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TEM analysis of tweed structure in high-palladium dental alloys

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Transmission electron microscopy and convergent-beam electron diffraction were used to study three high-palladium dental alloys: an as-cast Pd–Ga alloy, a cast Pd–Cu–Ga alloy aged at room temperature for over 5 years, and a cast Pd–Cu–Ga alloy annealed at 1023 K for 2 h and slowly cooled to room temperature. Bands containing a tweed structure in the Pd-Ga alloy were 120° twins with $(1\ \bar{1}\ 0)$ mirror planes. Within these bands the alloy had a face-centered tetragonal structure with a *c/a* ratio of 1.03. The aged Pd–Cu–Ga alloy contained a larger amount of tweed structure than the original as-cast alloy, along with randomly oriented bands and thin lath-like regions. The annealed Pd–Cu–Ga alloy contained rectangular particles of a secondary phase that may be Pd_2Ga, Pd_5Ga_2 or $Pd_{13}Ga_5$. The microtwinned band structure relieves the strain energy arising from transformation of the f.c.c. palladium solid solution on cooling.

1. Introduction

High-palladium casting alloys have become popular for metal–ceramic restorations and implant-supported prostheses [1, 2] because of their excellent mechanical properties, good porcelain adherence [3], and lower cost compared to gold alloys. Most commercial high-palladium alloys are based on either the Pd–Cu–Ga or Pd–Ga systems. The former can have relatively high values of Vickers hardness (> 300), and dental laboratories may consider that it is difficult to perform adjustments on castings fabricated from such alloys. In order to achieve suitable coefficients of thermal expansion for metal–ceramic bonding, adequate adherence to dental porcelain, and appropriate levels of mechanical properties such as yield strength and elevated-temperature creep, small amounts of other elements, e.g. Sn, In, Au and Ag, are also included in the alloy compositions [4]. Grain refinement is typically achieved by incorporating a small amount of Ru.

Recently, the ultrastructures of two representative Pd–Cu–Ga dental alloys and two representative Pd–Ga dental alloys were investigated using transmission electron microscopy (TEM) [5, 6]. Although the Pd–Cu–Ga alloys were substantially harder than the Pd–Ga alloys, all four alloys had the same very fine-scale tweed structure for both the as-cast and heat-treated conditions. The same ultrastructure had been previously observed by TEM in a Pd–Cu–Ga dental alloy [7], although it was not recognized as a tweed structure. Tweed structures have been observed by TEM in a wide range of metallic and ceramic systems [8–13]. The objective of this study was to employ conventional TEM and convergent-beam electron diffraction (CBED), as well as X-ray energy-dispersive spectroscopic analysis with the TEM, to provide further insight into the ultrastructure of representative high-palladium dental alloys.

2. Materials and methods

TEM foils were prepared from three high-palladium alloys: (1) as-cast 85Pd–10Ga–1In–2Au–1Ag Legacy (Jelenko, Armonk, NY, USA); (2) cast 76Pd–10Cu–5.5Ga–6Sn–2Au Liberty (Jelenko) that had been aged at room temperature for over 5 years [14]; (3) cast 79Pd–10Cu–9Ga–2Au Spartan Plus (Williams/Ivoclar, Amherst, NY, USA) that was annealed at 1023 K for 2 h and slowly cooled to room temperature. The Legacy foil had been used in an earlier TEM study in our laboratory [5, 6]. The other foils were prepared by the same combination of jet polishing, ion milling and plasma cleaning used in that study. The foils were examined by TEM (CM200, Philips, Eindhoven, The Netherlands), using bright-field two-beam imaging, dark-field two-beam imaging, selected-area electron diffraction (SAED) and conventional standardless X-ray energy-dispersive spectroscopic analysis (EDS).

CBED was also employed to gain greater insight into the ultrastructure of the high-palladium alloys. Convergent-beam patterns (CBPs) normally consist of a series of discs, each corresponding to a different Bragg

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reflection [15]. The intensity variation within the discs provides important information about the thickness, orientation and other properties of the specimen. In CBED the focused incident beam strikes the specimen at a range of angles. The range of angles in the cone of illumination corresponds to a disc in the diffraction plane, with each Bragg reflection giving rise to a disc. Every point in the disc corresponding to the incident beam (the bright-field disc) represents electrons exiting through the sample at a specific orientation; different points correspond to different orientations of the beam with respect to the crystal structure. Associated with each point in the bright-field disc is an equivalent point in the other discs corresponding to Bragg reflection from that particular angle. CBPs are usually obtained at low index zones in the diffraction pattern of the crystal and can be used for unit cell determination, phase identification, lattice parameter determination and crystal structure analysis [15].

