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Abstract: Nano-sized hafnium carbide was synthesized from organic-inorganic hybrid polymer based on polycondensation and carbothermal reduction reaction from pectin and hafnium tetrachloride followed by thermal treatment. Orthorhombic and monoclinic hafnia formed on pyrolysis which above 1300 oC transformed to hafnium carbide. Conversion of amorphous to crystalline hafnia was initiated at ~800 oC while the endothermic carbothermal reduction reaction started at ~1275 oC. Total yield of hafnium carbide was ~62%. The resulting carbide powders are equiaxed with narrow size distribution of crystallite size ~50 nm. SEM and EDX mapping confirm the uniform distribution of Hf and C. The high ceramic yield, uniform size particles, and simplicity of the process make it a promising route for polymer infiltration pyrolysis of carbon fibre/ultra high temperature composites.

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Reply to Reviewers

We wish to thank the Reviewer for the work of carefully reading the manuscript and pointing out some issues, which we could thus fix according to him/her recommendation, as described in the following.

In the revised manuscript, we have added/rearranged some explanation in the original manuscript in order to clarify the referee doubts. The list of changes and answer of reviewer comments hereafter are given below:

Reviewer #1:

The use of pectin in the synthesis of HfC is an interesting approach and also the low temperature synthesis could be convenient for the further development and cost reduction. Therefore, this article can be acceptable after minor reviews:

Q1. In the experimental section, authors must provide the Pectin to HfCl₄ ratio.

A1. Thanks to the reviewer for pointing out that. We have now inserted the ratio that is 1:4 of Hafnium tetrachloride and pectin in the experimental section.

Q2. Provide the heating rate used for pyrolysis study (Line no. 12).

A2. We have now provided the heating rate used in the pyrolysis process.

Q3. Line no. 36, argon flow rate used TG-DTA study.

A3. We have now provided the argon flow rate in the experimental section.

Q4. Authors mentioned about the endothermic peak at 165 °C (line no. 41) whereas, in the figure 2, it is labelled at 156 °C.

A4. We have now corrected it to 156 °C.

Q5. Reference needed to support the sentence, "DTA analysis reveals that the formation temperature of HfC by this method (<1500 °C) is lower than the conventional solid state synthesis which is above 1800 °C". (line no. 46-53).

A5. We have now put a reference to support this.

Q6. Line no. 36, mentions about the deconvolution peaks "are deconvoluted at 295, 563 and 724 °C", whereas in the figure 3, the first peak is at 360 °C rather than 295 °C.

A6. Thanks to the reviewer. We have now corrected it.

Low-temperature synthesis of nanosized hafnium carbide using pectin by solution processing route

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Abstract

Nano-sized hafnium carbide was synthesized from organic-inorganic hybrid polymer based on polycondensation and carbothermal reduction reaction from pectin and hafnium tetrachloride followed by thermal treatment. Orthorhombic and monoclinic hafnia formed on pyrolysis which above 1300 °C transformed to hafnium carbide. Conversion of amorphous to crystalline hafnia was initiated at ~800 °C while the endothermic carbothermal reduction reaction started at ~1275 °C. Total yield of hafnium carbide was ~62%. The resulting carbide powders are equiaxed with narrow size distribution of crystallite size ~50 nm. SEM and EDX mapping confirm the uniform distribution of Hf and C. The high ceramic yield, uniform size particles, and simplicity of the process make it a promising route for polymer infiltration pyrolysis of carbon fibre/ultra high temperature composites.

Keywords: Hafnium carbide; Pectin; Precursor; Carbothermal reduction

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1. Introduction

Hafnium carbide (HfC) has a high melting point ($>3900\text{ }^{\circ}\text{C}$), high hardness ($\sim 28\text{ GPa}$), high wear resistance, low vapour pressure, low electrical resistivity ($\sim 40\text{ }\mu\Omega\cdot\text{cm}$) and high chemical stability[1–4] which makes it a promising candidate for ultra-high-temperature applications in extreme environments in such as occur in hypersonic flight and rocket propulsion[1,2,5,6].

