Impact of Carbon Nanotube Defects on Fracture Mechanisms in Ceramic Nanocomposites

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Abstract

Carbon nanotubes (CNTs) can improve the fracture toughness of ceramic composites. It is widely believed that defects in the CNTs will alter key properties that ultimately dictate composite toughening. However, to date there have been no studies that directly correlate these specific properties to controlled defect levels in CNTs. This type of investigation is presented here, using ceramic nanocomposites with a polymer derived ceramic (PDC) matrix, reinforced with multiwalled CNTs. This work includes basic fracture measurements on full composite films, combined with careful testing of individual CNTs embedded in the same PDC matrix. The defect levels in these CNTs were controlled with high energy carbon ions. By using this approach, it was possible to directly correlate defect levels with the interfacial shear strength (IFSS) of the CNT/PDC interface, the CNT fracture strengths, and the pull-out lengths observed after fracture of the full composites. The radiation induced defects led to substantial increases in the IFSS, and

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only a marginal decrease is observed in the measured fracture strength. Based on this, the shorter pull-out lengths that occurred with higher defect levels were primarily attributed to stronger bonding at the CNT/PDC interface.

1. Introduction

The incorporation of CNTs into ceramic matrix composites can produce materials with a wide range of mechanical properties. For example, significant increases in fracture toughness on the order of 50-200% compared to the matrix material have been reported for moderate CNT volume fractions of 1-10%.[1-11] However, these improvements are not observed in all cases. These variations in composite properties are not surprising, given the wide range of CNT structures and processing methods that have been employed. Of particular interest here are predictions that variations in atomic scale defects in CNTs can have a significant impact on toughening mechanisms. For example, molecular dynamics models indicate that carbon interstitials can promote interwall load transfer and increase the CNT fracture strength under certain conditions.[12-15] On the other hand, vacancy clusters in CNTs are believed to decrease fiber strength.[16,17] To date, it has been difficult to evaluate these predictions with well controlled experiments. General comparisons show that CNTs with higher defect densities lead to shorter pull-out lengths during nanocomposite fracture,[18] however, this could be due to lower fracture strengths, to changes in the fiber/matrix interface, or both. A focused investigation that addresses these questions is presented here.

The starting materials for these investigations were multiwall CNTs with very low defect densities. Controlled defects were introduced in these CNTs via exposure to different doses of high energy carbon ions. By varying this radiation exposure, it was possible to directly control the defect levels in the CNTs. Nanocomposites were then produced by embedding CNTs with

different radiation levels in a ceramic matrix, and these were investigated with both single CNT pull-out measurements and by evaluating fracture in multi-CNT composite films. The combined results from these experiments provide direct correlations between defects in the CNTs, and their impact on both measured CNT properties and fracture.

2. Experimental

2.1 Carbon nanotubes and irradiation

The multiwalled CNTs used in this study were obtained from Mitsui Corporation. Tetrahydrofuran (Ward Hill, MA) was used to uniformly disperse the CNTs in 0.1 wt.%, with ultrasonication for 1 hour and then kept undisturbed for 2 hours to settle out large aggregates, before uniformly dip coating onto the Si wafers. The samples were then heated at 250 °C for several seconds to evaporate the solvent. The CNTs on Si wafers were irradiated by 3.15 MeV C^{2+} ions using the tandem accelerator at the University of Wisconsin-Madison. One batch of CNTs was irradiated to a fluence of 1.17×10^{17} ion/cm² and the other batch of CNTs was irradiated to 2.34×10^{17} ion/cm². In order to quantitatively compare damage in materials irradiated under different conditions (e.g., irradiation species, energy), we use the concept of the displacement-per-atom (dpa). Dpa corresponds to the number of times that an atom in the target material was displaced for a given irradiation fluence[19] and it can be determined using the SRIM code (Stopping and Range of Ions in Materials).[20,21] Since there is no model for CNTs in SRIM, we assume that CNTs dispersed on the Si wafer have a similar density as graphite and the same displacement threshold energy (33 eV) as C atoms in graphite.[22] Based on these assumptions, the fluence 1.17×10^{17} ion/cm² is found to correspond to 0.5 dpa and the fluence 2.34×10^{17} ion/cm² to 1.0 dpa. During the irradiation, the ion flux was kept around 4.1×10^{12} ion/

cm²s. Therefore, the irradiation time was about 8 hours for the 0.5 dpa sample and 16 hours for the 1.0 dpa sample. The irradiation temperature was controlled by a heating stage and the temperature was 125 ± 20 °C. The temperature was measured by two thermocouples buried into the sample holder.

