



Fabrication of low specific resistance ceramic carbon composites by colloidal processing using glucose as soluble carbon source

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Abstract. Ceramic carbon composites were fabricated by colloidal processing using glucose as soluble carbon source. Glucose is converted into conducting carbon at high temperature treatment. Ceramic carbon composites were sintered in flowing argon at 1400°C showing resistor behaviour even at low carbon content (1 wt%). In this work, ceramic carbon composites were fabricated using alumina–clay slurries with addition of glucose as a soluble carbon source. Morphology of the sintered samples was characterized by field emission gun (FEG) electron microscopy. Phase analysis was done by X-ray diffraction (XRD). Electrical properties of ceramic carbon composites were measured by broad band dielectric spectrometer. Carbon produced from glucose at high temperature was characterized independently by BET surface area, dynamic light scattering, field emission gun scanning electron microscopy, field emission gun transmission electron microscopy, XRD and Raman spectroscopy.

Keywords. Ceramic carbon composites; slip casting; carbonization; specific resistance.

1. Introduction

Semi-conductive materials have the electrical resistance in the range from 10^8 to $10^{-3} \Omega \text{ cm}$ [1,2]. A lot of materials have the electrical resistance in this range but conductive ceramics is attracting industrial interest due to its excellent performances in low and high temperature [3]. The electrical properties exhibited by the composites make them useful in many applications such as discrete resistors used in electronic circuits, pressure sensors used in piezo-resistive transducers and temperature sensors used in devices with self-adjusting power or current cut-outs [4,5]. Ceramic carbon composites consist of a mixture of an insulating phase and an electrically conducting phase. Ceramic carbon composites have been fabricated by two routes, dry mixing and wet processing. Generally the conducting phase in ceramic carbon composites has been provided by insoluble carbon sources (carbon black, graphite, carbon nanotube, graphene, etc.) [6–12]. However, in aqueous medium homogeneous dispersion of the insoluble carbon source in ceramic matrix is difficult due to the different nature of the materials. Ceramic materials are hydrophilic in nature while carbon sources are hydrophobic in nature. Soluble carbon sources (sucrose, glucose, fructose, etc.) are homogeneously dispersed in the ceramic matrix in an aqueous medium. Wet processing has better control on homogeneity of the conductive phase present in conductive ceramics. Menchavez *et al* [1,13] suggested a simple and direct approach to fabricate electrically conductive porous alumina ceramic using mechanically foamed alumina slurry by gel casting

process, followed by sintering. In the present work, ceramic carbon composites were fabricated by alumina–clay slurries with the addition of glucose as a soluble source of carbon. Ceramic carbon composites were sintered in flowing argon at 1400°C showing resistor behaviour in the frequency range from 1 to 10^5 Hz measured by broad band spectrometer.

2. Experimental

Ceramic carbon composites were fabricated using alumina–clay slurries with the addition of glucose as a soluble source of carbon by slip casting. Glucose (Glucon-D, Heinz) was added to the PVA (S-D fine chemical, molecular weight, 125,000) solution containing 26 vol% ceramic (alumina–clay in 35:65 weight ratio, alumina HIM30, Hindalco, clay, English India Clay, Kerala) in amounts which upon decomposition at high temperatures would lead to carbon in the range of 1, 1.5, 2, 5 and 9 wt% with respect to the ceramic. A dispersant, sodium polyacrylate (NaPAA) (1 ml/100 g of ceramic powder) and an anti-foaming agent, n-octanol (100 μl /100 g (powder basis) were added to the slurries. Zirconia grinding media (2–3 mm diameter) to alumina–clay weight ratio was 1:1 and grinding media was added to the slurries. The slurries were contained in a polypropylene bottle and milled on a pot mill for about 24 h. Ceramic carbon composites were fabricated by slip casting the slurries in ring-shaped plastic moulds placed on plaster of Paris base plates. Inner surface of the plastic moulds was coated with WD40 (WD Company) to minimize adhesion of

cast body to the moulds. Cast samples were removed from the plastic moulds after drying in ambient condition for 36 h followed by drying in an oven maintained at 50°C for 5 days. Sintering was done in flowing argon atmosphere at 1400°C. Thickness and diameter of each sample for electrical measurement was 5 and 20 mm, respectively. Samples with 1, 1.5, 2, 5 and 9 wt% carbon equivalent content have been coded 1, 1.5, 2, 5 and 9G, respectively. To understand the characteristics of the carbon produced from carbonization of glucose was independently characterized by BET, dynamic light scattering (DLS), field emission gun scanning electron microscopy (FEG-SEM), field emission gun transmission electron microscopy (FEG-TEM), X-ray diffraction (XRD) and Raman spectroscopy.