3. Results

The ultrastructure of as-cast Legacy has been previously reported as a series of parallel bands of up to 200 nm width which lie approximately along ⟨1 0 0⟩ directions and contain very fine tweed structure striations with spacings of approximately 20 nm [5, 6]. A dark-field image of this ultrastructure is shown in Fig. 1. Using EDS, no overall compositional difference could be detected between adjacent bands of the ultrastructure [16]. The overall compositions of the bands determined by EDS agreed very closely with the nominal percentages of Ga, Au and Ag provided by the manufacturer, whereas the concentration of Pd was 1–2 wt % higher than the nominal amount and In was not detected [16]. The 1 wt % nominal concentration of In could have been lost during the casting process or alternatively formed In–Au, In–Ag or In–Ru intermetallic compounds that might be difficult to detect because of the relatively small foil areas examined or the loss of these phases during specimen preparation [5, 6].

The [1 1 1] zone patterns were obtained for the alternating bands under different diffraction conditions. The distances (r-values) of the diffraction spots from the transmitted spot in the CBED (Fig. 2) and SAED (Fig. 3) patterns were measured accurately. Ten different measurements on ten [1 1 1] zone patterns, taken under different diffraction conditions for each set of bands, were made. It was found that the r-values for two ⟨1 1 0⟩ type pairs of spots were equal, whereas the r-value of the third pair of ⟨1 1 0⟩ type spots was consistently smaller by approximately 3.5%. Similar measurements on other condensed spot patterns of the [1 1 1] zone verified the tetragonality of the structure, and the procedure was repeated for the other set of bands. The lattice parameters of the tetragonal structure were $a = b = 0.386 \pm 0.008$ nm and $c = 0.398 \pm 0.006$ nm, giving c/a ratio of 1.023–1.037.

Indexing of the SAED patterns followed standard TEM procedures [15] for a tetragonal structure. Diffraction patterns of various zones in reciprocal space were obtained with the TEM for both sets of bands. The angles of the tilts required to reach these zones were recorded, and standard stereographic projections of both sets of bands were plotted [16]. The following orientation relationships (OR) between the bands were established by comparing the corresponding stereograms after 120° rotation: [0 1 1] || [1 0 1]; [1 0 1] || [1 1 0]; [1 1 0] || [0 1 1]. This OR was then confirmed by tilting the specimen to each of the zones for both sets of bands. It was concluded that these bands are 120° twins along the [1 1 1] zone axis, with a $(\bar{1}\ 1\ 0)$ mirror plane.

Figs 4–6 show bright-field images of cast Liberty that had been aged at room temperature for over 5 years [14]. While the regular tweed structure in aged Liberty (Fig. 4) was identical to that in as-cast Liberty and Legacy [5, 6], randomly oriented bands with a width of approximately

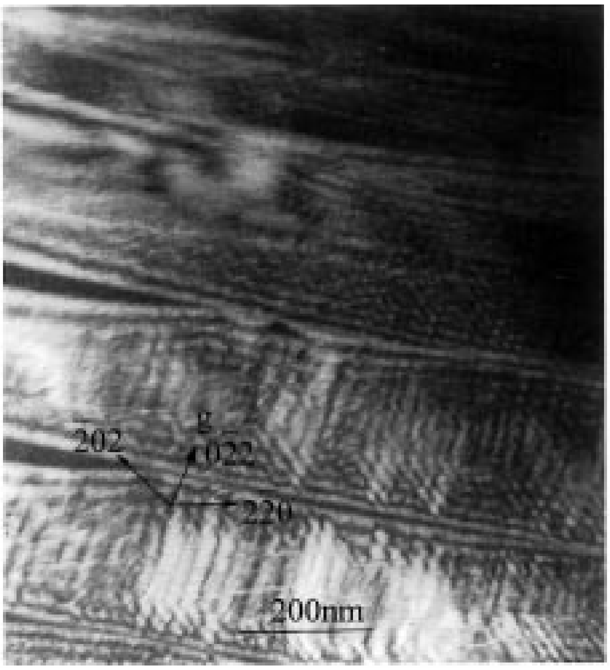

Figure 1 Dark-field image of as-cast Legacy, tilted along $g_{02\bar{2}}$ of the broad bands, and showing the directions of the tweed striations.

