



Theme: Ceramic, composite and polymeric materials

CARBON NANOTUBE REINFORCED AA6061 ALLOY FOR HIGH STRENGTH-LOW DENSITY STRUCTURAL APPLICATIONS*

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Abstract

High strength-light weight materials are very attractive for the transportation sector, particularly to the aerospace industry. High strength-age hardenable aluminium alloys are widely used in airframes due to their unique combination of strength, density, toughness, corrosion resistance, cost and easy processing. However, the hardening capacity of such alloys is somehow saturated due to thermodynamic issues related to the conventional processing. The production of aluminum-matrix composites is a promising strategy to overcome this limitation, resulting in strength levels that cannot be reached by actual commercial aluminum alloys. In the present work, multiwall carbon nanotubes were used to reinforce the AA6061 aluminium alloy. 1 and 2% weight percent of MWCNT were mixed to the alloy powder by high-energy ball-milling process. The blended powder was consolidated by hot extrusion. The obtained composite bars were submitted to heat treatment for the T6 condition in order to combine both CNT dispersion and precipitation hardening effects. Optical and scanning electron microscopy, as well as hardness testing, was used to characterize the bars. Typical wrought microstructure, free of defects, was observed on the extruded bars. Hardness of the composites was observed to increase by 20, 28 and 68% for 1% MWCNT 6 h milling, 2% MWCNT 6 h milling and 2% MWCNT 10 h milling, respectively, in the as-extruded condition. The better performance for the composites blended at higher milling time was attributed to a better nanotubes dispersion. Subsequent heat treatment to the T6 condition did not result in additional hardening.

Keywords: Carbon nanotubes; Aluminum matrix composites; AA6061 alloy; Powder metallurgy.

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1 INTRODUCTION

Over the past seventy years, aluminum alloys have dominated the market for the aerospace industry, due to a set of intrinsic properties and characteristics, as mechanical and corrosion strength, low density, easy processing and moderate cost. However, in the latest decades, the strength level of the commercial Al alloys seems to be stalled at around 600 MPa of ultimate strength, and conventional thermo-mechanical processing seems to be unable to reverse this picture.

Carbon nanotubes (CNT) is an emerging and promising class of material, exhibiting very interesting properties, among them, high strength and elastic modulus [1,2]. With nanometer dimensions, carbon nanotubes can be added to a set of ductile metallic materials in order to increase their strength by several mechanisms: stress fields at the metallic reticulate, Orowan, and the classic load-transfer mechanism of composite materials [3]. However, as their dimensions are nanometric, van der Waals forces promotes their agglomeration and make very challenging their homogeneous dispersion in composite materials.

High energy ball milling (HEBM) has been the most used route to produce CNT reinforced aluminum matrix composites (CNT-AMC), although the energy of the process could be deleterious to the reinforce phase integrity. Fragmentation and amorphization are the main risks to which HEBMilled CNT are subject [4]. However, it is believed that the ductile aluminum particles can hold the CNT particles at initial milling stages, protecting them from direct impacts from the milling media. As a result, several authors have reported success on CNT dispersion in aluminum by this process, keeping their structural integrity [5-8]. The final consolidation of the composites produced by HEBM can be obtained by several processes: hot extrusion, cold or hot pressing followed by conventional sintering, spark plasma sintering, cold or hot milling and plasma spraying are examples.

Most of the literature regarding the production of CNT-AMC is related to pure aluminum and a maximum of 5% by weight of the reinforcing phase [5-6,8,9-15]. Few works are related to precipitation hardenable aluminum alloys, more specifically to AA2024 [7,16-17], and the combined effect of precipitation hardening and CNT to the composite strength is rarely evaluated. Kondoh and co-workers [18] investigated the effect of the heat treatment on the AA6063 alloy reinforced by multi wall carbon nanotubes (MWCNT) produced by spark plasma sintering and hot extrusion, and observed that after aging to T6 condition both yield and ultimate tensile strength decreased, when comparing to the as-extruded condition. The authors argue that Mg matrix depletion, as a consequence of Al_2MgC_2 , MgO and/or $MgAl_2O_4$ formation around nanotubes, are responsible for the unsuccessful heat treatment. Less Mg atoms would be available for Mg_2Si hardening precipitation.