3. Experimental techniques

Specific resistance of the sintered samples were fabricated by the addition of glucose, which was measured using broadband dielectric spectrometer (Novo Control Technologies,

Germany, Concept 80) in the frequency range of 1 to 10^5 Hz at room temperature. The produced carbon from the carbonization of glucose at 1400°C was independently characterized by BET (Smart Sorb 92/93, Smart Instruments Co.), FEG-SEM (JEOL, JSM-7600F), FEG-TEM (JEOL, JEM-2100F), DLS (Beckman Coulter, Delsa Nano C particle analyzer), XRD measurement was performed with the scan rate of $20 \text{ degree min}^{-1}$ with Cu-K α source (Expert Pro, 40 kV, 30 mA, Panalytical) and Raman spectroscopy measurement was performed with the scan rate of $2000 \text{ cm}^{-1} \text{ min}^{-1}$ with 514 nm excitation source (Jobin-Yvon, France Ramnor HG-2S Spectrometer).

4. Results and discussion

Ceramic carbon composites were fabricated using glucose as soluble carbon source. Ceramic carbon composites were characterized by FEG-SEM, XRD and broadband spectrometer. SEM micrographs (a and b) as shown in figure 1 represent ceramic carbon composites 1 and 9G, respectively. It seems

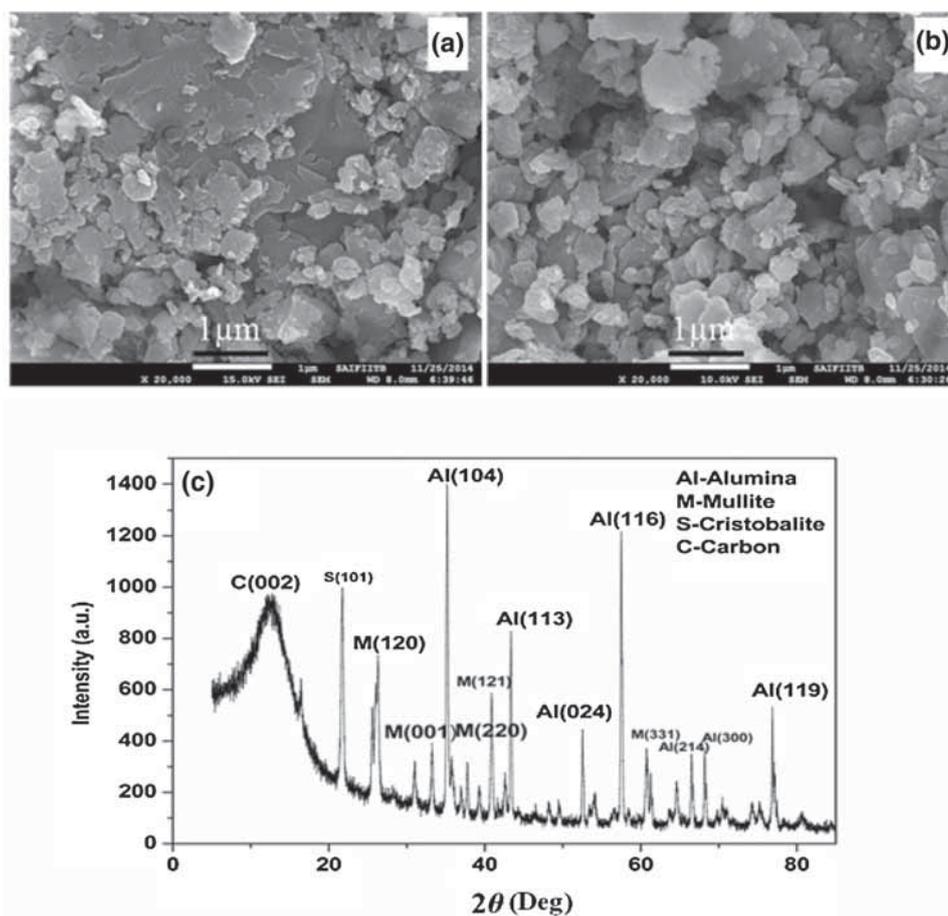


Figure 1. FEG-SEM micrographs of ceramic carbon composites: (a) 1 wt% carbon content (1G), (b) 9 wt% carbon content (9G) and (c) XRD of ceramic carbon composite with 2 wt% carbon content (2G) sintered at 1400°C.

