Rare Metal Materials and Engineering
Volume 47, Suppl. 1, July 2018
Cite this article as: Rare Metal Materials and Engineering, 2018, 47(S1): 072-077.

Anti-ablation Property of $ZrB_2/SiC/Ta_2O_5$ Coatings Prepared by Atmosphere Plasma Spraying

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Abstract: To improve the anti-ablation property of carbon/carbon (C/C) composites, the double-layer coatings with SiC/Al_2O_3 as an inner layer and $ZrB_2/SiC/Ta_2O_5$ as an outer layer were prepared by atmosphere plasma spraying. The phase composition, microstructure and element distribution of the coatings before and after ablation were analyzed using X-ray diffraction, scanning electron microscopy and energy dispersive X-ray spectroscopy, respectively. There are no cracks on the surface coating and the connection of two coatings and the SiC/Al_2O_3 coating with substrate is well. The distribution of elements Zr, Si and Ta on the coating are similar, which indicates the good homogeneity of coating. Ablation resistance of coated C/C was tested by the oxyacetylene flame at 1800 ℃. The mosaic structure formed during the ablation process is conducive to prevent the diffusion of O_2, and the Ta-Si-O glassy layer formed on the surface coating has a protective effect. The coating exhibits a good anti-ablation ability.

Key words: C/C; ablation; mosaic structure; Ta-Si-O glassy layer

With the increasing of velocity, some hot structure components of hypersonic vehicles will be applied at ultrahigh temperature which exceed the work temperature of conventional materials, such as nose cone and leading edge.

C/C composites are considered as one of the most promising materials for hot structure components of hypersonic vehicles, due to their excellent mechanical properties such as high strength, low density, high stiffness and good thermal shock resistance at high temperature[1,2]. However, C/C will be oxidized rapidly when the temperature is over 723 K in the oxidizing atmosphere[3]. The insufficient anti-ablation property limits the further application of C/C in hypersonic vehicles. Depositing the anti-ablation coatings is considered to be an effective way to improve the anti-ablation property of C/C[4].

As a kind of ultra high temperature ceramics (UTHC), ZrB_2 and ZrB_2-based ceramics are considered to be candidate materials of anti-ablation coatings for C/C, due to their high melting point, suitable CET, good mechanical and anti-ablation property at high temperature[5]. ZrB_2 combined with SiC shows a good oxidation resistance at temperature lower than 1700 ℃ due to the formation of a silica outer-layer[6]. As the flight speed of hypersonic vehicles increases, the temperature of thermal protection systems will exceed 1700 ℃ and the silica outer-layer of ZrB_2-SiC may be quickly removed[7], and cause the failure of coating. Therefore, it is necessary to improve the anti-ablation property of ZrB_2-SiC at temperature higher than 1700 ℃. To add oxides of appropriate melting point to coating material is one of the effective methods. Ta_2O_5 has a higher melting point of 1872 ℃ than SiO_2 and add it to the ZrB_2/SiC is hopeful to improve the anti-ablation property of coatings. In this study, the Ta_2O_5 was doped into ZrB_2-SiC by spray drying and it is the first time to adopt this method.

Atmosphere plasma spraying (APS) is an effective method to prepare the ultra high temperature ceramics coatings on the C/C composites. The temperature of plasma arc is higher than 10000 ℃, and its jet velocity is up to hundreds of meters per second. The jet gas can be controlled as inert atmosphere. The APS is especially suitable for the preparation of high melting point ceramic coating. B. Wen et al. [8] prepared the ZrC coating by APS. The coatings exhibited a dense structure, a good bonding with substrate and outstanding anti-ablation ability. X. Song et al.[9] prepared the YSZ coatings by APS successfully and studied the shock resistance of coatings. In the present work, the $ZrB_2/SiC/Ta_2O_5$ composite powder was synthesized and the coating was prepared by APS and it is the first time to adopt this method.

The phase and microstructure of the coatings was ana-

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lyzed. The ablation property was evaluated by oxygen acetylene flame. The anti-ablation and failure mechanism were studied.