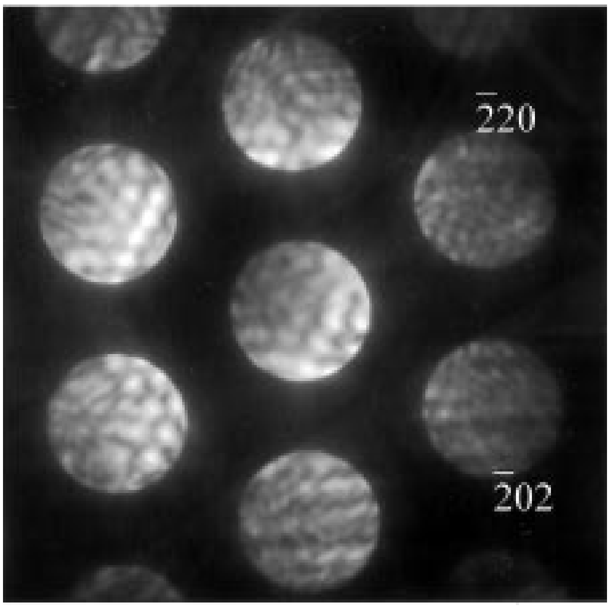

Figure 2 CBED pattern of the [1 1 1] zone for as-cast Legacy. The distances of the diffraction discs from the central transmitted disc revealed the tetragonality of the structure.

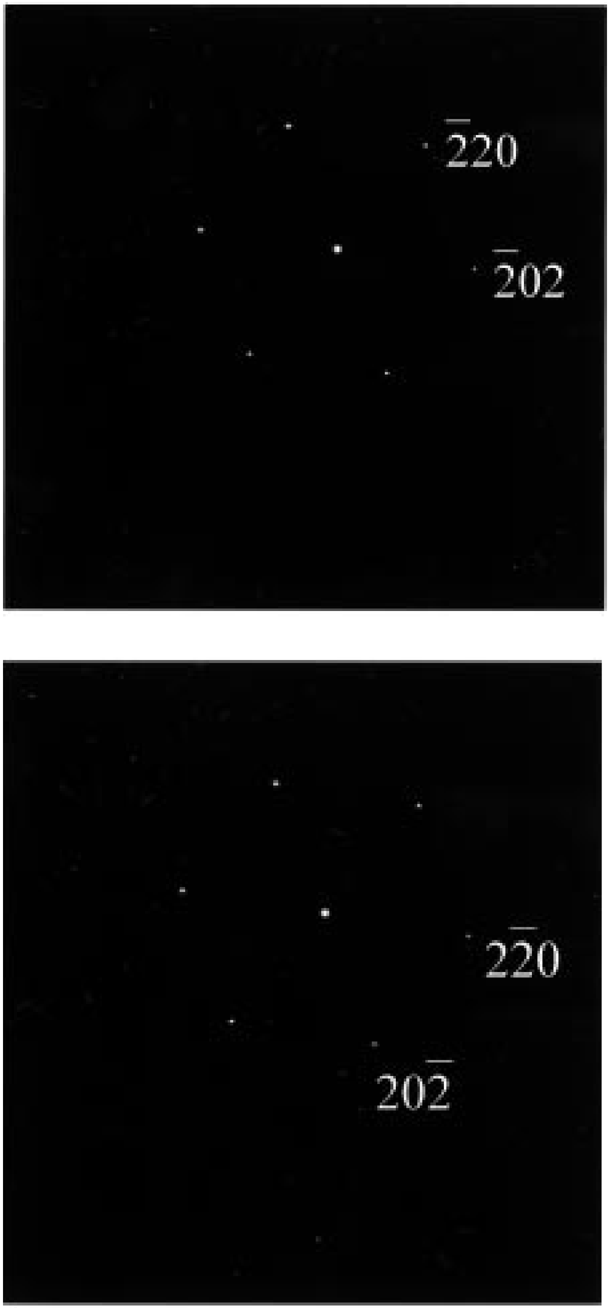

Figure 3 [1 1 1] zone patterns for each set of the tweed bands in as-cast Legacy. The bottom electron diffraction pattern can be obtained by a 120° counterclockwise rotation of the top electron diffraction pattern.