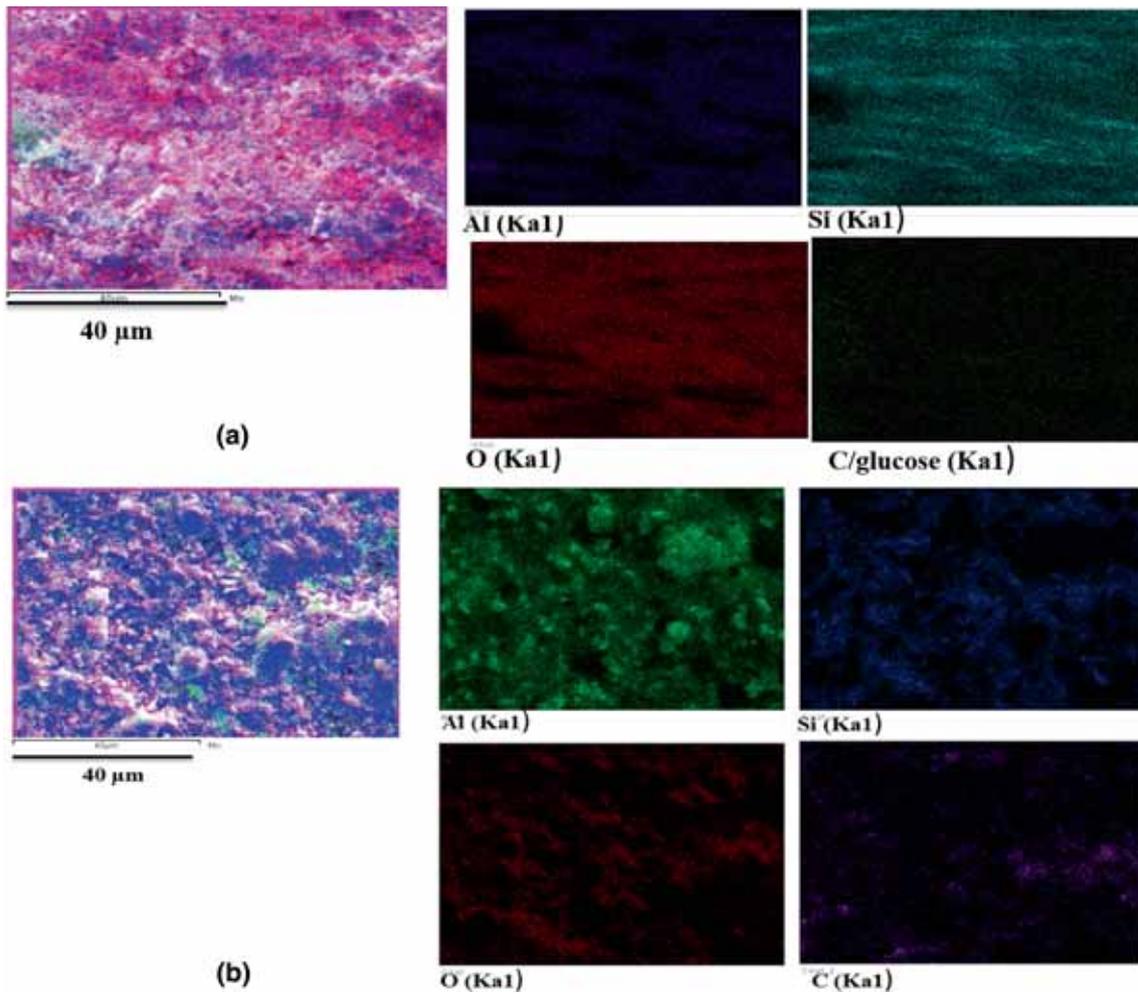


Figure 2. Elemental mapping of ceramic carbon composite with 1 wt% carbon content (1G): (a) green sample and (b) sintered sample.