In the present work, the effect of 1 and 2 % (in weight) of MWCNT reinforcing AA6061 AMC was evaluated by microhardness measurements, in the as extruded condition and after solution heat treatment followed by natural and artificial aging (T4 and T6 tempers, respectively). Optical and scanning electron microscopy were also employed to assess the microstructural development. AA6061 bars with no MWCNT reinforcement were also produced by the same processing route, for comparison purposes. It was found that the hardness was significantly increased after the addition of MWCNT to the alloy, in the as-extruded condition. However, subsequent heat treatment did not provide additional hardening for both unreinforced and reinforced material, when comparing to the as-extruded condition. Possible reasons for such behavior are discussed.

2 MATERIAL AND METHODS

AA6061 alloy powder, produced by inert gas atomization by ALPOCO – United Kingdom and having particles lesser than 50 μm , was employed in the present work. The nominal chemical composition of the alloy that complies with AMS-QQ-A-200/8 specification [19], is shown in Table 1.

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Table 1. Nominal chemical composition of AA6061 alloy used in the present work

| Element | Weight % |
|---------|----------|
| Si | 0,45 |
| Mg | 0,96 |
| Cu | 0,27 |
| Cr | 0,16 |
| Fe | 0,15 |
| Mn | 0,0023 |
| Al | Bal |

Bundles of MWCNT (Baytubes® C150P) produced by chemical vapor deposition process by Bayer Materials Science – Germany, with a minimum purity level of 95%, were employed as reinforcing phase. Figure 1 shows a transmission electron micrography of a typical isolated nanotube, where an aspect ratio of around 100 can be observed.

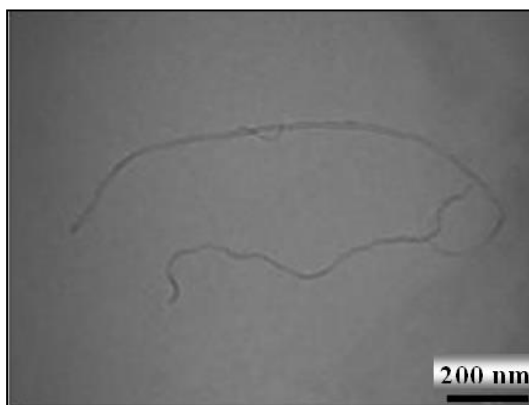


Figure 1. Aspect of isolated Baytubes® C150P, after ultrasonically assisted dissolution in acetone. For observation at the microscope, the MWCNT were captured from the solution by a carbon film covered Cu grid.

The AA6061 powder and the MWCNT were blended into a planetary ball mill Retsch PM4 in air atmosphere, using 250 cm³ stainless steel vials and 20 mm diameter hard steel balls. A ball to powder ratio of 10:1 at 200 RPM were employed and 0,5% in weight of stearic acid was employed as the process control agent (PCA). Composites having 1 and 2% in weight of MWCNT were produced. For comparison purpose, bars without reinforcement were also produced employing the same milling conditions. Milling times of 6 and 10 h were employed. For the composite milled for 10 h, the aluminum powder, bundles of MWCNT and PCA were simply loaded into the vials. For the composite milled for 6 h, a special mixing procedure was performed before loading into the milling vials. MWCNT was previously dispersed into acetone for 0,25 h under sonication. The AA6061 powder was added to this suspension with additional sonication for 0,25 h. The mixture was subsequently heated under magnetic agitation until a thick slurry was obtained. Final drying at 50°C for 24 h was performed before adding the mixture to the milling vials, with the PCA and balls. The Table 2 resumes the main process parameters employed to obtain the composite powders.

Raman spectroscopy was performed on samples containing 2% of MWCNT in order to assess their structural quality after milling, when comparing to the pristine condition. A micro-Raman Renishaw microscope system 2000, employing an argon laser (514.5 nm wavelength) was employed on this characterization.

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The powders obtained in the HEBM process were encapsulate into clean aluminum tubes and extruded at 450°C at 2 mm/s and an extrusion rate of 28:1, resulting in 8 mm diameter bars.

