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Improvement of tribological properties of titanium by DMGN

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Abstract

Tribological of 99.70% titanium was improved in ammonia at 1,000, 1,050 and 1,100 °C for 2, 6 and 10 h by direct metal-gas nitridation (DMGN). The flow rate of ammonia was set constantly at 10 cm^3 s^{-1}. By using an X-ray diffractometer (XRD) and an energy dispersive X-ray (EDX) analyzer, TiN and Ti_2N phases with the corresponding elements were detected. Vicker hardness (HV) of the sample was at the highest and pin-on-disk tribological test shown lowest of friction coefficient when it was processed at 1,100 ºC for 10 h. Formation of TiN, Ti_2N, could improve surface hardness and reduce friction coefficient leading to improve wear resistance of the 99.70% titanium.

Keywords: TiN; Ti_2N; Vicker hardness; Tribological; DMGN

1. Introduction

Titanium and its alloys are now vastly expanding into many field, such as aeronautical and chemical industries, marine, power generation, sports and leisure transportation, and biomedical devices, due to their high strength and excellent corrosion resistance, low density, high strength-to-weight ratio, low modulus and good biocompatibility. However, titanium and its alloys with low hardness usually have poor wear resistance and high friction coefficient, which limits their application in engineering [1]. Some titanium implants are intended for long term or permanent location, for example, as orthopaedic joint prostheses [2]. A clinical problem sometimes encountered with titanium implants and their abutments is that they are relatively soft and easy to damage. The addition of thin hard coating to the surface of titanium might overcome those problems, i.e. to protect titanium against oxidation and to improve surface hardness [3, 4]. Therefore, continuous research has been directed towards surface modification of titanium [5]. Research in the field of advanced ceramics has focused on the exploration of new routes to produce non-oxide materials, such as carbides, nitrides, borides and sulfides [6]. Among transition metals, titanium carbide and nitride may be used for improvement the poor surface properties due to their high hardness, wear resistance and chemical inertness [7]. In addition to, titanium carbonitride have been successfully introduced in the metal cutting industry [8]. Surface coatings of titanium nitride, carbide and carbonitride can be made by chemical vapor deposition (CVD), physical vapor deposition (PVD), anodizing, plasma and laser nitriding, thermal oxidation and ion implantation [9]. The CVD and PVD of titanium are rather expensive. They need high vacuum systems and toxic chemicals. The purpose of the present research is to improve tribological properties of titanium using direct metal-gas nitridation (DMGN) which is benign to environment and inexpensive. It can be done on a large scale as well.

2. Materials and methods

Samples were prepared from titanium rod (99.70%) with the impurities as follow: Fe 0.05 at%; C 0.05 at%; N 0.05 at%; O 0.05 at%; H 0.015 at%. The rod was cut into the disks with about 20 mm diameter and 1 – 2 mm thick. The disks were ground with SiC papers and polished with 0.30 µm alumina powder, and then they were cleaned with alcohol. Each of them was put in a high temperature reaction chamber made of ceramic as shown in Fig. 1. The air was removed by evacuation to 2.67 kPa absolute pressure and purified argon was slowly fed into the chamber. The process was repeated ten times. Each of the samples was heated in 10 cm^3 s^{-1} argon until the test temperature was obtained. Then 10 cm^3 s^{-1} ammonia were fed into the chamber. The process proceeded at 1,000, 1,050 and 1,100 °C for 2, 6, and 10 h. At the end of the process, the furnace, ammonia were turned off. The samples were cooled down to room temperature and brought for further analysis. The samples were measured ten times using 10 s dwelling time and 100 gf load for a Vicker micro-hardness tester (HV STARTECH SMV-1000), XRD (XRD LapX-6100), SEM equipped with EDX (Jeol: JSM-6335F) and pin-on-disk tester (Implant Science: ISC200).

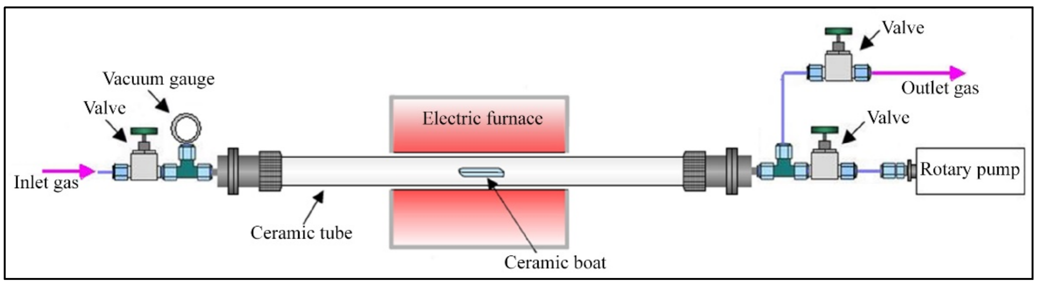

Fig. 1 Schematic of direct metal-gas nitridation (DMGN).