HfC powder can be prepared by different methods including solid state combustion[7], carbothermal reduction of metal oxides[8], vapour phase synthesis[9], sol-gel[10], laser and plasma chemical synthesis[11]. Since most carbides are conventionally made by sintering of powders, their properties depend to a great extent on the quality of the starting powders. However, due to the high temperature nature of the carbothermic process, the carbide produced has a relatively large particle size (e.g. micrometre scale) leading to micropore formation ($\sim 15\%$) during densification[12]. The processing routine could be simplified to improve sinterability by reducing the HfC powder particle size to nanometre scale thus increasing the surface free area. A simple, scalable, low temperature, non toxic technique is thus needed to synthesize HfC nanoparticles.

In carbon fibre/ultra-high-temperature ceramics (C/UHTCs) composites different techniques have been used to introduce UHTCs particles to the carbon fibre e.g. chemical vapour infiltration[13], reactive melt infiltration[14], slurry impregnation[15]. However, these processes have some disadvantages of inhomogeneous dispersion in the composites, especially the intra bundle areas of composites. Again, the volume content of the UHTCs is limited for the blocking effect of the fibre to the particles. Thus, the use of organometallic preceramic polymer liquid precursor route for UHTCs is a promising approach, as this technique allows improving homogeneous distribution of UHTCs particles in the composites, lower processing temperatures,

uniform and fine grain size distribution[16,17]. This technique can yield near net structures with complex shape and large size along with coating the UHTCs powder on every single individual carbon fibres.

Pectin is a galacturonic acid rich natural, non-toxic, inexpensive, amorphous and abundantly available polysaccharide. It is an eco-friendly candidate for biodegradable applications. Pectin is commonly used in the food industry as a gelling and stabilizing agent. The present study focused on synthesis of hafnium carbide using pectin as the source of carbon and chelation followed by carbothermic reduction. This technique offers some advantages compared to conventional powder processing techniques, such as lower reaction temperatures and shorter reaction times which is due to the intimate contact of the polymer with the organometallic salt[17]. This process reduces the kinetic barriers between the formed metal oxide and the carbon particles created in pyrolysis of metal alkoxide polymer due to the atomic level mixing of reactants in the precursor material. Pectin macromolecules allow uptake of several metal via electrostatic ion interaction. Pectin metal salt complexes are promising precursors for hafnium carbide because of its excellent metal ion chelation. The objective of this work is to explore a simple solution based method using a natural material to synthesize bulk hafnium carbide powder with uniform and fine nanoparticles using the cheapest hafnium salt and pectin as starting materials.

2. Experimental

Hafnium tetrachloride (HfCl_4) and pectin from citrus peel obtained from Sigma-Aldrich Company Ltd, Dorset, UK were used as the starting materials in the synthesis of HfC .

The pectin/hafnium complex (P/Hf) was prepared by dissolving pectin in distilled water with continuous magnetic stirring at 40 °C. Appropriate amount of HfCl_4 was added to the pectin