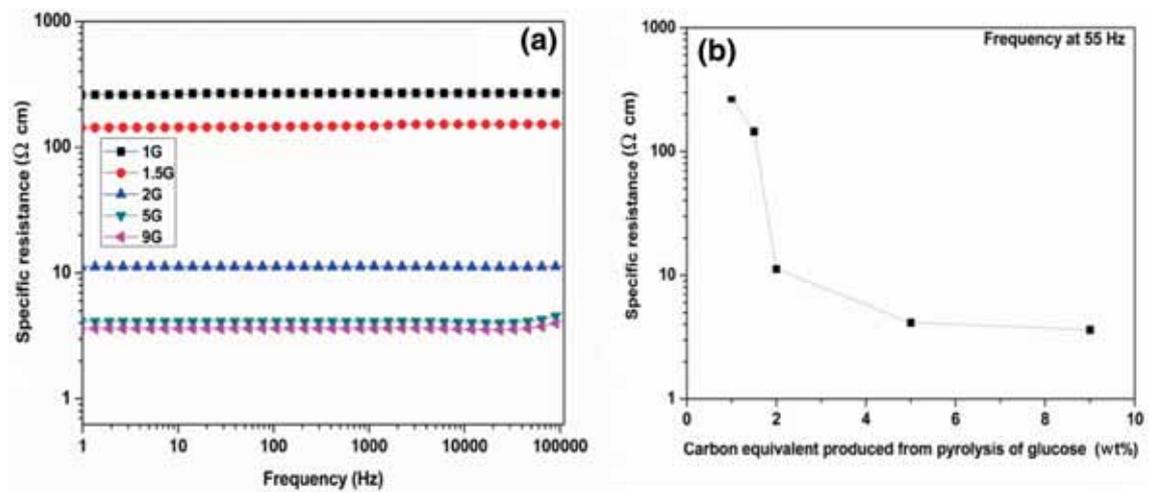


Figure 3. (a) Specific resistance vs. frequency and (b) specific resistance vs. different carbon content of the ceramic carbon composites sintered at 1400°C.