2.2 Raman Spectroscopy

The as-received and irradiated CNTs were characterized with a WITec alpha 300M+ Confocal Raman Microscope using a 532 nm laser. The Raman spectra in Fig. 1 are the average of large area scans of $10\mu\text{m} \times 10\mu\text{m}$, 50×50 points, with integration time of 70 ms. The I_D/I_G ratios were calculated by Lorentzian peak fitting of the D and G bands. Previous Raman studies have shown that the ratio between the D and G peaks can be related to the defect density in ion-irradiated graphene and this relation can be described by the following expression:[23]

$$n_D \left(\text{cm}^{-2} \right) = \frac{(1.8 \pm 0.5) \times 10^{22}}{\lambda_L^4} \left(\frac{I_D}{I_G} \right) \quad (1)$$

Here n_D is the defect density, λ_L is the laser wavelength (in nanometers), and I_D and I_G are the intensities of the D and G peaks, respectively. Table 1 reports the calculated defect density and the corresponding average distance between defects obtained with this equation.

2.3 Composite Fabrication

Nanocomposite films were fabricated with a PDC matrix that was produced with a silicon alkoxide ($\text{Si}(\text{OR})_4$) precursor where some OR sites were substituted by hydride and vinyl groups. The liquid PDC precursor (CSO-230) and platinum catalyst (CLC-PL005) were obtained from Extreme Environment Materials Solutions (Saratoga Springs, NY). These were combined to obtain the mixed liquid PDC precursor (weight ratio of 100:1), which was then diluted to 30 wt.% in isopropanol and infiltrated into the dispersed CNTs on the Si wafer using a spin coater.

These films were cross-linked at 100 °C for 30 min followed by pyrolysis in a tube furnace under continuous flow of forming gas (95% Ar and 5% H₂) at a flow rate of 100 mL/min. The resulting films were ~2 μm thick, with CNT volume fractions that were estimated to be 20-30% based on SEM images and the relative amounts of material used to prepare the films. Substantial stresses occurred in these films, due to both densification of the PDC and the thermal expansion mismatch between the composites and the Si substrates. These stresses led to cracks in the CNT-PDC nanocomposite films[18], which made it possible to observe the fracture surfaces by SEM (LEO 1530 VP).

2.4 Single CNT Pull-out and Fracture Tests

Single tube pull-out tests were conducted to measure the IFSS between individual CNTs with/without irradiation and the PDC matrix. This approach has been reported in previous publications.[18,24,25] To summarize briefly, a thin layer of prepared PDC precursor was first dropped onto the sample shuttle of a custom-designed micromechanical device. Individual CNT were then carefully loaded onto this previously prepared PDC layer, and several more drops of PDC were transferred onto the CNT to fully cover it. The whole device together with the embedded was put into a tube furnace under continuous flow of a mixture of 95% N₂ and 5% H₂ at 100 mL/min. After this heat treatment, Pt was deposited on the other end of the CNT in an FEI Helios 660 SEM/FIB to firmly bond it to the other sample shuttle of the device. For the pull-out test, a quantitative Agilent nanoindenter with displacement resolution of 1 nm was employed to actuate the device and also to measure the load and displacement independently. Calibration of this device was described previously.[26] The complete pull-out test was recorded by video to monitor the process and to ensure the test validity. The strength of CNTs with and without

radiation was measured in the same apparatus, but with a different specimen configuration. Both ends of CNTs were anchored with either PDC, Pt, or epoxy.

