Effects of nanostructured, diamondlike, carbon coating and nitrocarburizing on the frictional properties and biocompatibility of orthodontic stainless steel wires

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ABSTRACT

Objective: To evaluate and compare the effects of nanostructured, diamondlike, carbon (DLC) coating and nitrocarburizing on the frictional properties and biocompatibility of orthodontic stainless steel archwires.

Materials and Methods: Plasma-enhanced chemical vapor deposition technology was applied to coat DLC films onto the surface of austenitic stainless steel wires, and salt-bath nitrocarburizing technology was employed to achieve surface hardening of other wires. Surface and cross-sectional characteristics, microhardness, modulus of elasticity, friction resistance, corrosion resistance, and cell toxicity of the modified and control wires were analyzed.

Results: The surfaces of the DLC-coated and nitrocarburized wires were both smooth and even. Compared with the control, the DLC-coated wires were increased in surface hardness 1.46 times, decreased in elastic modulus, reduced in kinetic friction coefficient by 40.71\%, and decreased in corrosion current density by two orders of magnitude. The nitrocarburized wire was increased in surface hardness 2.39 times, exhibited an unchanged elastic modulus, demonstrated a decrease in maximum static friction force of 22.2\%, and rose in corrosion current density two orders of magnitude. Cytotoxicity tests revealed no significant toxicity associated with the modified wires.

Conclusions: DLC coating and nitrocarburizing significantly improved the surface hardness of the wires, reduced friction, and exhibited good biocompatibility. The nanostructured DLC coating provided excellent corrosion resistance and good elasticity, and while the nitrocarburizing technique substantially improved frictional properties, it reduced the corrosion resistance of the stainless steel wires to a lesser extent. (Angle Orthod. 2016;86:782–788.)

KEY WORDS: Orthodontic wire; Nanostructured, diamondlike, carbon coating; Nitrocarburizing; Frictional properties; Biocompatibility

INTRODUCTION

During fixed orthodontic treatment, friction is generated by the relative motion between the archwire and bracket. This friction must be overcome before force can be transferred from the oral device to the teeth.\textsuperscript{1–3} Sliding mechanisms are now widely used in fixed appliances,\textsuperscript{4} which means that friction from the treatment process is becoming a crucial concern that affects the performance and efficiency of appliances.\textsuperscript{5,6} Indeed, subtle changes in brackets, archwires, and ligation methods designed to reduce friction may improve anchorage control and shorten the orthodontic treatment period. Many orthodontists use austenitic stainless steel wires to close extraction spaces; however, a major shortcoming of this is the weak mechanical properties of the material.\textsuperscript{7} This has led to a global research focus on using mechanical processes to reduce the friction coefficient and improve overall efficiency of treatment.

The rapid development of biomedical engineering has resulted in researchers exploring a variety of surface modification methods to improve the perfor-
mance of biomedical metallic materials. Very recently, owing to its extreme hardness and substantial wear resistance, diamondlike, carbon (DLC) coating has emerged as a new type of surface coating. In particular, studies have shown DLC coating of orthodontic appliances may indeed improve their frictional properties. Traditional DLC films, however, tend to shed from the substrate due to the large residual stress, which has greatly limited any industrialization or further application of DLC coating in orthodontics.

Nanomaterials with unique properties such as high strength and good plastic deformation have begun to move the field of orthodontic materials forward. Nanostructured DLC films, defined as a series of amorphous carbon materials with nanoparticles or a membrane layer, not only reduce the internal stress of DLC film, but also increase its adhesiveness. Research into surface modification techniques using nanostructured DLC films and coatings, however, is still in its initial stages.

Another technique to harden the surface and reduce the friction coefficient of austenitic stainless steel is nitrocarburizing, which uses two major methods: gas-plasma and salt-bath. The salt-bath method excels owing to its simplicity, low cost, and stable processing temperature. It has been reported that the gas nitriding technique has improved the frictional properties and wear resistance of dental titanium. However, use of salt-bath nitrocarburizing surface modification for orthodontic materials has yet to be investigated.

