gradient morphologies of the LDQS substrate are clearly shown: the surfaces of laser transformation-hardened regions are rather smooth; a lot of fine micro-holes exist in the transition zones; there are many micro-dimples in the original substrate. Furthermore, the novel method of dissolving coatings with sharp interfaces may be used to reveal the structural features of a substrate/coating system, explore the effect of the substrate on the initial microstructure and morphologies of coatings, and check the quality of the coated-parts.

Keywords: Interface; Electroplating; Chromium; Laser-discrete quenching; Dissolution edge effect

1. Introduction

Chromium electrodeposits have been widely used as protective coatings on engineering composites and tools such as work rolls, aircraft landing gear and barrels of gun/cannon tubes etc. owing to their excellent wear and corrosion resistance, high melting point and low coefficient of friction, high hardness [1–4]. However, under severe service conditions (e.g. high temperature, gas erosion and severe stressing), damage would be caused easily at the substrate/chromium interface and result in spallation of the local chromium coatings along the interface [5–7]. With operating conditions becoming more and more severe, the traditional single chromium plating cannot meet practical requests. In order to improve the damage-resistance of the substrate/Cr plating interface, various duplex surface techniques based on chromium plating, such as the combinations of chromium plating plus laser-surface hardening (or plasma nitriding), were proposed and investigated [8–11]. Among these hybrid techniques, the duplex process of substrate laser pre-quenching plus chromium post-depositing was successful for improving the service life of the chromium-coated parts [12,13]. In order to reveal its mechanism, our previous work has shown that laser-quenching of a steel substrate cannot only reduce the steep hardness gradient at the substrate/chromium interface but also alter the morphologies and microstructure of the initial electrodeposited chromium [14].

It is well known that the microstructural and morphological features of a substrate surface have an important influence on the interfacial structure and service life of coatings. To reveal the surface topographic characteristics of the LDQS substrate before plating, a novel method of dissolving coatings was put forward and used to characterize the hierarchical structure of a LDQS substrate/chromium system in the present paper.

2. Experimental

An as-quenched and tempered 30CrNi2MoV steel plate (main chemical ingredients: 0.28C, 0.7Cr, 2.27Ni, 0.20 Mo, 0.21V, all in wt.%) was used as substrate material. The detailed

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preparation process on laser-quenching of the steel plate and chromium electroplating can be found in Ref. [14]. Etching was performed by using the modified Murakami's reagent and Nital 2% in volume to observe the cross-sectional characteristics of the duplex electroplated chromium layers and LDQS substrate, respectively. The alcohol solution with hydrochloric acid 6–8% in volume was used to dissolve chromium coatings. Samples 10×5×5 mm in dimension were prepared using electro-sparking machining with the longest sides perpendicular to the laser scanning direction. Two groups of specimen (G1 and G2) were prepared. G1 was hold in the chemical reagent for 3 h. G2 was hold for longer time (e.g. 12 h) to remove the top HC chromium thoroughly. Finally, all samples were ultrasonically cleaned in alcohol. Morphological observations were carried out by using optical microscope (OM) and high resolution scanning electron microscope (HRSEM) (FEI Sirion 400NC) with EDS.

3. Results

3.1. Cross-sectional features

OM observations on the cross-section of the LDQS substrate/as-deposited chromium system are shown in Fig. 1. As can be seen, the duplex chromium coatings are composed of top HC and underlying LC chromium layers. The micro-cracks embedded in the former are longer in size and more in number than those in the latter. And the laser-quenched tracks appear crescent-shape, resulting from the Gaussian distribution of laser beam energy density. The special surface gradient structure of the substrate was generated via laser-discrete quenching. Thus, the hierarchical structure with graded mechanical properties in the LDQS substrate/chromium system is produced by the duplex technique of laser pre-quenching plus chromium post-depositing.