The fracture statistics were analyzed with a standard Weibull distribution:

$$P_f = 1 - \exp \left[- \left(\frac{\hat{\sigma}}{\sigma_0} \right)^m \right] \quad (2)$$

where P_f is the fracture probability, σ_0 is again the average fracture stress for a gauge length L_0 , and the $\hat{\sigma}$ values are fracture strengths due to the distribution of strength limiting flaws. The latter is defined for specimens of the specified size (i.e., corresponding to L_0). Because each of the measurements was based on a different fiber diameter, d , and suspended length, L , $\hat{\sigma}$ has to be normalized to the specimen size:

$$\hat{\sigma} = \left(\frac{d^2 L}{d_0^2 L_0} \right)^{1/m} \sigma \quad (3)$$

For the data collected here, $L_0 = 5.56 \mu\text{m}$ and $d_0 = 93.5 \text{ nm}$ are the average values for the CNTs where fracture strengths were measured. The standard Weibull plot in Fig. 4 is then based on Eq. (6), with the size adjusted fracture stresses that are described by Eq. (7).

3. Results and Discussion

Raman spectra before and after ion damage are shown in Fig. 1. The D band is attributed to point defects in graphene and CNT structures, and thus these results demonstrate that the radiation exposures increase defect concentrations. The relative intensities of the D and G bands were also inserted in Eq. (1) to estimate relative defect concentrations. For pristine CNTs, the intensity ratio (I_D/I_G) of the D peak at 1360 cm^{-1} and the G peak at 1580 cm^{-1} is 0.17, which indicates that these are high-quality CNTs with very low defect levels. The ion doses of 0.5 dpa

to 1.0 dpa lead increasing I_D/I_G (0.41 to 0.52, respectively), suggesting that a significant number of defects were generated during radiation. Quantitative results from this analysis are included in Table 1.

Fig. 1. Raman spectra of Mitsui CNTs, as a function of the exposure to 3.15 MeV C^{2+} ions. The spectra are normalized based on the G peak of pristine CNTs.

Table 1. Impact of C^{2+} ion exposures on measured properties of CNTs.

Property	Pristine CNTs	Irradiated CNTs with 0.5 dpa Exposure	Irradiated CNTs with 1.0 dpa Exposure
Elastic Modulus [GPa]	399.2 ± 39.5	333.9 ± 65.5	270.2 ± 22.2
Fracture Strength [GPa]	11.5 ± 6.5	10.3 ± 5.8	9.7 ± 6.7
IFSS [MPa]	9.6 ± 1.9	14.8 ± 3.1	27.5 ± 5.8
I_D/I_G (Raman)	0.17	0.41	0.52
Defect Density [nm ⁻²]	1.30×10^{-3}	2.74×10^{-3}	3.36×10^{-3}
Average Distance between Defects [nm]	27.7	19.1	17.2
Average Pullout Length [μm]	2.79	1.90	1.58

Nanocomposite films with the aforementioned PDC matrix were prepared using CNTs with the different defect levels. Examples of fracture surfaces in these specimens are shown in Fig. 2. The average pull-out lengths in Table 1 clearly show that the C^{2+} ion exposures lead to shorter pull-out lengths. The extensive pull-out observed here is typically associated with increased toughness in fiber-reinforced ceramics. This type of behavior has been the subject of

extensive continuum mechanics modeling. As an example of the type of result obtained with these analyses, the following approximate relationships describe the average pull-out length, $\langle h \rangle$, and work of fracture due to pullout, W_p : [27,28]

Fig. 2. Fracture surfaces for PDC matrix nanocomposites fabricated with: (a) untreated CNTs; (b) CNTs with 1.0 dpa exposure.

$$\langle h \rangle = \frac{\lambda(m)}{4} \left(\frac{\sigma_0 r L_0^{1/m}}{\tau} \right)^{m/(m+1)} \quad (4)$$

$$W_p = \frac{\gamma(m)}{3\lambda(m)} f \left(\frac{\sigma_0 \tau L_0}{r} \right)^{1/(m+1)} \langle h \rangle \quad (5)$$

where τ is the fiber-matrix interfacial sliding resistance, f is the fiber volume fraction, σ_0 is the average fiber strength over a gauge length L_0 , r is the fiber radius, and m is the Weibull modulus for fiber fracture. The coefficients γ and λ depend only on m , and can be approximated with:

$$\gamma(m) \cong \frac{1.87}{m^{0.75}} + 0.50 \quad (6)$$

$$\lambda(m) \cong \frac{0.664}{m^{0.6}} + 0.716 \quad (7)$$

This model is based on unidirectional composites with global load sharing. Additional considerations are needed to address local load sharing effects, and to describe the random fiber orientations in our composites. However, Eqs. (4) – (7) provide a relatively simple framework

for interpreting the trends in our data. Here, the observed pull-out lengths are described in terms of two physical processes – fiber fracture (i.e., σ_0 , L_0 , and m) and the sliding resistance, τ .