Samples from the bars were cut, degreased and submitted to heat treatment according to SAE-AMS2772E specification [20]. Solution heat treatment was performed in air by heating at $530 \pm 5^\circ\text{C}$ for 1 h and quenched in water. For T4 temper, solubilized samples were allowed to age at room temperature for 96 h minimum. For T6 temper, T4 samples were aged at $175 \pm 5^\circ\text{C}$ for 8 h and cooled in air.

Metallographic examination was performed on samples in the as-extruded, T4 and T6 conditions. The samples were prepared by conventional grinding procedures and polishing with diamond past and colloidal silica suspension. Samples were observed in an Olympus BH-2 optical microscope and in a Hitachi S-4800 FEG scanning electron microscope, equipped with EDS microanalysis. Vickers microhardness tests using load of 1 kg applied for 10 s were performed on the samples. A total of 5 measurements were performed in each sample, and the highest and lowest values were discarded. Results were expressed as the average of the 3 remaining values.

Table 2. Milling conditions employed for the production of composites

| Sample | %MWCNT | MT | SM | RPM | B/P ratio |
|---------------|--------|------|-----|-----|-----------|
| 6061-NR-6h | - | 6 h | yes | 200 | 10:1 |
| 6061-1CNT-6h | 1,0 | 6 h | yes | 200 | 10:1 |
| 6061-2CNT-6h | 2,0 | 6 h | yes | 200 | 10:1 |
| 6061-NR-10h | - | 10 h | no | 200 | 10:1 |
| 6061-1CNT-10h | 1,0 | 10 h | no | 200 | 10:1 |
| 6061-2CNT-10h | 2,0 | 10 h | no | 200 | 10:1 |

NR= no reinforcement; %MWCNT in weight; MT= milling time; SM= Special mixing procedure of the powders before milling; B/P= balls to powder ratio

3 RESULTS AND DISCUSSION

The powders obtained after milling presented and homogeneous aspect and did not stick to the vials or the balls, showing that the amount of PCA added to the process was satisfactory. Raman spectroscopy presented in Figure 2 shows that typical D and G bands are present in all conditions. As the D band is frequently related to structural disorders of carbon based materials, the D to G band intensity ratio (ID/IG) is commonly used to monitor induced defects during nanotubes processing [21-22]. From Lorentzian fitting of the peaks, it seems that ID/IG ratio slight increase at milled samples (around 1,10), when comparing to the pristine condition (1,05), showing that small structural disorders are introduced to MWCNT during milling. It is also observed the presence of a shoulder at the right side of the peak of the pristine spectrum. This shoulder evolves to a more defined peak at around 1620 cm^{-1} as the milling time increases, and can be attributed to the D' band originate from a double resonance processes. The small increase of ID/IG observed suggests that MWCNT were minimally damaged during the HEBM process.

Figure 3 shows the microstructure of the sample 6061-2CNT-6h in the as-extruded condition. This microstructure is typical for all as-extruded bars, and is similar to the microstructure of un-recrystallized wrought commercial products. Insoluble precipitates consisting mainly of $\text{Fe}_3\text{SiAl}_{12}$ and Mg_2Si [23] are visible, aligned with the extrusion direction. In 3A few bigger particles are observed. Higher magnification in 3B enables to identify extrusion flux lines around such particles, suggesting some

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sort of contamination probably from the milling media. Figure 4 shows the microstructure of the sample 6061-2CNT-10h in T4 condition, that is representative for all bars at both T4 and T6 heat treated conditions. This microstructure shows great similarity with the bars in the as-extruded condition, although visible $\text{Fe}_3\text{SiAl}_{12}$ and Mg_2Si precipitates seem to be less abundant. This is consistent with the heat treated condition that dissolves much of these precipitates that re-precipitates in a smaller size during aging. From Figure 4, it is also possible to verify some voids arising after heat treatment. These voids, indicated by arrows at the Figure 4, are aligned to the extrusion direction and can result from the expansion of entrapped gases, during solution heat treatment.