Therefore, the present study was undertaken to evaluate and compare the effects of a nanostructured DLC coating and salt-bath nitrocarburizing technique on the frictional properties and biocompatibility of orthodontic stainless steel archwires, to provide an experimental basis for the application of surface modification technology in orthodontics.

MATERIALS AND METHODS

As-received austenitic, stainless steel archwires with cross-sectional dimensions of 0.019 × 0.025 inch (3M Unitek, Monrovia, Calif) were used as controls. DLC coatings were deposited on these stainless steel wires using plasma-enhanced chemical vapor deposition (PECVD). All wires were fixed on a worktable, and deposition was carried out at an offset voltage of 60 V, under a pressure of 0.5 Pa, and a radio frequency power of 100 W. The substrate temperature was 200 °C and the total time of deposition was 8 minutes. For the salt-bath nitrocarburizing procedure, the wires were finished in the salt-bath nitrocarburizing arc furnace at 565 °C for 10 minutes. The specific medium for austenitic stainless steel was 16% wt K2CO3, 24% wt KCl, and 60% wt urea.

Raman Analysis

A Labram HR800 laser confocal Raman microscope (Jobin Yvon Inc, Paris, France) was used to analyze the structural characteristics and quality of the DLC coating. A 514.532-nm Ar+ laser was available with the excitation source inside. Maximum power of the laser was 25 mW, with the Raman shift ranging from 100 cm−1 to 4000 cm−1 (200–2000 wavenumbers).

Scanning Electron Microscopy

To observe the surface and cross-sectional topography of the wires, all specimens were examined using scanning electron microscopy (SEM) (Ultra Plus, Carl Zeiss, Sydney, Australia) operating at 5 kV. The surface of the wires was cleaned by ultrasonic irrigation for 20 minutes before a 10-mm length of each wire was fixed to a specimen holder.

Microhardness Tests

Microhardness of the control, DLC coated, and nitrocarburized wire surfaces were assessed using a DHV-1000 digital Vickers microhardness tester (Shanghai Electric Machine Tool I & E Co Ltd, Shanghai, China). The normal load applied was 1.96 N for 15 seconds. Five pinpointed locations at least 1 mm apart were selected on the surface of each wire for testing. The mean of the hardness values from these five locations was considered to be the microhardness value (HV) of the wire. Five wires were tested for each type of wire.

Modulus of Elasticity Tests

A TI-950 nanoindentation test apparatus (Hysitron Inc, Minneapolis, Minn) was used to detect changes in the elastic moduli of the wires. All tests were completed using a Berkovich indenter (Hysitron) at 25°C. The measurement sites were selected using an optical microscope and charge-coupled device camera linked to the apparatus. Each test consisted of three segments: 10-second loading to the peak value, 1-second hold at the peak load (6 mN), and 10 seconds for unloading. The slope of the load-depth curve at the initial stage of unloading was defined as the elastic modulus for each wire. Five wires were tested for each type of wire.

Friction Tests

The frictional force generated by each archwire-bracket combination was tested under dry conditions at 25°C using a frictional testing apparatus mounted on the crosshead of a universal testing machine (Instron).
Three maxillary first premolar brackets for each type of wire were used in the study. The conventional stainless steel brackets (Victory Series, 3M Unitek) had a slot dimension of 0.022 inch and a mesiodistal width of 3.2 mm. Each bracket was bonded to the end of a stainless steel plate before a 5-cm-long wire was ligated to the bracket with an elastomeric ligature (AlastiK Easy-to-Tie Ligatures, 3M Unitek). Each wire was drawn through the bracket at a crosshead speed of 10 mm/min for a distance of 20 mm. The kinetic and static frictional coefficients and maximum static friction were calculated using load-displacement curves.