40 nm were found in one region of the foil (Fig. 5). Any boundaries between different orientations of the bands could not be distinguished. Thin, parallel, lath-like regions that did not exhibit internal striations were also observed (Fig. 6). The microstructure was dominated by the presence of bands, with few regions of the lath-like constituents.

Specimens of Spartan Plus, annealed at 1023 K and slowly cooled to room temperature, had complete absence of tweed morphology (Figs 7 and 8). Instead, randomly oriented, approximately rectangular phases were visible in the matrix; these phases showed no internal striations on tilting the specimen. EDS analyses revealed that the rectangular phase had higher Cu and lower Pd than the matrix region, and closely corresponded to the composition Pd_6Cu_2Ga.

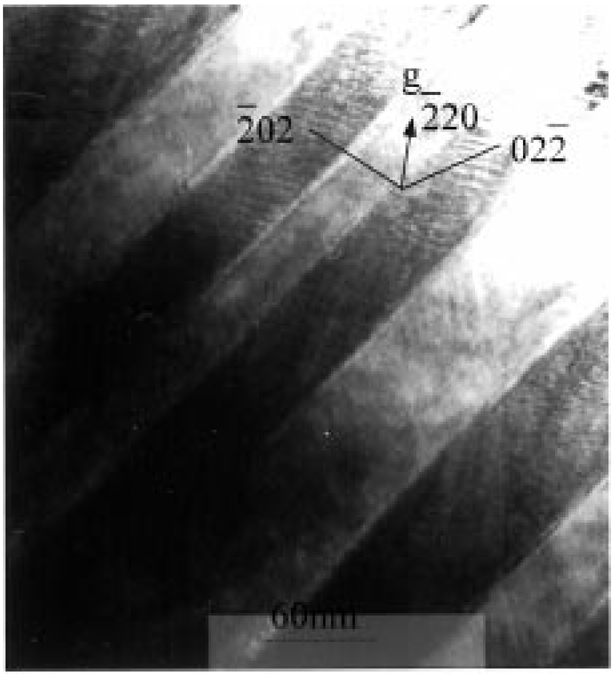

Figure 4 Bright-field image of Liberty specimen aged at room temperature for over 5 years.

Figure 5 Bright-field image of aged Liberty with the same two-beam condition as in Fig. 4, but in a different region of the foil specimen.

4. Discussion

In previous research on the high-palladium alloys [5–7], the nature of the bands in the ultrastructure was not firmly established. The present electron diffraction analysis confirms that these bands have an overall face-

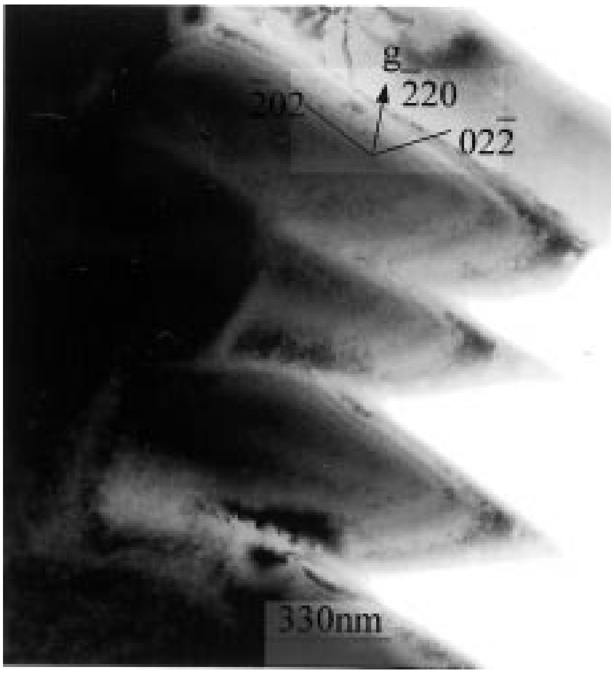

Figure 6 Bright-field image of aged Liberty with the same two-beam condition as in Fig. 5, showing the presence of thin lath-like precipitates.