1 Experiment

1.1 Raw materials and spray drying process

The ZrB_2 (1~3 μm, purity>99.9%, China New Metal, CNM), SiC (0.5~1.5 μm, purity>99.9%, China New Metal, CNM), and Ta_2O_5 (0.5~1.5 μm, purity>99.9%, Jiangxi Branch Material Co. Ltd) particles were chosen as the raw materials. The volume content of ZrB_2, SiC and Ta_2O_5 was 67.5%, 22.5% and 10%, respectively. The solid solution ratio was 40%. The raw materials, water glass adhesive, deionized water were mixed in stirring ball mill device for 2 h. The composite powder was obtained by spray drying

1.2 ZrB_2/SiC/Ta_2O_5 coatings preparation

The C/C was provided by the Hunan Jiuhua Carbon Hi-Tech Co. Ltd with a density of about 1.7 g/cm^3. The dimension of samples is Φ25.4 mm×6 mm, which were cut from bulk 2D C/C. The anti-ablation coating has two layers. The bonding layer was SiC/Al_2O_3 coating and the thickness was 0.1 mm. The surface layer was ZrB_2/SiC/Ta_2O_5 coating and the thickness was 0.2 mm. The coatings were both prepared by APS (SG-100, Praxair Surface Technologies, U.S.). The main parameters of ZrB_2/SiC/Ta_2O_5 coating are primary gas (Ar), second gas (He) and powder feed rate.

1.3 Ablation test

The anti-ablation property of coatings was tested by oxygen acetylene flame which was caused by FP-73 (PRAXAIR-TAFA Inc, USA). The flow rate of C_2H_2 was 50 L/min and that of O_2 was 25 L/min. The distance between the nozzle tip of the oxygen acetylene flame gun and the surface of coatings was 70 mm. The temperature of coating surface was measured by infrared temperature measuring device (Marathon MR).

The ablation behavior of coatings was assessed under 1800 ℃ at 30 and 60 s. The anti-ablation property was characterized by mass ablation rate and the value was the average ablation rates of coatings that assessed at different time and it is 3.209×10^{-4} g s^{-1}.

1.4 Characterization

The phase composition, microstructure and element distribution of the powder and coating were analyzed by X-ray diffraction (XRD, D8, Bruker-AXS, Germany) and scanning electron microscopy (SEM, S-4800, HITACHI, Japan) equipped with energy-dispersive spectroscopy (EDS).

2 Results and Discussion

2.1 Characteristics of the composite powder

The composite powder is nearly spherical according to Fig.1a, which is good for the preparation of coatings. The cross-section morphology shown in Fig.1b illustrates the composite powder is homogeneous and there are no cracks. The size range of powders are from 10 μm to 100 μm and the most are between 40 μm to 60 μm, which is consistent with the observation results of SEM and meets the requirements of APS.

The micromorphology of composite powder is shown in Fig.2. The combination of grey particles and dark substance is close. The distribution of element Si and Ta is similar, indicating that the SiC and Ta_2O_5 are mixed uniformly under the effect of water glass glue. The size of ZrB_2 is larger and the grey particles are mainly ZrB_2 as shown in the result of EDS and the composite powder is suitable for coating preparation.