**Corrosion-resistance Tests**

To evaluate the corrosion rates of the three different types of wires, a potentiostatic, anodic polarization experiment was conducted. Three electrodes were used on the electrochemical workstation CHI760D (Chenhua Instrument Co Ltd, Shanghai, China), including the working electrode (using various sample wires), the auxiliary electrode (using a platinum gauze electrode), and the reference electrode (using a saturated calomel electrode). A special artificial saliva (pH = 6.8, 37°C) was used as the medium. The corrosion rate of each wire was proportional to the corrosion current density that was measured using the Tafel curves from the linear potential sweep method. The sample size of each wire was 5.

**Cytotoxicity Tests**

A 3-(4,5-dimethyl-2-thiazolyl)-2,5-diphenyl-2H tetrazolium bromide (MTT) colorimetric assay was applied to evaluate the in vitro cytotoxicity of the archwires. Human gingival fibroblasts were collected and cultured with the impregnation liquid from each archwire sample in Dulbecco’s Modified Eagle Medium (GIBCO-BRL, Bethesda, Md) supplemented by 10% heat-inactivated fetal bovine serum. Optical density (OD) values were read at 490 nm using an automatic microtiter plate reader (Spectramax 190, Molecular Devices Inc, Sunnyvale, Calif). The cell proliferation rate (P%; P = the mean OD value of every concentration group/negative control group) was calculated to provide toxicity levels (all approximate): level 0: 100; level 1: 80; level 2: 60; level 3: 40; level 4: 20. The sample size for each wire was 5.

**Statistical Analysis**

Statistical analysis was performed with the Statistical Package for the Social Sciences V17.0 software (SPSS Inc, Chicago, Ill). It was hypothesized...
that the DLC coating and salt-bath nitrocarburizing technique do not affect the frictional properties and biocompatibility of orthodontic archwires. Since the data for the frictional properties, microhardness, and elastic modulus were normally distributed (Levene test), values among the three wire types were compared using one-way analysis of variance followed by the least significant difference test ($P < .05$).

### RESULTS

#### Raman Analysis and SEM Observation

For the DLC-coated wires, the Raman spectra and Lorenz curves show peaks D (sp$^3$ bonding state of carbon for diamondlike) and G (sp$^2$ bonding state of carbon for graphitelike), broadening significantly (Figure 1). The D peak appears at 1347 cm$^{-1}$ and the G peak at 1557 cm$^{-1}$, which is typical for DLC structures.$^{22}$ SEM photomicrographs from a cross-section of the DLC-coated wires clearly show the coating to have a thickness of approximately 1 $\mu$m (Figure 2E). Diameters of the ultrafine crystal grains in the films were all below 100 nm (Figure 2D), and therefore, defined as nanocrystals. The surface of the nitrocarburized wires was greyish-black and relatively smooth compared with the control wire.

#### Microhardness

After surface modification, microhardness of the DLC-coated wires (685.17 Hv) was increased 1.46 times compared with the control wires (468.42 Hv), while the microhardness of the nitrocarburized wires (1119.58 Hv) was increased nearly 2.39 times compared with the control wires (Table 1; $P = .0001$). The nanoindentation test revealed that the elastic modulus of the DLC-coated wires (74.17 GPa) obtained from the 6 mN load was significantly lower than that of the control wires (201.24 GPa; $P = .0001$). The elastic modulus of the nitrocarburized wires (208.03 GPa) was similar to that of the control wires ($P = .845$).

#### Static and Kinetic Friction

Table 2 shows that the kinetic friction coefficient of the DLC-coated wires was reduced 40.71% compared with the control wires ($P = .001$), and the static friction coefficient of the nitrocarburized wires was reduced 15.24% compared with the control wires ($P = .067$). The maximum static friction of the nitrocarburized wires was significantly lower than those of the other two types of wires, and it decreased 22.2% compared with the control wires ($P = .001$).

#### Electrochemical Corrosion Experiments

The mean value of the corrosion potential and corrosion current of the control wires were 1.325 V and 3.41e-5, respectively. For the DLC-coated wires, the values were $-0.487$ V and 5.89e-7, respectively, with the polarization current decreasing by two orders of magnitude compared with the control wires. The mean corrosion current of the nitrocarburized wires obtained from the Tafel curve was 1.65e-4, an increase of one order of magnitude relative to the control wires (Figure 3). Therefore, our results demonstrate that DLC coating improves the corrosion resistance of the archwires, while such is true to a lesser extent for nitrocarburizing.