3.2. Low-magnified surface features

SEM micrographs of the typical overall morphologies of the LDQS substrate/chromium system in G1~2 are presented in Fig. 2a–b, respectively. As shown in Fig. 2a, the surface morphologies of the steel substrate, LC and HC chromium layers (from up to down) are extremely different. A lot of network cracks can be observed on the HC chromium layer, while no cracks in the LC chromium layer are clearly seen. And the periodical topographic features of the LDQS substrate aren't distinctly exposed due to shorter etching time. Obviously, Fig. 2b shows the periodical morphological characteristics of the laser-transformation hardened zone, transition zone and original substrate (marked A–C, respectively) after the top HC chromium was thoroughly removed away. Few cracks in LC chromium can still be observed in Fig. 2b. According to Fig. 2, it can be well concluded that the dissolution edge effect of chromium coatings results in the step-like morphologies of the substrate, LC and HC chromium layers. Thus, the hierarchical structure of a LDQS substrate/as-plated chromium system can be simultaneously characterized by dissolving coatings.

3.3. Surface characteristics of HC and LC chromium layers

EDS mapping of Cr on G1 is shown in Fig. 3. As can be seen, distribution of Cr (Fig. 3b) is consistent well with the surface morphology (Fig. 3a), and there is no residual chromium left on the exposed substrate. Moreover, no significant difference was found between the Cr distributions in

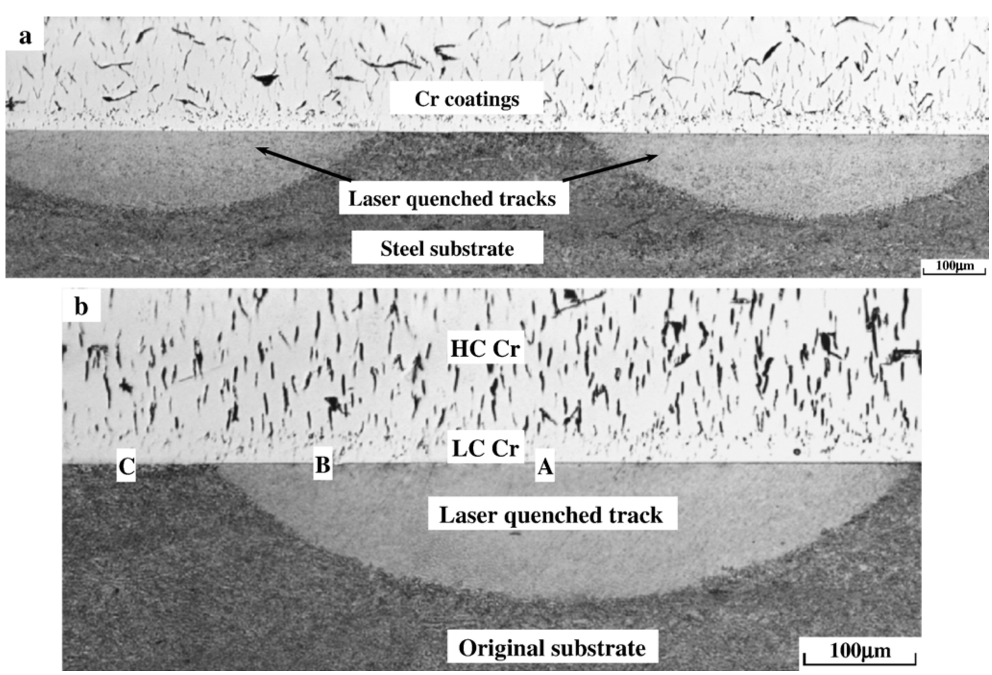

Fig. 1. Cross-sectional OM view of the laser-discrete–quenched substrate/Cr specimen; A–C in (b): laser-transformation hardened zone, transition zone and original substrate, respectively.

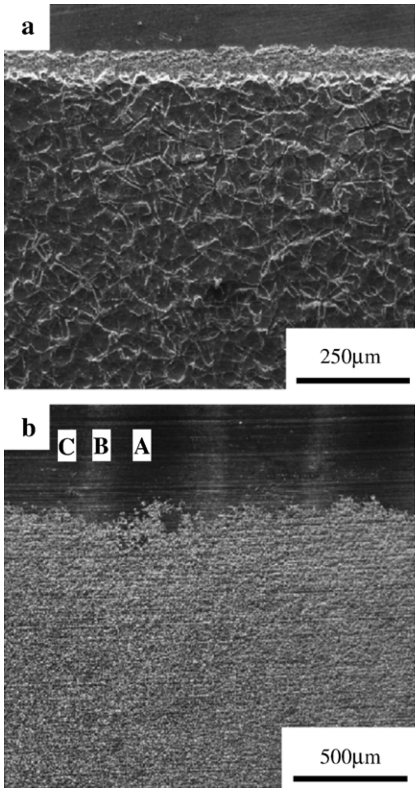

Fig. 2. Low-magnified SEM micrographs of the surface morphologies of the laser-quenched substrate/duplex chromium layers; (a)–(b): G1–2, respectively.