Information about the impact of radiation on the fracture and interface properties described above was obtained with single CNT pullout experiments. The apparatus and procedure for these measurements is presented elsewhere,[18,24] and reviewed in the Experimental section. The specimens were produced by embedding individual CNTs in the same PDC matrix that was used for the composite films. These investigations made it possible to measure the CNT modulus, CNT fracture strengths, and interface bonding. The latter is reported here as τ_b , the IFSS, which is calculated as:

$$\tau_b = \frac{F_{\max}}{2\pi r l_{\text{emb}}} \quad (7)$$

where $F_{\max}$ is the maximum measured force (applied to the CNT) and l_{emb} is the length of the CNT embedded in the PDC matrix.

Fig. 3 shows two examples of irradiated CNTs with 1.0 dpa exposure pulled out from PDC (Figs. 3a-3c), and tensile test of a pristine CNT (Figs. 3d-3f). The CNTs with short embedded length in PDC are likely to be pulled out of PDC (Fig. 3b), while those CNTs with either longer embedded length in PDC or high density of defects will break in the suspended area (Fig. 3e). The remained shell of PDC in the inset of Fig. 3b suggests the full contact between the CNT and PDC matrix in Fig. 3a. The video recording the entire pull-out process of the CNT can be found in the Supporting Information Video S1. The corresponding load-displacement curve is shown in Fig. 3c. The IFSS of the CNT debonding from PDC in Figs. 3a and 3b is calculated to be 36.2 MPa. Number of pull-out of pristine and irradiated CNTs under the similar testing condition and with different embedded length were carried out. The average IFSS of pristine CNTs, irradiated CNTs with 0.5 dpa and 1.0 dpa exposures pulled out from PDC is 9.6 ± 1.9

MPa, 14.8 ± 3.1 MPa, and 27.5 ± 5.8 MPa, respectively. Details of diameter and embedded length of CNTs, critical pull-out force, maximum normal stress, and IFSS are summarized in Table 2. In these single pull-out tests, there is some uncertainty in determining whether τ_b is dictated by debonding or frictional sliding during pullout. With this in mind, τ_b sets an upper bound on τ .

Fig. 3. Tensile tests of CNTs. (a) and (b) SEM images of a CNT with 1.0 dpa exposur before and after pull-out test from PDC matrix. The diameter of the irradiated CNT is 98.9 nm. The inset in (b) is the high-magnification SEM image of remained PDC shell. (c) Load-displacement curve of the CNT in (a) pulled out from PDC. (d) and (e) SEM images of a pristine CNT before and after tensile test. The diameter of the pristine CNT is 100.2 nm. The inset in (e) is the TEM image of fracture surface of the CNT in (d) with a sword-in-sheath fracture mode. (f) Stress-strain curve of the pristine CNT in (d).

Table 2. Interfacial properties between CNT and PDC.

Sample #	Radiation dose [dpa]	Embedded depth [nm]	Nanotube diameter [nm]	Critical pullout force [mN]	Maximum nominal stress [GPa]	IFSS [MPa]
1	0	5180.6	74.9	0.0106	2.40	8.7
2	0	2042.1	77.2	0.0061	1.31	12.4
3	0	3220.3	79.1	0.0083	1.70	10.4
4	0	3557.9	86.3	0.0087	1.48	9.0
5	0	3000.4	103.9	0.0075	0.88	7.6
1	0.5	1493.5	90.5	0.0037	0.57	8.7
2	0.5	4420.5	85.0	0.0203	3.57	17.2
3	0.5	5129.3	72.2	0.0192	4.69	16.5
4	0.5	7691.5	82.4	0.0319	5.99	16.0

5	0.5	2631.2	94.4	0.0122	1.75	15.7
6	0.5	5430.6	96.4	0.0246	3.37	15.0
1	1.0	3326.6	98.9	0.0375	4.88	36.2
2	1.0	887.6	78.6	0.0052	1.06	23.5
3	1.0	2298.0	100.0	0.0180	2.29	25.0
4	1.0	2532.5	78.3	0.0138	2.87	22.2
5	1.0	1706.3	94.9	0.0155	2.19	30.5