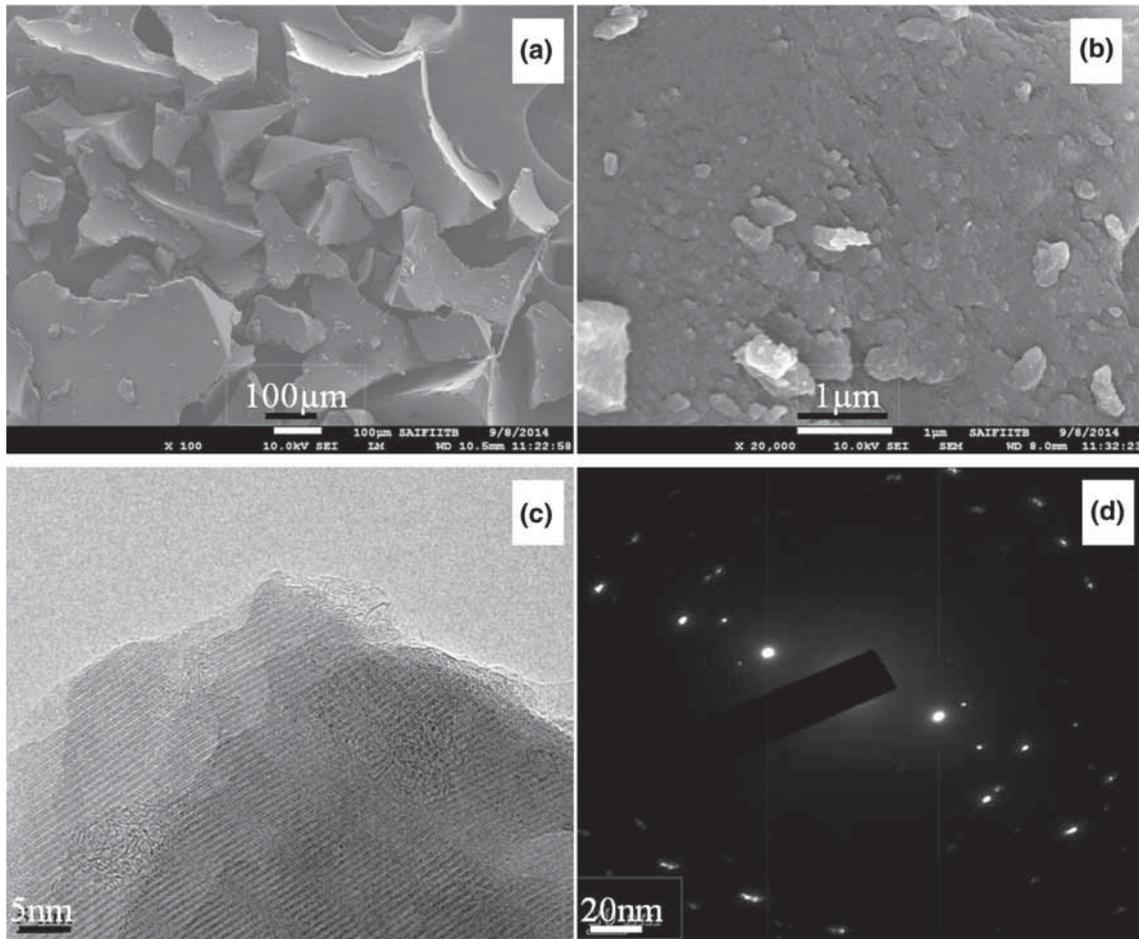


Figure 4. FEG-SEM micrographs (a) at low magnification and (b) at high magnification, (c) FEG-TEM micrographs at high magnification. (d) Diffraction pattern of carbon produced from carbonization of glucose at 1400°C.

from micrographs that platelet-type particles with particle size in the range of half micron to 1 μm are clay particles and particles with particle size more than 1 μm seem to be alumina particles. Carbon particles produced from carbonization of glucose are fine in nature and difficult to see in the micrographs. XRD analysis of the representative ceramic carbon composite, 2G shows that four phases are present in the composite as shown in figure 1c. Clay may have played two roles in ceramic carbon composites—one as an inorganic binder to bind alumina particles and another to form *in-situ* mullite crystals and free silica (cristobalite low) crystals as shown in XRD (figure 1c) which is expected to contribute to strengthening of the body. Alumina phase was also confirmed by XRD pattern (figure 1c). Elemental mapping of a representative green and sintered sample (1G) was done to see the distribution of the alumina, clay and glucose/carbon as shown in figure 2a and b. Figure 2a shows the near uniform distribution of alumina, clay as well as glucose in the green sample while figure 2b shows uniform distribution of alumina, clay and carbon as obtained from carbonization of glucose at high temperature in the sintered sample. Ceramic carbon

composites fabricated by addition of glucose were characterized by Broadband dielectric spectrometer to measure the specific resistance of the composites. Specific resistance of the composites was measured in the frequency range from 1 to 10^5 Hz at room temperature. Specific resistance of the ceramic carbon composites is constant with varying frequency as shown in figure 3a. This is the property of the resistor used for electrical applications. Ceramic carbon composites fabricated by the addition of glucose show of the resistor behaviour even at low carbon content 1G (1 wt% carbon equivalent). As the amount of the graphitized carbon increases in the composites, value of the specific resistance in the composites decreases and it is constant with varying frequency as shown in figure 3a and specific resistance vs. carbon equivalent of ceramic carbon composites is shown in figure 3b. Ceramic carbon composite with 9 wt% carbon content (9G) shows the minimum specific resistance value ($3.6 \Omega \text{ cm}$), while sample with 1 wt% carbon content (1G) shows the maximum specific resistance value ($268 \Omega \text{ cm}$). Kumar and Bhargava observed the resistor behaviour of the ceramic carbon composites made by slip casting using carbon