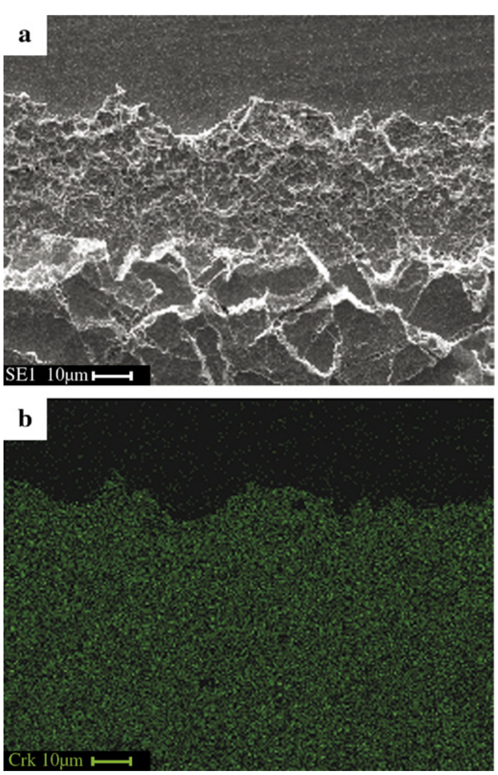

Fig. 3. EDS elemental mapping of Cr in G1.

HC and LC. The step-like morphology formed by the substrate, LC and HC chromium layers verifies soundly the remarkable dissolution edge effect of chromium coatings. Therefore, the dissolution edge effect of duplex chromium layers implies a convenient way to investigate the hierarchical structure features of the LDQS substrate/chromium system.

Closer observations on the HC, LC chromium layer and their boundary were performed and typical results are given in Fig. 4a–c. As shown, the microstructure and morphology of the HC and LC chromium layer are distinctly different. There are long and wide network cracks on the top HC chromium layer and some smaller micro-cracks exit inside the large and wide net-like cracks; the HC chromium near the micro-cracks is prone to preferentially be dissolved away (seen in Fig. 4a).The surface morphologies of HC chromium layers show layer-like features. Compared to HC chromium, the LC chromium layer with fine pole-like cracks (marked by arrows in Fig. 4b) is more equally dissolved and its topography is more uniform. In

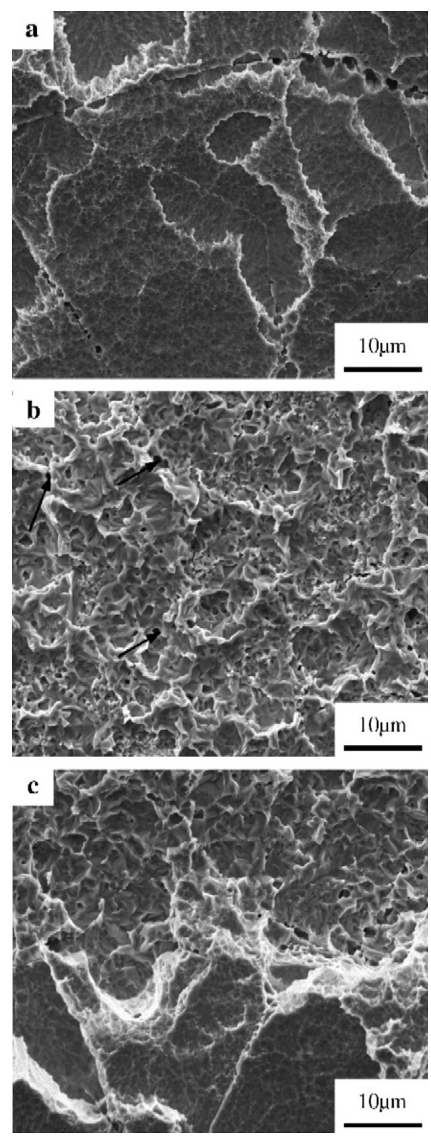

Fig. 4. SEM micrographs of the HC and LC chromium layers; (a)–(c): HC, LC and HC/LC boundary, respectively.