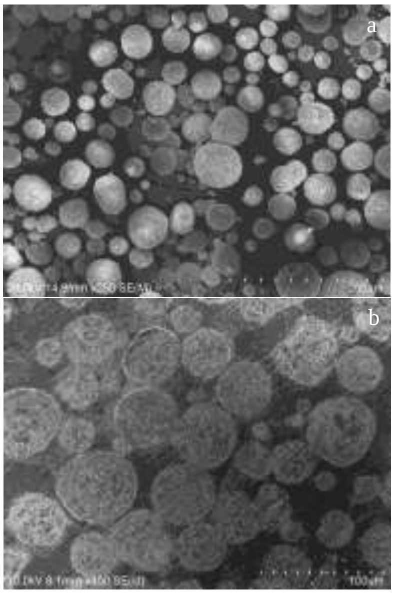

Fig.1 Morphologies of composite powder: (a) surface and (b) cross-section

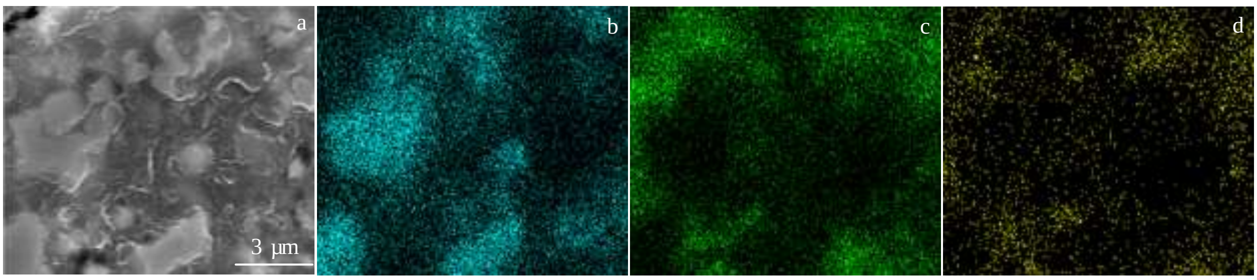

Fig.2 Morphology of cross-sectional composite powder (a) and element distribution of Zr (b), Si (c), and Ta (d)

2.2 Characteristics of the coating

Fig.3 shows the macrograph of the $ZrB_2/SiC/Ta_2O_5$ coated sample. It can be seen that the coating is integrity and uniform. There are no cracks on the surface of coating, which is conducive to protect the C/C.

Fig.4 shows the XRD pattern of the coatings. The main phase are ZrB_2, SiC and ZrO_2. During the process of coating preparation, ZrB_2 is oxidized to form the ZrO_2. The Ta_2O_5 are not detected due to the small amount.

The $ZrB_2/SiC/Ta_2O_5$ composite powders were semi-melted and deposited directly on the SiC/Al_2O_3 coated C/C substrate during the plasma spraying. Fig.5a shows the morphology of surface coating. It can be seen that there are some voids distributed on the coating, which may be due to the evaporation of gases such as SiO and B_2O_3 produced during the spraying process at high temperature. Since the melting point of composite powders is high, the particles are not totally melted in the spraying process and formed cluster structure. Fig.5b shows the enlargement of Fig.5a. The composite powders were combined during the process of spraying, forming the lamellar structure. Some particles were melted completely and separated out during cooling, forming the flocculent particles which deposit on the lamellar substance shown in Fig.5b. The distribution of elements Zr, Si and Ta are uniform shown in Fig.6. The raw materials were mixed uniformly by spray drying. And the component of coating is uniform, which is conducive to the protection of coatings.

The cross-section image of substrate, SiC/Al_2O_3 coating and $ZrB_2/SiC/Ta_2O_5$ coating is shown in Fig.7. The coating presents a typical lamellar structure. No obvious crack or void is found at the interface between inner layer and outer layer, indicating that the connection of two coatings and the SiC/Al_2O_3 coating with substrate is well. The SiC/Al_2O_3 coating relieves the mismatch of thermal expansion coefficient between C/C and $ZrB_2/SiC/Ta_2O_5$ coating. It is beneficial to improve the stability of coatings during ablation. Fig.8 shows the enlarged morphology of the $ZrB_2/SiC/Ta_2O_5$ coating and there are no

Fig.3 Morphology of specimen

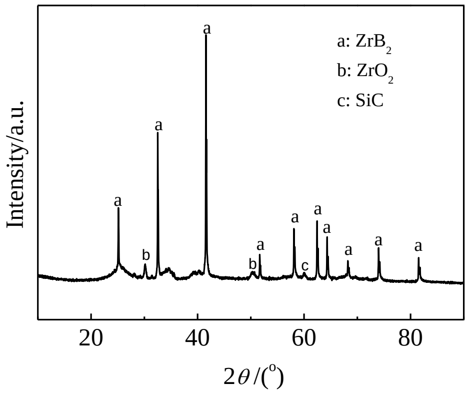

Fig.4 XRD pattern of coatings

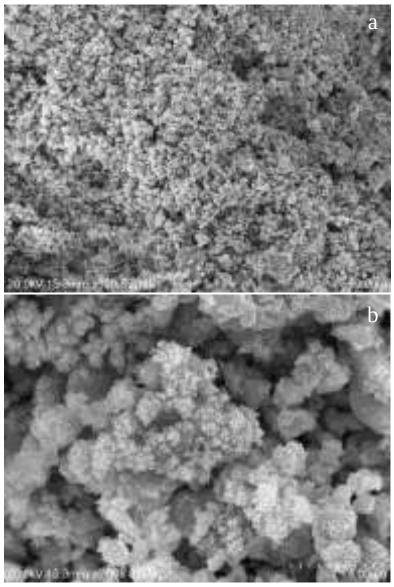

Fig.5 SEM surface morphology of coating (a) and its magnification (b)