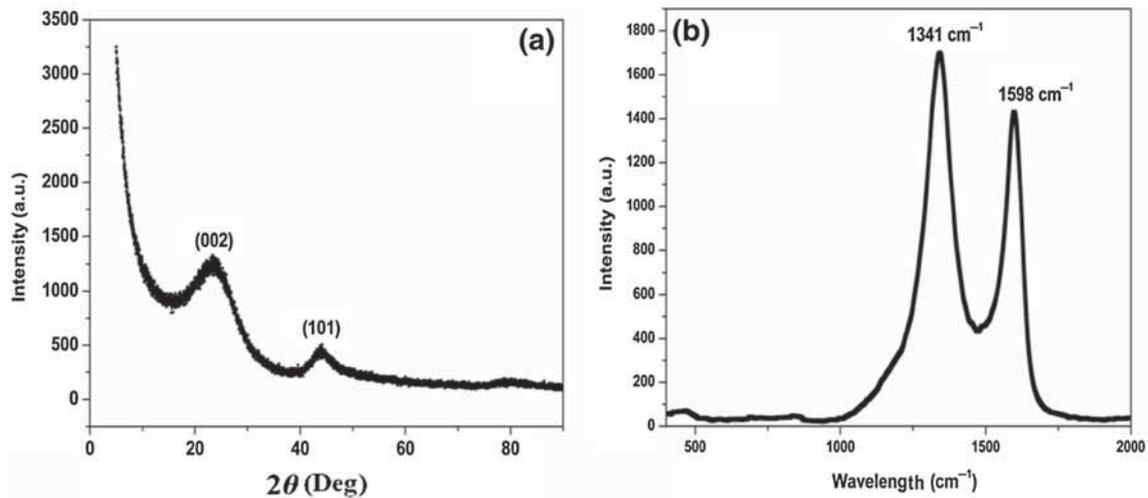


Figure 5. (a) Raman spectroscopy and (b) XRD pattern of the carbon produced from the carbonization of glucose at 1400°C.

black as carbon source but the value of the specific resistance was exceptionally high ($6.7 \times 10^7 \Omega \text{ cm}$ at 2 wt% carbon black content, $11.21 \Omega \text{ cm}$ at 9 wt% carbon black content measured at frequency 55 Hz) [14]. The use of soluble carbon source (sucrose [15] and polymers etc.) has better homogeneous distribution of the carbon particles rather than insoluble carbon source at low carbon content (graphite, carbon black, carbon nanotubes, graphene etc.). It may be the fact that soluble carbon source (glucose) molecules were adsorbed on the alumina–clay particle surfaces and converted in conducting fine carbon particles at high temperature in flowing argon. Carbon produced by carbonization of glucose was characterized independently and following observations were obtained. BET measurement was done to measure the surface area of the produced carbon and it was found to be $7 \text{ m}^2 \text{ g}^{-1}$. The particle size of the produced carbon was measured by DLS and average particle size (d_{50}) was obtained 620 nm. FEG–SEM micrograph as shown in figure 4a and b shows the morphology of the produced carbon. Figure 4a shows the flake like morphology of the produced carbon and figure 4b shows that flakes are made from fine particles. It was observed by FEG–TEM as shown in figure 4c and d that produced carbon has crystalline nature (figure 4c) and it was also confirmed by diffraction pattern (figure 4d). Two peaks were observed in the XRD pattern of the produced carbon and these peaks are corresponding to the crystalline reflections from (002) and (101) planes as shown in figure 5a. The 2θ values at which the intensity maximum observed for (002) and (101) planes are 23.37 and 44.33, respectively. Carbon produced from glucose at high temperature has turbostratic graphite structure. Raman spectrum of the produced carbon showed two prominent bands at 1341 and 1598 cm^{-1} as shown in figure 5b. Band at 1341 cm^{-1} is known as D band, band at 1598 cm^{-1} is known as G band. D band is a subscription of the disorders (like vacancies, bond disruption and defects

etc.) formed in the carbon lattice, while G band is a common feature of the graphitic structures and produces because of the in-plane vibrational modes of the sp^2 bonded carbon atoms [16]. The I_D/I_G ratio of the produced carbon was calculated using Raman spectroscopy data and it was obtained as 1.18. This value showed graphitic nature of the produced carbon and it was also confirmed by SAD pattern of FEG–TEM as shown in figure 4d.

5. Conclusions

Ceramic carbon composites fabricated by slip casting using glucose as soluble carbon source show resistor behaviour even at low carbon content. Specific resistance of the composites decreases as the amount of the graphitized carbon increases in the composites. Characterizations of the carbon produced from the carbonization of glucose independently show that the produced carbon has crystalline nature. Crystalline nature of the produced carbon is responsible for low electrical specific resistance of the ceramic carbon composites.

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