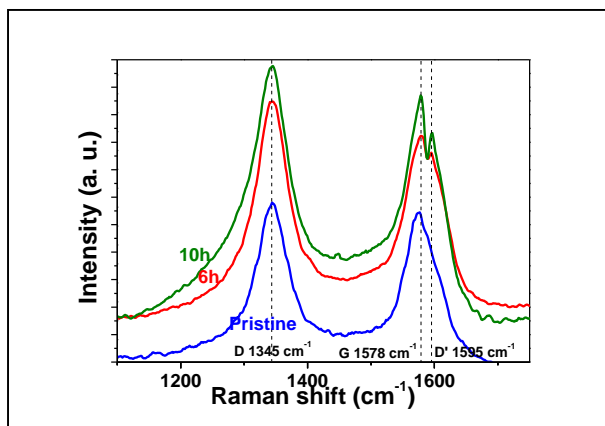


Figure 2. Raman spectroscopy of the samples containing 2% (weight) of MWCNT, after milling for 6 and 10 h. A spectrum from the isolated nanotubes in the as-received condition is also presented for comparison purpose.

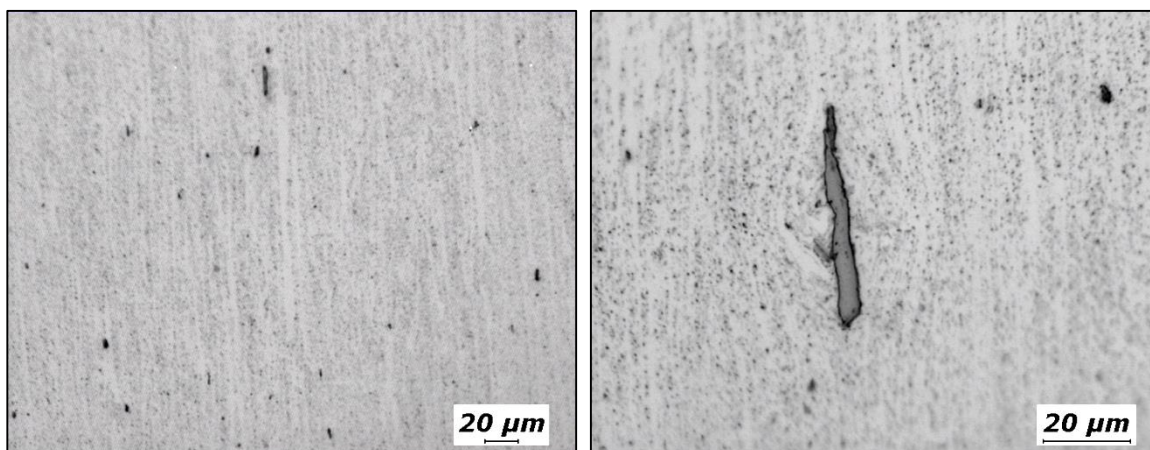


Figure 3. Optical micrographs of samples containing 2% of MWCNT milled for 6 h (6061-2CNT-6h), in the longitudinal as-extruded condition: 3A- overall aspect showing fine precipitation; 3B- higher magnification showing extrusion lines around a bigger particle.

Scanning electron microscopy performed on the sample 6061-NR-6h shows in detail (Figure 5) one particle that is similar to the bigger particles mentioned in the Figure 3B. Quantitative microanalysis performed resulted in a composition similar to 3XX series austenitic stainless steel, confirming that such particles are contaminants from the milling media (vials).

The results from microhardness testing performed on samples in the as-extruded, T4 and T6 conditions are presented in Table 3 and Figure 6. It can be easily observed the contribution of MWCNT additions to the hardness of the bars. This contribution is