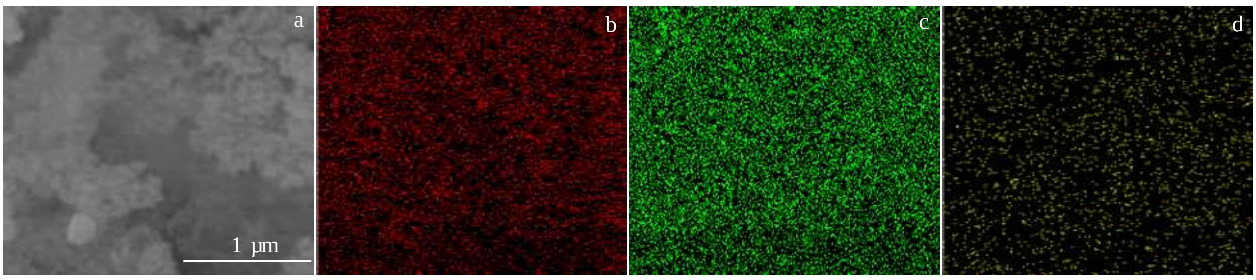

Fig.6 Morphology of coating surface (a) and element distribution of Zr (b), Si (c), and Ta (d)

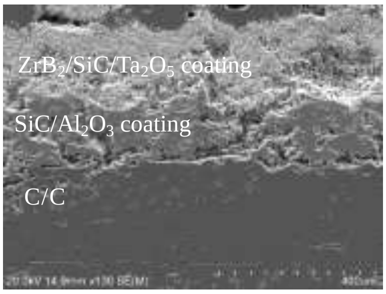

Fig.7 SEM image of the cross section of coating

obvious cracks and the holes are small, which may be caused by the escape of gas. The distribution of elements Zr, Si and Ta are similar, indicating that the homogeneity of coating is well.

2.3 Ablation test

The phases of the coating after ablation are mainly ZrO_2 and ZrB_2 according to the result of XRD shown in Fig.9. SiC was oxidized into SiO_2 during the ablation, which has a great loss. The molten SiO_2 and Ta_2O_5 have a rapid solidification in the ablation cooling process, which may be the reason why it is not detected.

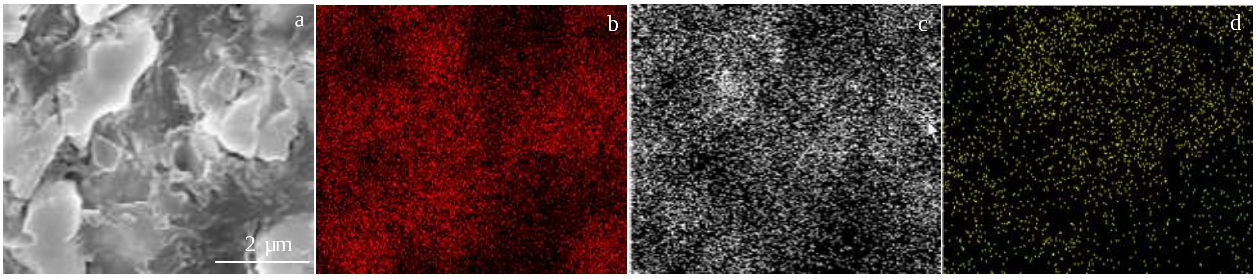

Fig.8 Morphology of cross section of ZrB_2/SiC/Ta_2O_5 coating (a) and elements distribution of Zr (b), Si (c), and Ta (d)

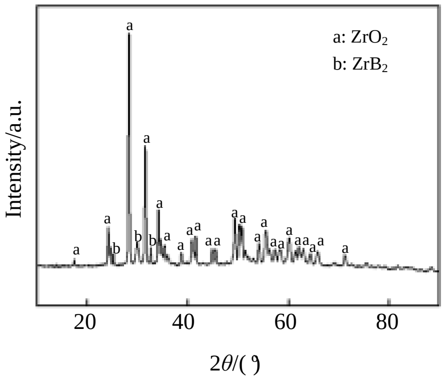

Fig.9 XRD pattern of the coating after ablation

The temperature of ablation flame decreases gradually from ablation center to the edge, leading to the different conditions of glass phase material produced during ablation. And the surface morphology of the coating is different. After ablation at 1800 ℃ for 30 s, the surface of coating can be divided into center, transition and margin three parts shown in Fig.10a, 10b, 10c, respectively.