addition, the step-like dissolution features of the top HC chromium layer at HC/LC boundary are shown in Fig. 4c and may result from the long and wide network cracks in HC chromium. Thus, the surficial features of the LC and HC chromium layers are clearly revealed owing to the dissolution edge effect of chromium coatings.

3.4. Surface features of the laser-discrete quenched substrate

The typical high-magnified morphologies of one laser-quenched track with LC chromium in G2 are shown in Fig. 5. Similar to Fig. 2a, Zones A–C in Fig. 5a are corresponding to laser-transformation hardened zone, transition zone and original substrate, respectively. Detailed observations on Zones A–C near the substrate/LC chromium boundary are shown in Fig. 5b through d. And the corresponding EDS mappings of Cr in Zone A and C are given in Fig. 5e and f, respectively. As can be seen, the morphologies of the three zones are extremely different. The surface in Zone A is rather smooth, while that of Zones B and C is much rougher compared with Zone A. For example, there are many micro-holes in Zone B and some dimples exist in Zone C. Similar to Fig. 3, the EDS mapping of Cr in Fig. 5e and f are also consistent with the surface morphology in Fig. 5b and d, respectively. Some islands of deposit (arrowed by arrows in Fig. 5) are left on the substrate as the LC chromium layer is dissolved. Interestingly, some micro-dimples in original substrate are still filled with Cr, while the others are empty. This indicates that the Cr islands are left randomly during etching, because the LC chromium layer in the deeper micro-dimples is surrounded by the steel substrate and removed slowly.

Fig. 6 presents the high-magnified morphology of the LDQS substrate far from the LC chromium in Fig. 5a. Fig. 6a–c was taken in the laser-transformation hardened zone, transition