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4 solution ratio of (1:4) hafnium tetrachloride and pectin. The solution mixture was stirred for 3 h
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6 at 40 °C. All samples were pre-dried at 110 °C for 24 h in an oven to remove water and crushed
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8 to powder in a glass mortar. The crushed powder was further heated for 30 mins at 200 °C under
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10 vacuum to promote cross-linking of the precursor and volatilisation of solvent. Finally, pyrolysis
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12 was carried out from 30 to 1550 °C at a heating rate of 10 °C.min⁻¹ under controlled flow of argon
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14 (99.99% purity, 50 mL.min⁻¹) in a tube furnace in order to avoid oxidation. The dwell time was
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16 given at 1550 °C for 1 hour. Synthesized pectin and hafnium tetrachloride complex was coded as
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18 P/Hf. In P/Hf-110 °C, 110 °C represents the drying temperature of the P/Hf complex in air
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20 whereas in P/Hf-200 °C, the 200 °C represents the drying temperature of the sample under
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22 vacuum.
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29 Fourier transform infrared spectra (FT-IR) of pectin, hafnium tetrachloride and the complex
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31 of P/Hf were acquired in the range of 4000–400 cm⁻¹ in attenuated total reflection mode using a
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33 Nicolet iS10 instrument from Thermo scientific FT-IR spectrometer Company Ltd, Waltham.
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35 USA. All spectra were baseline corrected and normalized thereafter to the highest peak. Thermal
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37 analysis was carried out in a simultaneous thermogravimetry-differential thermal analyzer (TG-
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39 DTA, NETZSCH STA 449 F1 Jupiter, Selb, Germany) under argon (flow rate 60 ml/min) as well
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41 as in air at a heating rate of 10 °C min⁻¹. X-ray diffraction (XRD) patterns were obtained using a
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43 computer controlled (PANalytical Xpert³ diffractometer, Cambridge, UK) X-ray diffractometer
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45 using Cu K α 1 radiation (λ =1.540598 Å). The X-ray tube was operated at 40 kV, 40 mA with
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47 scanning at a step width of 0.030 (2 θ). The crystallite sizes were determined from the broadening
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49 of the XRD diffraction lines using the Scherrer equation. The lattices calculated from all the
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51 major peaks have been fitted according to Nelson and Riley function (a_0 Vs $\cos^2 \theta / \sin^2 \theta + \cos^2$
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53 θ / θ) and the intercept is the precise lattice parameter. The morphology of the HfC was observed
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under a SEM (JEOL JSM 6010 LA, Tokyo, Japan) using secondary electron imaging. Semi-quantitative energy dispersive X-ray analysis (EDX) was used for mapping the elements of the powder.

3. Results and Discussion

FT-IR spectra of starting materials (pectin and hafnium tetrachloride) and the synthesized P/Hf complex powders dried in two different conditions (Fig. 1a-b) were obtained in order to understand the structural changes and the principal interactions between pectin and the metal ion. In the FTIR spectra for the as-received pectin (Fig 1a), the broad ($\nu(\text{O-H})$) stretching band at 3352 cm^{-1} ; a small intensity ($\nu(\text{C-H})$) band at 2930 cm^{-1} ; and the peaks at 1747 , 1649 , and 1452 cm^{-1} in the carboxylic group region are assigned to ($\nu(\text{C=O})$) stretching of methylated carboxyl groups to antisymmetric and symmetric stretching modes of ($\nu(\text{COO}^-)$), respectively. The vibrations at 1149 , 1106 , 1043 , 1013 and 954 cm^{-1} correspond to skeletal ($\rho(\text{C-O})$) and C-C bands of glycoside bonds and a pyranoid ring. For hafnium tetrachloride, the respective assignments for the broad vibration band between 3328 cm^{-1} is associated with the ($\nu(\text{O-H})$) stretching of water molecules (physisorbed molecular water) while a small band at 3146 cm^{-1} is assigned to ($\nu(\text{C-H})$). The band at 1590 cm^{-1} corresponds to the bending vibration of water molecules coordinated to the cations[18]. Evident differences of FTIR spectra between the P/Hf complexes and pectin (organic ligands) are revealed (Fig 1b) when the ligands of pectin coordinate to hafnium. For the hybrid complex P/Hf-110 °C (Fig 1b), the characteristic peaks assigned to $\nu(\text{O-H})$ get broader and stronger indicating that O-H participates in forming the hybrid complex. When pectin chelates to hafnium a cyclic structure forms. Therefore, the peaks of $\nu(\text{C=O})$ and $\nu(\text{C=C})$ located at 1737 and 1615 cm^{-1} shift to lower wave numbers. For the hybrid complex P/Hf-200 °C in vacuum which is analogous to the conditions of pyrolysis, the

$\nu(\text{C}=\text{O})$ absorption peak of pectin disappears, leaving the strong peak of $\nu(\text{C}=\text{C})$. These results indicate that the $\nu(\text{C}=\text{O})$ absorption peaks display significant red shifts after hafnium ion chelation, suggesting that the $-\text{CO}-$ group takes part in the complexation. The peak at about 660 cm^{-1} $\nu(\text{Hf}-\text{O})$ appears due to ring distortion in FTIR.