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higher as the CNT content increases from 1 to 2% in weight. The increase of the hardness with the milling time is observed only in the composite bars. It seems that a better dispersion of MWCNT is obtained as the milling time increases from 6 to 10 h, resulting in better properties. When compared to un-reinforced bars, the hardness of the samples 6061-1CNT-6h, 6061-2CNT-6h, 6061-1CNT-10h and 6061-2CNT-10h, increased by 20, 30, 57 and 68% respectively. This increase is remarkable, but surprisingly, after heat treatment, an additional contribution from precipitation hardening could not be observed at T4 and T6 conditions for any sample. In some cases, the hardness even decreased after heat treatment. Similar behavior has been observed for AA6063 alloy [18], but only when reinforced by CNT. In this reference work, the composites were not produced by HEBM as in the present work. It seems that microstructural benefits resulted from HEBM as strain hardening and/or the development of a subgrain structure [24] that could manifest in the as-extruded condition could be lost during solution heat treatment, which could compensate the precipitation hardening obtained by heat treatment. Furthermore, the presence of hard reinforcing phases in ductile matrices generates internal stresses [25] that can accelerate the precipitation kinetics. High defects concentration produced by HEBM process [24] can account for similar behavior, due to the higher concentration of favorable nucleation sites for precipitates. Under such conditions, heat treatment procedures applicable to commercial alloys that are produced by conventional thermo mechanical processing, could lead to overaging of the composites produced by HEBM.

As far as precipitation hardening in HEBM processed materials is concerned, the literature also point out that the grain refinement reduces the potential for precipitation hardening in some alloys [3,25-26]. In this case, when the grain becomes too small, the volume of the grains (were precipitation would be effective for hardening) diminishes in comparison to the grain boundary area. As a consequence, precipitates could form at grain boundaries, were precipitation is more favorable, but less effective for hardening. This is another aspect to be investigated in order to assess the behavior of CNT reinforced aluminum alloys produced by HEBM during subsequent precipitation hardening heat treatments.

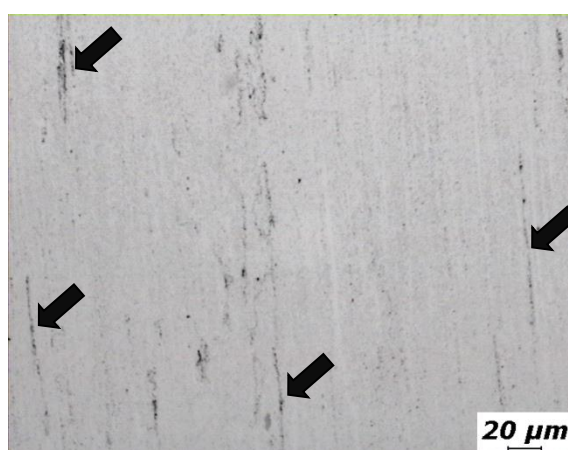


Figure 4. Optical micrograph of sample containing 2% of MWCNT milled for 10 h (6061-2CNT-10h), in the longitudinal T4 condition. Some of the voids originating after solution heat treatment are indicated by arrows.

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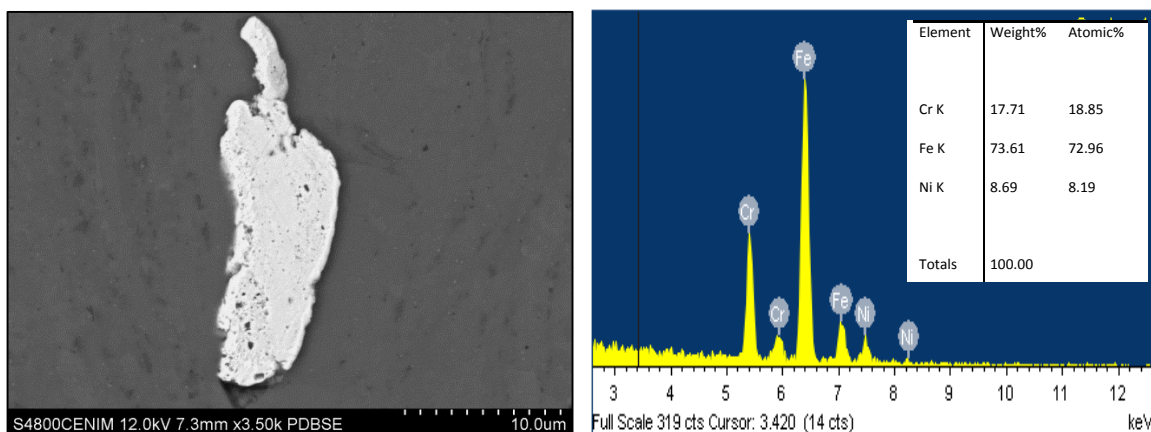


Figure 5. Scanning electron micrograph of the sample 6061-NR-6h, in the longitudinal as-extruded condition. The particle in the center of the micrograph refers to stainless steel contamination from the milling vials, as confirmed by EDS microanalysis in the left.