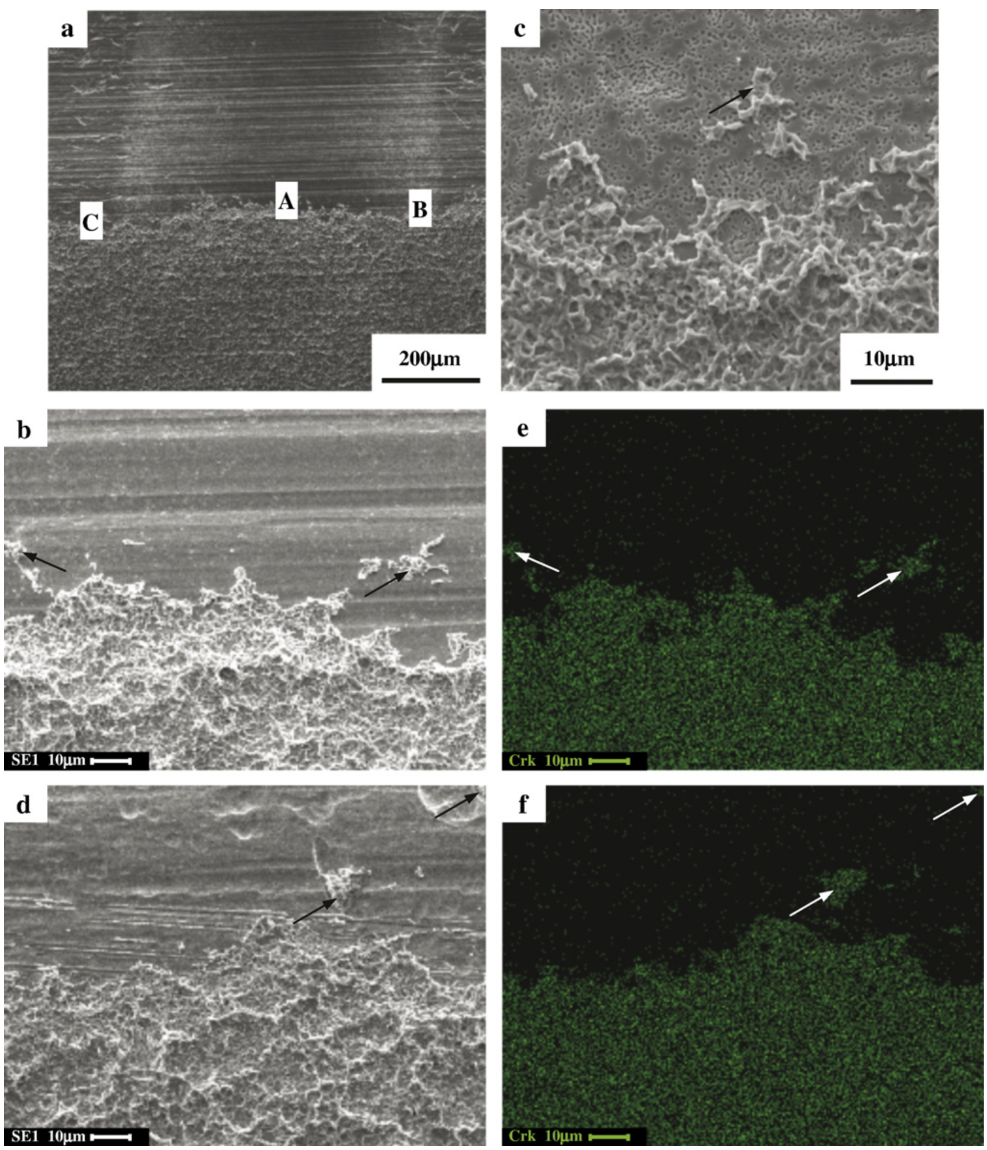

Fig. 5. Surface morphological features and EDS elemental mapping near the substrate/LC chromium boundary; (a): one periodical micrograph; (b)–(d): taken in Zones A–C in (a), respectively; (e) and (f): EDS mapping of Cr element.

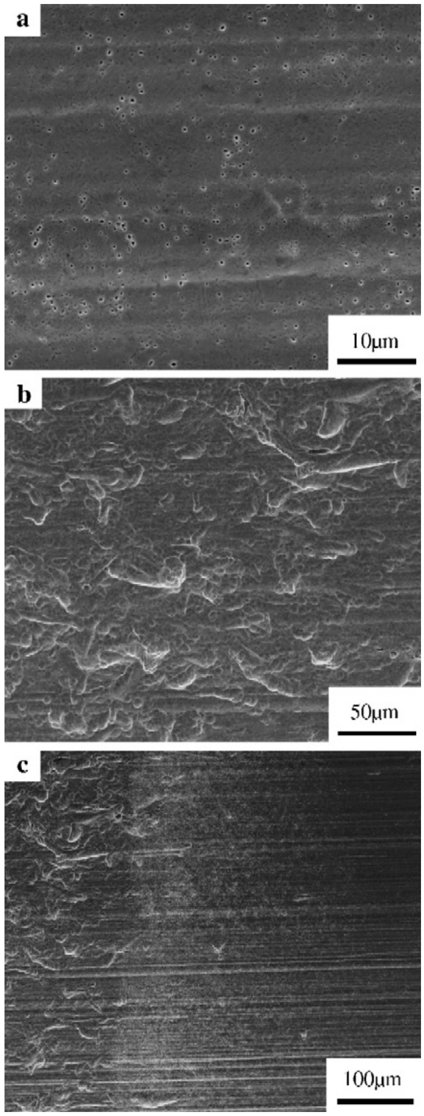

Fig. 6. Surface features of the laser-discrete quenched substrate far away from the LC chromium in Fig. 5a; (a)–(c): laser-transformation hardened zone, transition region and original substrate, respectively.