A mosaic structure is formed on the center region according to Fig.10a. The granular particles were covered by the molten substance and its main composition is ZrO_2 according to the results of EDS shown in Fig.11a. The element distribution of Si and Ta on the center region is similar and the coating is compact without cracks according to Fig.12. During the ablation, a Ta-Si-O glassy layer[10] is formed on the coating, which coats the ZrO_2 and plays a positive role in preventing the penetration of O_2. Since the temperature of flame is high and the air erosion is larger, the molten substance loses a lot. The melting point of SiO_2 is lower than that of Ta_2O_5, and it is easier to evaporate. The gradual loss of molten substance causes the exposure of ZrO_2. The distribution of element Ta is uniform, which is good to form a uniform layer of glass barrier, prevent the diffusion of O_2 and protect C/C.

Fig.10b shows the region of transition. It is relatively smooth and there are no cracks and pores. The margin region has pores according to Fig.10c. Some obvious cracks occur on the margin region shown in Fig.10d, which can be attributed to the volume change of SiO_2 during solidification and cooling. It can be seen that the spherical particles are distributed on the margin region, which is formed by the molten droplets during cooling under the action of surface tension.

The evaporation of glass phase material and the impact of flame on the center region is bigger. The ZrO_2 particles play a supporting role and the molten substances fill the pores. It is beneficial to protect the ZrO_2 from blowing off and stopping the infiltration of O_2. The temperature of transition region is lower and the ZrO_2 is surrounded by the glass phase material, forming a dense structure. The temperature of margin is lowest and the amount of glass substance cannot be sufficient to fill the defects like cracks.

During the ablation, the materials of coating was oxidized and formed the oxidation products consisting of ZrO_2, B_2O_3, SiO_2, CO and CO_2. The B_2O_3 was quickly evaporated in the process of ablation due to the low melting point and high vapor pressure. Some of it will possibly react with SiO_2 or dissolve into it to form a borosilicate glass with a higher melting point. The molten Ta_2O_5 can fill the defects of the coating

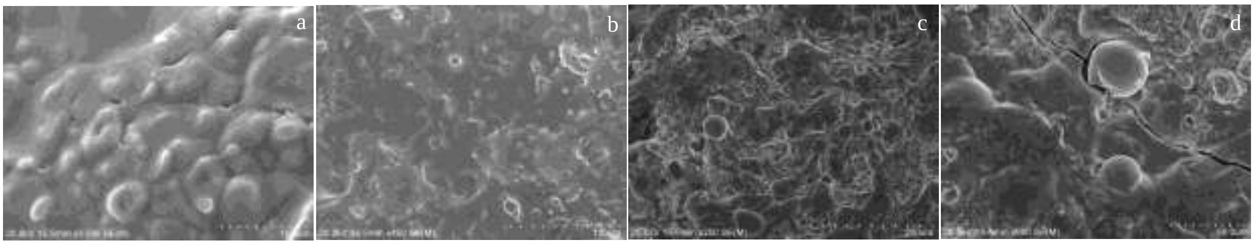

Fig.10 Morphologies of surface coating after ablation for 30 s: (a) center, (b) transition, (c) margin, and (d) enlarge of Fig.10c