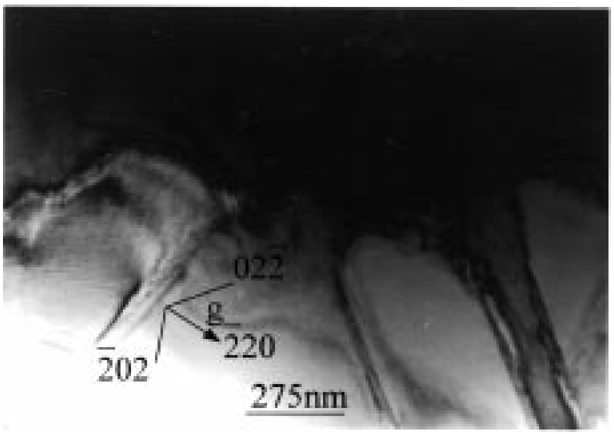

Figure 7 Bright-field image of heat-treated Spartan Plus, showing absence of tweed structure.

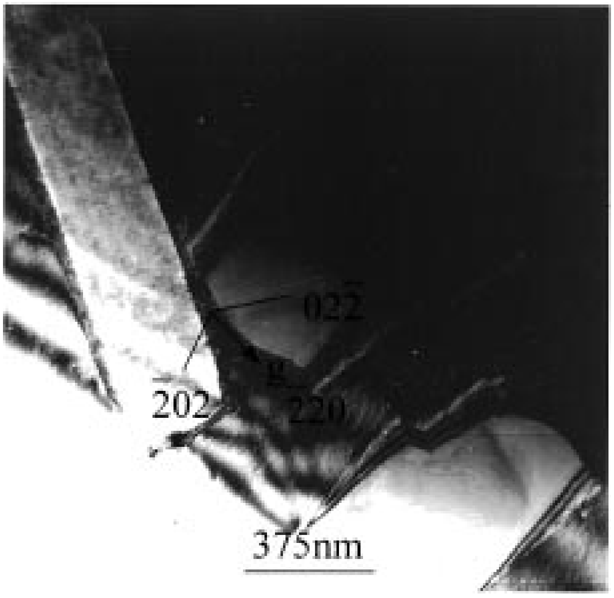

Figure 8 Different region of the specimen in Fig. 7, tilted along the $g_{\bar{2}\,2\,0}$ direction.

centered tetragonal (f.c.t.) structure [7]. The region where no bands are present is face-centered cubic (f.c.c.). Previous experimental results also indicated that the bands and tweed structure formed rapidly after casting or quenching following heat treatment [5, 6].

The present EDS analyses showed that within the limit of experimental error there is no significant difference in composition between the two sets of bands in the ultrastructure of as-cast Legacy, which suggests that it is highly unlikely that the bands are two phases with different c/a ratios as previously proposed [7]. The two sets of bands were found to have identical c/a ratios from both the SAED and convergent-beam patterns. While it is assumed that this result would be found for all high-palladium dental alloys, similar TEM analyses should be performed on other Pd–Cu–Ga alloys and Pd–Ga alloys to verify this hypothesis. The lattice parameter of the palladium solid solution in as-cast Legacy determined from the electron diffraction patterns was 0.386 nm, which agrees well with the value previously found [17] using X-ray diffraction. Short atomic movements required for the formation of a tetragonal structure from the parent f.c.c. structure can be associated with a proposed martensitic transformation of the palladium solid solution [5, 6].

The present study reveals the bands to be 120° microtwins, with a $(\bar{1}\ 1\ 0)$ mirror plane. Twins are a common microstructural feature in f.c.c. metals, and twinning is a significant mechanism to accommodate plastic deformation in tetragonal and h.c.p. crystal structures, since they have fewer slip systems. The shear strain associated with the f.c.c.–f.c.t. martensitic transformation in high-palladium alloys may be easily accommodated by twinning. The 120° twin about a [1 1 1] axis can also be described in terms of a $\Sigma 3$ coincident site lattice [18]. Since the twin boundaries contain a high density of coincident sites, they have very low interfacial energies and hence low activation energy for nucleation. This would then represent a very stable structure, which explains the predominant occurrence of tweed contrast in high-palladium alloys. The tweed bands can be expected to form wherever the martensite nucleates in the solid solution, and the growth process would be enhanced by the low activation energy.