<p>| Table 1. Microhardness and Elastic Modulus of Control, DLC-coated, and Nitrocarburized Wires |
|-----------------------------------------------|-----------------------------------------------|-----------------------------------------------|
| Control ($T = 5$)                             | DLC-coated ($T = 5$)                           | Nitrocarburized ($T = 5$)                      |</p>
<table>
<thead>
<tr>
<th>Mean</th>
<th>SD</th>
<th>Mean</th>
<th>SD</th>
<th>Mean</th>
<th>SD</th>
<th>$P$ Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Microhardness (Hv)</td>
<td></td>
<td></td>
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<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>468.42$^a$</td>
<td>17.19</td>
<td>685.17$^b$</td>
<td>51.57</td>
<td>1119.58$^c$</td>
<td>17.04</td>
<td>.000</td>
</tr>
<tr>
<td>Elastic modulus (GPa)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>201.24$^a$</td>
<td>25.56</td>
<td>74.17$^b$</td>
<td>6.51</td>
<td>208.03$^a$</td>
<td>25.11</td>
<td>.000</td>
</tr>
</tbody>
</table>

$^a,b,c$ Mean values having the same superscript letter are not statistically significant after ANOVA ($P > .05$).

<p>| Table 2. Kinetic and Static Friction Coefficients and Maximum Static Friction of Control, DLC-coated, and Nitrocarburized Wires |
|---------------------------------------------------------------|---------------------------------------------------------------|---------------------------------------------------------------|
| Control ($T = 30$)                                           | DLC-coated ($T = 30$)                                        | Nitrocarburized ($T = 30$)                                    |</p>
<table>
<thead>
<tr>
<th>Mean</th>
<th>SD</th>
<th>Mean</th>
<th>SD</th>
<th>Mean</th>
<th>SD</th>
<th>$P$ Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\mu_{\text{kinetic}}$</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>47.63$^a$</td>
<td>9.38</td>
<td>28.24$^b$</td>
<td>9.17</td>
<td>48.43$^a$</td>
<td>11.03</td>
<td>.001</td>
</tr>
<tr>
<td>$\mu_{\text{static}}$</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>105.40$^a$</td>
<td>10.89</td>
<td>107.33$^a$</td>
<td>27.28</td>
<td>89.34$^a$</td>
<td>13.84</td>
<td>.067</td>
</tr>
<tr>
<td>$F_{\text{max}}$ (N)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.36$^a$</td>
<td>0.04</td>
<td>0.33$^a$</td>
<td>0.08</td>
<td>0.28$^a$</td>
<td>0.04</td>
<td>.001</td>
</tr>
</tbody>
</table>

$^a,b$ Mean values having the same superscript letter were not statistically significant after ANOVA ($P > .05$).

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*Angle Orthodontist, Vol 86, No 5, 2016*
Cytotoxicity

An inverted microscope for culture observations at 24, 48, and 72 hours was used, revealing an increase in cell numbers from the DLC-coated, nitrocarburized, and control groups. The means of the OD values are listed in Table 3. Results of the MTT colorimetric assay showed that cell proliferation rates for the DLC-coated group were between 91.92% and 115.32%, while for the nitrocarburized group they were between 84.76% and 110.11%. The toxicity level of both modification groups was 0, indicating no significant cytotoxicity.

DISCUSSION

Orthodontic archwires must meet certain requirements in order to be considered effective oral devices, for example, high strength, low stiffness, high plasticity, excellent frictional properties, corrosion resistance, abrasion resistance, and biocompatibility.23,24 Many techniques have been investigated to modify the surface of metallic materials to improve their overall performance. Surface nanoengineering might enhance both the surface properties and performance of materials by changing surface organization and structure.25 In this study, we successfully deposited even and dense nanostructured DLC films onto orthodontic stainless steel archwires. The ultrafine grains and wider atomic spacing resulting from the nanostructured DLC films, provided excellent characteristics compared with traditional archwires.