Table 3. Vickers microhardness values obtained in the bars, in AE, T4 and T6 conditions

| Sample | AE | T4 | T6 |
|---------------|-------------|-------------|-------------|
| 6061-NR-6h | 72,3 ± 3,1 | 54,7 ± 6,1 | 71,7 ± 2,9 |
| 6061-1CNT-6h | 86,0 ± 3,5 | 68,7 ± 3,6 | 75,3 ± 4,9 |
| 6061-2CNT-6h | 93,3 ± 0,6 | 79,0 ± 4,6 | 79,3 ± 3,8 |
| 6061-NR-10h | 69,7 ± 1,9 | 53,5 ± 4,1 | 61,5 ± 4,3 |
| 6061-1CNT-10h | 113,5 ± 4,4 | 100,3 ± 3,2 | 103,3 ± 6,2 |
| 6061-2CNT-10h | 121,3 ± 1,2 | 119,7 ± 0,6 | 113,7 ± 3,1 |

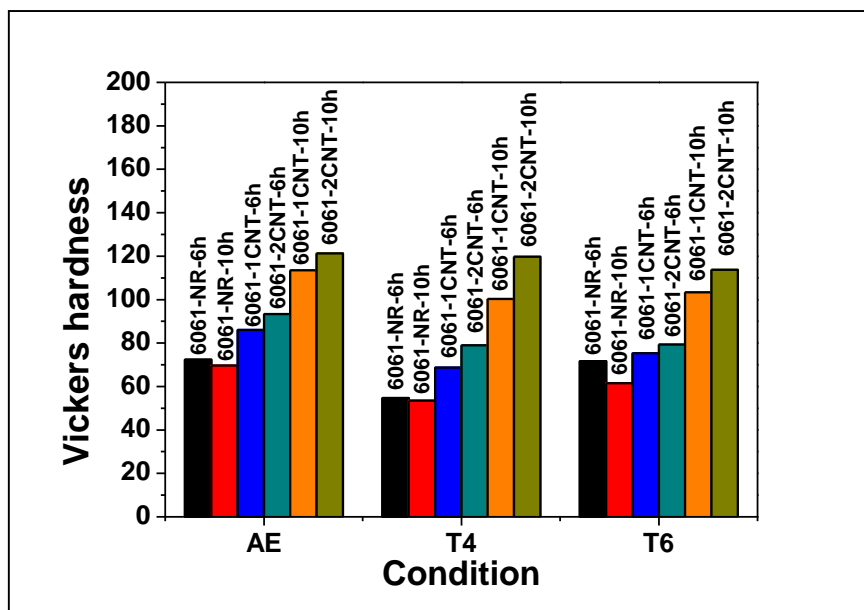


Figure 6. Microhardness measurements of the composite and non-reinforced bars produced, at the as-extruded, T4 and T6 conditions.

4 CONCLUSION

AA6061 alloy reinforced by MWCNT composites were successfully produced by HEBM – hot extrusion processing route. The benefits of MWCNT to the alloy strength, as verified by microhardness measurements, were remarkable. Vickers hardness increased by 20 and 30% with additions of 1,0 and 2,0% of MWCNT (in weight) respectively, when comparing to the unreinforced alloy produced by the same route.

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The benefits were even higher when the milling time was increased from 6 to 10 h, resulting in hardness increments by 57 and 68% for the same MWCNT additions. A better dispersion of nanotubes is supposed to occur with the higher milling time, resulting in higher strength of the composite.

The combination of MWCNT dispersion and alloy precipitation to the composite hardening was not observed in the present work, at least with the heat treatment procedure recommended for the commercial alloy. It seems that microstructural benefits arising from HEBM process could be lost during solution heat treatment, mainly for long periods (1 h in the present work). Furthermore, both the precipitation kinetics and grain boundary precipitation could be accelerated in fine grain HEBM composites, making conventional heat treatment procedures of commercial alloys inapplicable for such materials. However, the strength level reached in the as-extruded condition is already very promising for structural applications.

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