region and original substrate, respectively. As can be seen in Figs. 5 and 6, the surface topographies of the substrate far from the LC chromium resemble those at the LC/substrate boundary, and the former are more distinct. The micro-roughness of the original substrate surface is much higher than that of laser-transformation hardened zones. The graded morphologies of transition zones are clearly shown in Fig. 6c. The special morphological features of the LDQS substrate are formed by the combined actions of laser-quenching and pre-treatment processes (such as acid pickling and anodic etching) prior to plating. It is well known that the microstructure and properties of the steel can largely be altered via laser-quenching. And the corrosion resistance of laser-transformation hardened zones is much better than that of transition zones and original substrate. When the LDQS substrates are pretreated by acid pickling and anodic etching before plating, Zones A–C will present the distinctly different morphologies owing to their dissimilar microstructure and chemical properties. The especial surface characteristics of the LDQS substrate consist with those of the initial chromium electrodeposits [14]. Thus, it is verified that the surficial microstructure and morphology of the substrate have an extremely important influence on the nucleation and growth, and topography of the initial electrodeposited layer.

4. Discussions

Based on the experimental results, it is obvious that the hierarchical structural features of the LDQS substrate/chromium system can be clearly revealed using dissolution edge effects of duplex chromium layers in the hydrochloric acid and alcohol solution. It is well known that the edge and top portions of homogenous solid materials are preferentially etched in chemical reagent and the corrosion resistance of LC chromium is better than that of HC chromium. When the edge portions of the top HC chromium are preferentially dissolved away in corrosive solutions, the underlying LC chromium near the edge will be exposed. In addition, HC chromium are faster to remove away than LC chromium, because the micro-cracks in HC chromium are longer and wider than those in LC chromium and chromium near the micro-cracks is prone to preferentially be dissolved away in corrosive solutions. After the near-edge underlying LC chromium is exposed, the surface features of the laser-quenched substrate, underlying LC and top HC chromium layers will be simultaneously shown with dissolving of HC and LC chromium layers. Thus, the special dissolution effect of duplex chromium layers can be utilized to reveal the surface morphologies of the substrate and coating.

The special surface features of the LDQS substrate (see in Fig. 1 and Figs. 5 and 6) will play an important role in the substrate/coating interfacial structure and performances of coatings. First, the micro-dimples and micro-poles in original substrate and transition zones can increase the substrate/coating interfacial areas and mechanical interlocking [15,16]. Second, although the laser-transformation hardened zones are smooth, the abundant dislocations and other defects in their surface will provide more nuclei for the deposition of Cr and so the refinement of grains, which can enahance the coating/substrate interfacial adhession [17]. Third, the higher hardness of laser-transformation hardened zones can reduce the steep hardness gradient at the substrate/chromium interface and improve the load-bearing capacity of chromium coatings [14]. Moreover, the mesoscopically periodical structure of the substrate surface will result in the formation of a mechanically and compositionally graded three-dimensional interface between the substrate and coatings, which can improve the damage-resistance of chromium coatings [15,16]. Under severe service conditions such as high temperature and high-frequent mechanical stresses, the hierarchical structure of the LDQS substrate/chromium system with graded properties may mainly be responsible for the longer service life of the chromium-coated parts. Therefore, modification of the mesoscopic microstructure and morphologies of the substrate surface may be one effective way to enhance the performances of coatings with sharp interfaces.

In addition, the two methods of removing-substrate and dissolving-coating are used to effectively reveal the periodical graded interfacial features of a LDQS substrate/as-deposited chromium system according to the investigations of the substrate surface and initial electroplated chromium layer [14]. In future, it is convenient to characterize the surface features of the hierarchical structure in a substrate/coating system with sharp interfaces using the two methods.

5. Conclusions

The dissolution edge effect of duplex chromium layers was utilized to reveal simultaneously the surface characteristics of the steel substrate, LC and HC chromium layers. The periodical gradient surface morphology of the LDQS substrate results in the formation of a three-dimensional interfacial structure with mechanically graded properties between the steel substrate and chromium electroplate. Modification of the mesoscopic microstructure of the substrate surface is important for enhancing the performances of coatings with sharp interfaces. The concept of dissolving coatings with sharp interfaces may be useful for studying the structural features of a substrate/coating system, exploring the effect of substrate surface features on the microstructure and morphology of coatings and evaluating the quality of the coated parts.

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