In the salt-bath nitrocarburizing technique, CNO effectively removed the passivation film from the archwire surface, permitting the nitrogen and carbon atoms to infiltrate the internal wire to achieve surface hardening without special pretreatment. With no ion-etching effect in the salt-bath procedure, the nitrocarburized wires acquired a smooth surface that benefited their frictional properties.18

The primary task in achieving effective and efficient orthodontic treatment is to decrease friction between the bracket and the wire. Factors affecting friction include the material used, archwire size, and ligation methods, to name a few.11,26,27 Surface roughness has a positive correlation with friction, while archwire hardness is negatively correlated with friction. In the present study, our DLC-coated wires displayed a smoother and harder surface compared with the control wire (Table 1), which possibly resulted from the larger proportion of sp3 bonds in the DLC coating. In support of this argument, the D peak from Raman spectra moved to lower wavenumbers (Figure 1). The

Table 3. Optical Density (OD) Values From the MTT Assay Test and Toxicity Levels of Control, DLC-coated, and Nitrocarburized Wires

<table>
<thead>
<tr>
<th>Concentration of Impregnation Liquid</th>
<th>24 h OD Value</th>
<th>24 h P/%</th>
<th>Level</th>
<th>24 h OD Value</th>
<th>24 h P/%</th>
<th>Level</th>
<th>24 h OD Value</th>
<th>24 h P/%</th>
<th>Level</th>
</tr>
</thead>
<tbody>
<tr>
<td>Control (T = 5)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>25%</td>
<td>0.6512</td>
<td>99.43</td>
<td>0</td>
<td>1.1766</td>
<td>105.38</td>
<td>0</td>
<td>1.4465</td>
<td>104.98</td>
<td>0</td>
</tr>
<tr>
<td>50%</td>
<td>0.6523</td>
<td>99.60</td>
<td>0</td>
<td>1.2064</td>
<td>108.05</td>
<td>0</td>
<td>1.4542</td>
<td>105.38</td>
<td>0</td>
</tr>
<tr>
<td>75%</td>
<td>0.6445</td>
<td>98.50</td>
<td>0</td>
<td>1.2042</td>
<td>107.85</td>
<td>0</td>
<td>1.4599</td>
<td>105.47</td>
<td>0</td>
</tr>
<tr>
<td>100%</td>
<td>0.6312</td>
<td>96.38</td>
<td>0</td>
<td>1.1796</td>
<td>105.65</td>
<td>0</td>
<td>1.4879</td>
<td>107.82</td>
<td>0</td>
</tr>
<tr>
<td>DLC-coated (T = 5)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>25%</td>
<td>0.6323</td>
<td>97.10</td>
<td>0</td>
<td>1.2104</td>
<td>102.74</td>
<td>0</td>
<td>1.4177</td>
<td>112.86</td>
<td>0</td>
</tr>
<tr>
<td>50%</td>
<td>0.6245</td>
<td>95.90</td>
<td>0</td>
<td>1.2398</td>
<td>105.24</td>
<td>0</td>
<td>1.3599</td>
<td>108.26</td>
<td>0</td>
</tr>
<tr>
<td>75%</td>
<td>0.6265</td>
<td>96.21</td>
<td>0</td>
<td>1.1845</td>
<td>100.53</td>
<td>0</td>
<td>1.4487</td>
<td>115.32</td>
<td>0</td>
</tr>
<tr>
<td>100%</td>
<td>0.5986</td>
<td>91.92</td>
<td>0</td>
<td>1.1754</td>
<td>99.77</td>
<td>0</td>
<td>1.4101</td>
<td>112.51</td>
<td>0</td>
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<tr>
<td>Nitrocarburized (T = 5)</td>
<td></td>
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<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>25%</td>
<td>0.6523</td>
<td>97.66</td>
<td>0</td>
<td>1.2465</td>
<td>106.78</td>
<td>0</td>
<td>1.5255</td>
<td>110.11</td>
<td>0</td>
</tr>
<tr>
<td>50%</td>
<td>0.6413</td>
<td>96.02</td>
<td>0</td>
<td>1.2366</td>
<td>105.93</td>
<td>0</td>
<td>1.4612</td>
<td>105.47</td>
<td>0</td>
</tr>
<tr>
<td>75%</td>
<td>0.6534</td>
<td>97.83</td>
<td>0</td>
<td>1.2201</td>
<td>104.51</td>
<td>0</td>
<td>1.3751</td>
<td>99.26</td>
<td>0</td>
</tr>
<tr>
<td>100%</td>
<td>0.6366</td>
<td>95.31</td>
<td>0</td>
<td>1.1906</td>
<td>101.99</td>
<td>0</td>
<td>1.1743</td>
<td>84.76</td>
<td>0</td>
</tr>
</tbody>
</table>