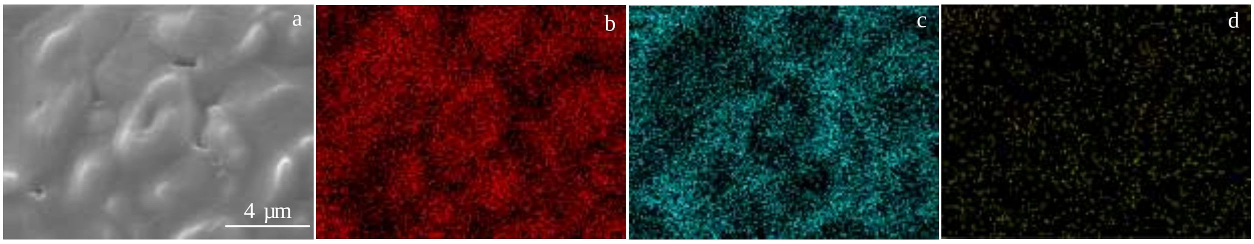

Fig.11 Morphology of center region after ablation for 30 s (a) and elements distribution of Zr (b), Si (c), and Ta (d)

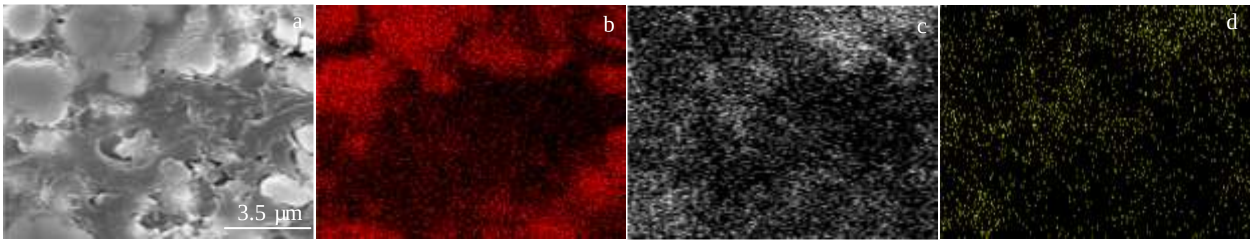

Fig.12 Cross section morphology of center region after ablation for 30 s (a) and elements distribution of Zr (b), Si (c), and Ta (d)

and prevent the further penetration of O_2 at a higher temperature, forming the protection at the whole temperature range.

During the ablation, the glass phase material covered the surface of coating and formed a dense structure around the cavity after cooling. With the ablation time increasing, the evaporation loss of glass materials causes the lack of sealing the pores and the single ZrO_2 particles can be blown away by oxyacetylene flame with high temperature, high velocity and pressure, leading to the diffusion of O_2 and the failure of the coating.

3 Conclusions

1) $ZrB_2/SiC/Ta_2O_5$ coating is prepared by APS on the surface of SiC/Al_2O_3 coated C/C composites. The combination of two coatings and the SiC/Al_2O_3 coating with substrate is well, which relieves the mismatch of thermal expansion coefficient between C/C and $ZrB_2/SiC/Ta_2O_5$ coating.

2) The distribution of elements Zr, Si and Ta are similar, indicating that the homogeneity of coating is well and it is conducive to protect the C/C. The mosaic structure formed during the ablation process is conducive to prevent the diffusion of O_2, and the Ta-Si-O glassy layer formed on the surface coating has a protective effect.

3) The oxidation products form the protection for C/C in the whole temperature range. With the ablation time increasing, the evaporation loss of glass materials and the wastage of ZrO_2 cause the failure of coatings.

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等离子喷涂制备 $ZrB_2/SiC/Ta_2O_5$ 涂层抗烧蚀性能研究

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摘　要：为了提高C/C复合材料的抗烧蚀性能，通过等离子喷涂法在C/C表面制备了SiC/Al_2O_3内层和$ZrB_2/SiC/Ta_2O_5$外层的双层涂层，通过XRD，SEM和EDS分析了涂层烧蚀前后的物相组成、微观结构和成分分布。烧蚀前涂层表面没有裂纹并且内层与基体、内层与外层之间结合良好。元素Zr、Si、Ta在涂层表面的分布相近，涂层表面成分分布均匀性良好。通过氧乙炔火焰在1800 ℃下对涂层的抗烧蚀性能进行考核。烧蚀过程中形成的镶嵌结构有利于阻挡氧气的渗入，Ta-Si-O玻璃层的形成封填了涂层孔隙，对基体有良好的保护效果，涂层表现出了较好的抗烧蚀性能。

关键词：C/C；烧蚀；镶嵌结构；Ta-Si-O玻璃层

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