Forbidden reflections or superlattice spots were previously observed in the electron diffraction patterns of high-palladium alloys [5–7]. It was conjectured [5] that the bands were domains of an ordered structure separated by antiphase boundaries (APBs). However, the present study proves that the bands form because of twinning of the ordered f.c.t. structure and are therefore not APBs. The reason for the occurrence of the tweed contrast within the bands is not clear. A one-to-one correspondence between streaks in diffraction patterns and striations in the bright-field image was previously observed in high-palladium alloys [5, 6], and similar tweed contrast was observed in a 63 at % Ni–Al alloy system [8–10], where it was suggested that the striations may be a premartensitic effect. The present tweed striations could arise from small regions of ordered structure within the bands separated by antiphase boundaries or from still finer-scale microtwinning to accommodate the strain energy associated with the f.c.c.–f.c.t. transformation. More TEM research is required to elucidate the exact nature of the striations.

The Liberty specimen aged at room temperature for over 5 years [14] revealed a qualitatively larger amount of the tweed morphology compared to the as-cast sample. The occurrence of randomly oriented bands in this specimen could be attributed to diffusion-based growth of these regions due to aging, with the regions impinging and possibly growing into each other. While such a structure might be expected to show greater hardness than the f.c.c. palladium solid solution due to an increased resistance to dislocation motion, the hardness of aged and as-cast Liberty were not significantly different [14].

Specimens of Spartan Plus, annealed at 1023 K for 2 h and cooled slowly to room temperature, contained a rectangular phase with the approximate composition Pd_6Cu_2Ga. If Cu largely occupies the atomic sites of Ga in the Pd–Cu–Ga alloys, the rectangular phase could correspond to the Pd_2Ga, Pd_5Ga_2 or $Pd_{13}Ga_5$ phase in the revised Pd–Ga phase diagram [19]. Further TEM study is required to determine the composition of this phase unambiguously.

The tweed structure appears to represent a metastable room temperature constituent in these alloys. It is conjectured that the tendency to undergo very fine-scale microtwinning might account for the failure of the tweed structure to serve as a substantial strengthening mechanism, since this ultrastructure is present in both Pd–Cu–Ga and Pd–Ga alloys that differ substantially in hardness [5, 6]. The stability of this structure might be expected to enhance the corrosion resistance and prevent the *in vivo* dissolution of these alloys in metal–ceramic restorations. It was previously found [5] that the high-palladium alloys investigated in this study have excellent *in vitro* corrosion resistance, as measured by anodic polarization in both saline and artificial saliva solutions.

5. Conclusions

The metallurgical structure of three high-palladium dental casting alloys was investigated by transmission electron microscopy (TEM) and convergent-beam electron diffraction. Under the conditions of this study, the following conclusions can be drawn:

1. The bands in the ultrastructure of high-palladium dental alloys are a face-centered tetragonal phase; in the as-cast Legacy alloy, the c/a ratio was approximately 1.03. The lattice parameter of the palladium solid solution found from TEM investigation of the as-cast Legacy alloy was approximately 0.386 nm.
2. Adjacent bands containing the internal tweed structure have the same c/a ratio and are microtwins misoriented by 120° along the [1 1 1] zone axis. The mirror planes separating these bands are $(\bar{1}\ 1\ 0)$ planes.
3. The ultrastructure of the cast Liberty alloy specimen aged 5 years at room temperature shows thin, lath-like regions and some randomly oriented bands containing the tweed structure.
4. After annealing at 1023 K for 2 h and slowly cooling, the cast Spartan Plus alloy contained rectangular precipitates of approximate composition Pd_6Cu_2Ga in the matrix. This phase could be Pd_2Ga, Pd_5Ga_2 or $Pd_{13}Ga_5$, if the Cu atoms are assumed to largely reside on the Ga sites.
5. Further TEM investigation is needed to elucidate the nature of the tweed striations within the bands of the ultrastructure of the high-palladium dental alloys.

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