Fig 1. FTIR spectra of (a) as-received pectin and HfCl_4 , (b) hybrid complex (P/Hf) after drying at $110\text{ }^\circ\text{C}/\text{air}$ and crosslinking at $200\text{ }^\circ\text{C}/\text{vacuum}$.

Thermogravimetric analysis has been used to investigate the decomposition, stability, purity and yield by various investigators[17,19–23]. Fig 2 shows the TG-DTA curves of P/Hf complex obtained in argon atmosphere from 30 to $1550\text{ }^\circ\text{C}$. TG analysis of the complex shows a considerable weight loss of $7\text{ wt\%}$ occurs up to $\sim 200\text{ }^\circ\text{C}$ due to the evaporation of physisorbed water. The sharp decrease in mass (20%) up to $500\text{ }^\circ\text{C}$ is due to decomposition of the sugars from pectin resulting in carbon formation. The mass loss tends to be stabilised after $500\text{ }^\circ\text{C}$. A small change in mass ($\sim 3\%$) occurred in the hybrid complex from 500 to $1250\text{ }^\circ\text{C}$ due to evaporation of organic/inorganic impurities. The final mass loss started at $\sim 1300\text{ }^\circ\text{C}$ due to the carbothermal reaction being initiated to form hafnium carbide. The thermal history of the hybrid complex was examined by DTA. An apparent endothermic peak at $156\text{ }^\circ\text{C}$ was observed in the DTA curve due to water evaporation. A broad endothermic peak appeared for the hybrid starting at $300\text{ }^\circ\text{C}$ to $700\text{ }^\circ\text{C}$ due to formation of $\text{Hf}-\text{O}$. The carbothermal reaction started at $\sim 1275\text{ }^\circ\text{C}$ with a clear endothermic peak which ends at $1500\text{ }^\circ\text{C}$. DTA analysis reveals that the formation temperature of HfC by this method ($<1500\text{ }^\circ\text{C}$) is lower than the conventional solid state synthesis which is above $1800\text{ }^\circ\text{C}$ [2].

Fig 2. TG-DTA curve of the dried synthesized P/Hf hybrid complex in argon.

To further examine the particle size distribution and homogeneity, TG analysis of the HfC powder obtained at 1550 °C was performed as in the studies of Roebuck et al. and others[17,24] who explain that the cubic transition metal carbides show a lower and smaller oxidation range when the particles are small (e.g. nanometre size) and homogeneous. The oxidation behaviour of the HfC powder synthesized at 1550 °C was studied using TG-DTA in flowing air (Fig. 3). TG reveals that the onsets of oxidation starts at ~220 °C with an increase in mass of 12% at 620 °C and then decreases by ~6.6% at 760 °C. However, for commercial HfC powder (<1.5 µm), the onset of oxidation start at 300 °C and was relatively rapid with 11.1% mass gain as observed by Epshteyn et al.[25]

The oxidation of our synthesized sample starts over a narrow and relatively low temperature range indicating homogeneous grain size distribution of the HfC powder. However, the oxide polymorph (HfO₂) transformation temperature (1600 °C) is higher than ZrO₂ which is 1050 °C[2]. DTA reveals overlapped broad bimodal exothermic peaks due to a multistep process which are deconvoluted at 360, 563 and 724 °C (Fig. 3) with maximum mass increase from 360 and 563 °C. The exotherm at 563 °C is due to oxidation of the Hf component of HfC with formation of carbon and HfO₂, hence the increase in mass. The exotherm at 724 °C is associated with CO₂ evolution by combustion of free carbon resulting in a mass loss[26]. The mass loss for the synthesized nano HfC powder sample at temperatures above 600 °C was much more rapid, and by 1200 °C it was 7%. The mass loss at higher temperatures was due to the conversion of HfO₂ to HfO, which is more stable at higher temperatures[27]. Oxygen loss is significantly more rapid at