The strengths of CNTs with and without radiation were measured in the same apparatus, but with a different specimen configuration. Figs. 3d and 3e show an individual pristine CNT before and after mechanical failure. The diameter of the CNT is 100.2 nm. Fig. 3e and associated inset (TEM image) show the CNT fracture surface with a sword-in-sheath morphology. The surface is severely torn. Fig. 3f is the stress-strain curve of the CNT. The corresponding video can be found in the Supporting Information Video S2. The elastic modulus and fracture strength of the CNT in Fig. 3e are subsequently calculated to be 398.9 GPa and 9.5 GPa, respectively. The average elastic modulus of pristine CNTs, irradiated CNTs with 0.5 dpa and 1.0 dpa exposures is 399.2 ± 39.5 GPa, 333.9 ± 65.5 GPa, and 270.2 ± 22.2 GPa, respectively. The average fracture strength of above three kinds of CNTs is 11.5 ± 6.5 GPa, 10.3 ± 5.8 GPa, and 9.7 ± 6.7 GPa, respectively. Because of the high CNT strengths and the inherent challenges with these measurements, failure usually occurred at the point where the CNTs were bonded to the deposited Pt or epoxy. Because of this, attempted measurements on more than 30 specimens yielded only 7 successful failure events that led to the average values in Table 1. The large error bars here are a direct result of the limited number of successful tests. Based on these data, it appears that the defects induced by radiation lead to a small decrease in the fracture strength. However, given the substantial scatter in this data it is instructive to apply a standard Weibull analysis to all of the successful measurements (irrespective of dpa). This gave a best fit with $m = 3$ and the resulting Weibull plot shown in Fig. 4. Both of the successful measurements with 1.0 dpa exposures are slightly below the median trend line, which is consistent with the idea that

radiation damage produced a small drop in the fracture strength. However, all of these points fall within the range of the inherent experimental scatter.

Fig. 4. Weibull plot of measured fracture strengths for individual CNTs.

The full range of measured fracture strengths are consistent with prior reports for CVD grown CNTs.[29-31] These values are well below the expected CNT strengths due to isolated point defects. Based on this, others have proposed that strengths are limited by larger vacancy clusters.[16] There is also some evidence which indicates that radiation can enhance the formation of these larger defects in the outer wall.[32] Note also that the pull-out lengths show that the density of strength limiting defects is far below the estimated defect densities in Table 1. For example, one strength limiting defect in a 5 μm length of the CNT used here corresponds to an areal density (per graphene layer) of $\sim 10^{-8} \text{ nm}^{-2}$. This further supports the conclusion that the vast majority of the defects induced by the C^{2+} ions do not lead to fracture. In addition to limiting the fiber strength, it is also possible that some internal defects might enhance interwall bonding. For example, previous computational work predicts that this kind of coupling can alter fracture in multiwalled CNTs by decreasing sensitivity to flaw size and increasing the strength (for a given critical flaw size).[12] There is no direct evidence for the latter in our measurements, however, decreased flaw size sensitivity could contribute to the limited impact that radiation has on fracture strength.

Although the results in Fig. 4 do not provide a full description of the fracture statistics as a function of dpa, these measurements still provide important input for our assessment of pull-out lengths. Based on the relationship in Eq. (1), note that the experimentally observed decrease in $\langle h \rangle$ at the highest dpa would require that σ_0 decrease by roughly a factor of 2 (based on typical values of m and with τ constant). However, the CNT fracture results in Fig. 4 indicate that any decrease in σ_0 is significantly smaller than this. Thus, it appears that the measured increase in τ is the dominant factor that leads to a decrease in $\langle h \rangle$. As noted above, the IFSS is not necessarily equal to τ . However, the general agreement with the relative change in $\langle h \rangle$ suggests that the energies for interfacial sliding and interfacial debonding are both scaling in similar ways with an increase in CNT defects.