a MTT = 3-(4,5-dimethyl-2-thiazolyl)-2,5-diphenyl-2H tetrazolium bromide.
b P/% indicates cell proliferation rate.
harder surface of the nanostructured DLC-coated wires reduced not only kinetic friction (Table 2), but also the effects of binding and notching.

This study also clearly demonstrated that the nitrocarburizing process decreased maximum frictional force (Table 2), which is related to the solid-solution strengthening effect in the salt-bath procedure. Therefore, initial movement of the teeth should be accelerated efficiently. The DLC coating on the stainless steel wires revealed a lower elastic modulus compared with the surface layers on the control wires (Table 1). This result is similar to that obtained by Muguruma et al., who deposited a DLC film onto stainless steel archwires using a plasma-based ion implantation/deposition method. 

DLC-coated wires with a lower elastic modulus show superior flexibility, a desirable characteristic of orthodontic wires.

Various chemical substances in the saliva at mouth temperature lead to electrochemical corrosion reactions on the wire surfaces, resulting in possible adverse reactions such as allergies, tooth discoloration, and toxic effects. The study of Kobayashi et al. showed that DLC coating on nickel-titanium archwires greatly reduced the release of nickel ions. 

In this study, Tafel curves obtained from the electrochemical test indicate that DLC coating significantly reduces the corrosion rate of stainless steel wire in artificial saliva (Figure 3). As the DLC-coated wires exhibited an even microstructure composition and smoother surface, the oxide layer of the wires were better protected. By contrast, the corrosion resistance of the nitrocarburized archwire declined to some extent, which may have been due to the destroyed passive film on the wire surface.

Primary acute toxicity screening provides a fast, simple, reproducible, and inexpensive method to detect material biocompatibility. Our MTT assay results showed that no significant cytotoxicity was associated with either the DLC-coated or the nitrocarburized wires. After 72 hours of cell culture, cell proliferation rates in different concentrations of cell-impregnating solution were slightly increased relative to the control. The reason for this might be that the DLC coating suppressed release of the nickel ions into the cell culture, which should be further investigated.

Some limitations are raised in the present in vitro study since this investigation was conducted under ideal laboratory conditions, whereas in the oral cavity the presence of saliva, plaque, corrosion, and other variables could influence the frictional properties of wires. Moreover, in order to simulate what occurs clinically during orthodontic tooth movement, further research on the corrosion resistance of wires is needed to evaluate the changes in different situations.

CONCLUSIONS

- Nanostructured DLC coating and nitrocarburizing processes both significantly improved the surface hardness and reduced the friction of stainless steel archwires as well as exhibiting good biocompatibility.
- Nanostructured DLC coating provided excellent corrosion resistance and improved elasticity.
- Though the nitrocarburizing technique was outstanding in improving frictional properties, it reduced the corrosion resistance of the stainless steel wires to a lesser extent.

ACKNOWLEDGMENT

This work was supported by the National Natural Science Foundation of China (grant 81371179), the Natural Science Foundation of Jiangsu Province (grant BK20150048), and the Project Funded by the Priority Academic Program Development of Jiangsu Higher Education Institutions (grant 2014-37).

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