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4 higher temperatures in the nanopowder sample than in the commercial hafnium carbide because
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6 of the nanoparticle size of the produced HfO_2 .
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10 Fig 3. TG and DTA of oxidation of HfC obtained after 1 h heat treatment at 1550 °C in air.
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13 XRD of powders heat treated at different temperatures is plotted in Fig. 4 revealing increase
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15 in crystallinity with increasing temperature and that 1000 °C is sufficient to form crystallized
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17 monoclinic hafnia with minor orthorhombic hafnia. At 1200 °C, the orthorhombic hafnia
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19 transforms to monoclinic HfC revealed at 1300 °C along with some monoclinic hafnia. Upon
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21 increasing the temperature to 1400 °C, HfC peaks become predominant and no other secondary
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23 phase is seen at 1550 °C. The complete conversion to HfC is due to the atomic level mixing of
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25 the powder synthesis route used, giving better contact of hafnium with carbon and thus making
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27 the diffusion path much shorter. On the other hand, the crystallite size of HfC powder obtained
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29 after 1h at 1550 °C was calculated applying Scherrer equation. The X-ray lines broadening for all
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31 peaks corresponding to HfC was taken into consideration while performing this calculation. The
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33 average crystallite size of HfC is 57.5 nm with a standard deviation of 2.97 nm. The lattice
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35 parameter of cubic HfC calculated from XRD patterns is given in Fig 5. The calculated lattice
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37 parameter was 4.63015 Å. The lattice parameter is almost the same as the reported value of
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39 (4.6377 Å) in the JCPDS database (JCPDS No. 39-1491).
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47 Fig 4. XRD of the pyrolyzed hybrid precursors for HfC at different temperature in flowing argon.
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50 Fig. 5. Estimate of lattice parameter of HfC powder heated at 1h at 1550 °C using Nelson-Riley
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52 extrapolation function.
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4 An SEM image and corresponding EDX (X-ray dot maps) from HfC powder obtained after
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6 1h at 1550 °C are shown in Fig. 6. HfC powder exhibits uniform particle size in the range of 300–
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8 600 nm. As shown in Fig. 6, only Hf (Fig 6c) and C (Fig 6d) with a trace of O are detected using
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10 EDX analysis, indicating that the precursor has almost completely been transformed into HfC
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12 which is in strong agreement with XRD analysis (Fig 4). The elements Hf and C were well
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14 distributed in the HfC powder indicating the powder is homogeneous.
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21 Fig. 6. (a) SEM image, (b) EDX cumulative spectrum of the same area, and (c) Hf and (d) C
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23 distribution maps in HfC powder obtained after 1 h heat treatment at 1550°C in argon.’
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29 **Conclusions**

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32 Nanosized hafnium carbide was obtained from hafnium chloride and pectin by carbothermal
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34 reduction. Hafnium carbide formation started at ~1300 °C. Formation of hafnium carbide
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36 increased on increasing temperature. The onsets of oxidation begin at ~220 °C, and ended at ~620
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38 °C with a 12 % increase in mass. The ceramics yield was ~62 wt%. The low temperature, non-
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40 toxic starting materials pectin which is having ‘excellent ability of metal ion chelation and
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42 controlled morphology’ makes it suitable precursors for polymer infiltration pyrolysis. The added
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44 incentive of this work is the utilization of natural resources for the realization of materials with
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49 excellent properties.
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51 **Acknowledgement**

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54 contract number N62909-13-1-N055 is gratefully acknowledged.
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