Each of the four types of measurements used in this investigation is only capable of providing limited information about the impact of CNT defects on the mechanical properties of interest. However, by combining these techniques we have been able to determine key relationships between radiation induced defects and toughening mechanisms in ceramic nanocomposites. The three key elements of this can be summarized as follows:

- The increase in the IFSS implies that radiation damage creates defects in the outer wall which promote bonding to the PDC matrix. It appears that these defects also increase τ (based primarily on the interpretation of pull out lengths discussed above).
- These defects have a smaller impact on CNT fracture. This is consistent with the idea that fracture is dictated by flaws that are larger than a single point defect.
- The reduction in fiber pullout due to radiation induced defects can be attributed to both a reduction in CNT strength and an increase in τ , however, the latter appears to have a larger impact here.

These relationships are fully consistent with the experimental observations reported here. A key result is that the defects incorporated during C^{2+} ion exposure can both increase τ and decrease σ_0 . Although both of these effects are consistent with the shorter measured pull-out lengths, they have different implications for toughness. As seen in Eq. (2), a decrease in σ_0 is generally detrimental, while an increase in τ can enhance toughness. In conventional ceramic composites these are typically viewed as independent properties, where surface modifications are widely used to control interfacial debonding / sliding, and defects in the fibers determine the fracture strength. However, σ_0 and τ can be interrelated at the very small length scales that are inherent in CNTs. Thus in these CNT reinforced composites, optimizing toughness is associated with a tradeoff between increasing τ and decreasing σ_0 (i.e., these properties are not independent). The measurements reported here do not allow us to evaluate this tradeoff precisely, largely because a quantitative relationship between IFSS and τ for our materials is not available. Additional research to attain this is ongoing.

Fig. 5. Proposed impact of defects on CNT fracture strength and IFSS. (a) Carbon ions introduce new defects, but larger pre-existing defects appear to control fracture. (b) The increase in the overall defect density leads to stronger overall bonding to the PDC matrix. (c) Summary of the experimental measurements from Table 1, which support the interpretations in parts (a) and (b).

For the case investigated in this work, we have concluded that the high energy carbon ions introduce a significant number of well dispersed defects which increase τ , but that there is only limited (if any) corresponding increase in large defect clusters that cause CNT fracture. Simplified schematics which illustrate key elements of this interpretation are presented in Fig. 5. The central idea is that each of the defects contributes to the increase in IFSS, while fracture is dictated by only the largest defect. More generally, this interpretation of our results indicates that the distribution of defects in CNTs is extremely important in determining the tradeoff between these two properties.

Ultimately, an improved understanding of the relationships between defects and composite properties requires more detailed information about specific defect structures. Based on previous molecular dynamics simulations, the most prolific defects due to ion irradiation of CNTs are C adatoms and vacancies (either isolated or in the form of multi-vacancy clusters).[33,34] Density functional theory calculations have found that clusters formed by more than five vacancies tend to spilt into smaller vacancy clusters because of the lower defect formation energy of the smaller clusters.[35] However, larger holes (about 1 nm) have also been simulated by molecular dynamics[36] and observed by transmission electron microscopy analysis of the surface of irradiated multiwall CNTs,[37] so the possibility of forming similar large vacancy holes on our irradiated multiwall CNT samples cannot be excluded. Based on these considerations, it is possible that the same type of defects dictate both CNT fracture and interfacial properties. For example, as already noted it is logical to attribute the measured increase in the IFSS to defects in the outer wall, and other work has reported that large vacancy clusters in the outer wall dictate CNT fracture. However, it is also possible that fracture is

dictated by defects in the inner walls. This points to another way in which the distribution of defects in CNTs is likely to have an important impact on the tradeoff between τ and σ_0 , and thus on toughening mechanisms in nanocomposites.

4. Conclusions

The primary impact that the C^{2+} ion exposure investigated here has on nanocomposite fracture is the creation of defects in the outer wall of the CNTs, which increases the IFSS significantly as the dpa increases. This appears to be correlated with a corresponding increase in the interfacial sliding resistance, which leads to the observed decrease in fiber pullout during nanocomposite fracture. A small decrease in fracture strength was also measured. This is within the experimental measurement error, which indicates that CNT fracture is relatively insensitive to the large number of additional defects created by ion damage. Thus, the specific results presented in this paper illustrate a case where introducing individual point defects can have a relatively large effect on τ , along with a relatively small decrease in σ_0 . This is expected to be an effective strategy for improving toughness in ceramic nanocomposites. Additional investigations of these relationships and the resulting properties are needed.

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