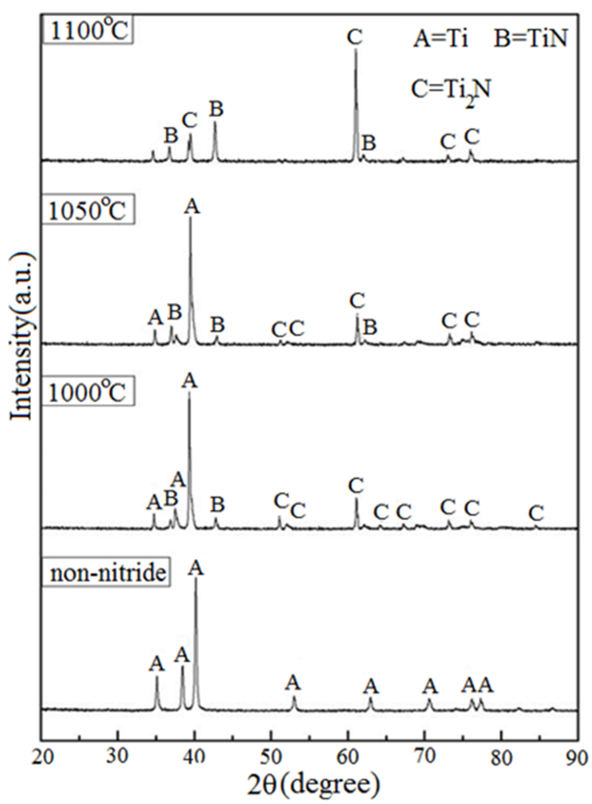

Fig. 2 XRD spectra for non-nitride and nitride at 1000, 1050 and 1100 °C for 10 h.

3. Results and Discussion

X-ray diffraction

XRD spectra are shown in Fig. 2 for non-nitride and nitride of Ti at 1,000, 1,050 and 1,100 °C for 10 h. There is only HCP-Ti peaks in the pattern of non-nitride sample. The pattern of the nitrided samples at 1,000 and 1,050 °C for 10 h show peaks of Ti, TiN and Ti_2N but at 1100 °C for 10 h show only peaks of TiN and Ti_2N.

At 1,000 and 1,050 °C, Ti were detected show that nitride layer could be too thin to shield the underneath Ti matrices. At 1,100 °C, nitride layer could be too thick to shield the underneath Ti matrices therefore, a mixture of TiN and Ti_2N phases were detected. During the nitridation process, NH_3 reacted with Ti to form TiN [10] and Ti_2N by the reaction,

$$Ti(s) + NH_3(g) \rightarrow TiN(s) + 1.5H_2(g)$$

$$2Ti(s) + NH_3(g) \rightarrow Ti_2N(s) + 1.5H_2(g)$$

TiN, Ti_2N phases were detected (JCPDS numbers 06-0642 for TiN:cubic, and 17-0386 for Ti_2N:tetragonal) [11]. TiN(s) and Ti_2N(s) deposited on the titanium surfaces, and H_2(g) were drained off into the ambient atmosphere [12].

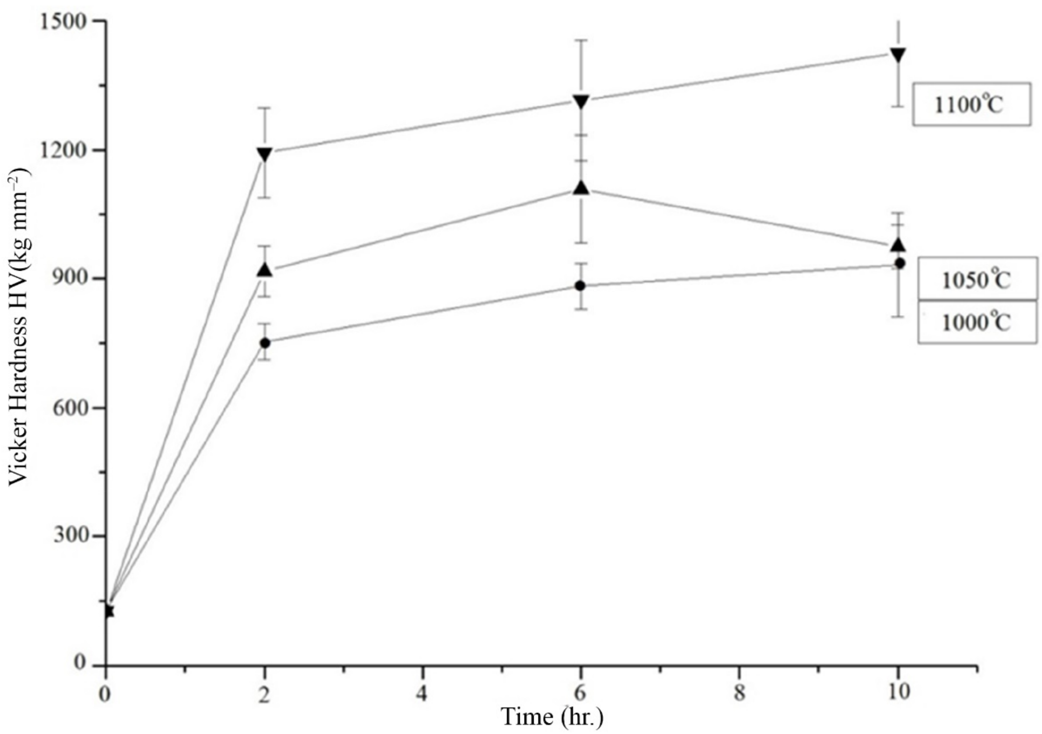

Fig. 3 Hardness for non-nitride and nitride at 1,000, 1,050 and 1,100 °C .

Vicker hardness

HV average value was calculated and shown in Fig. 3. HV value of the substrate before processing was 126.90 ± 6.42 kgf mm^{-2}. The maximum HV value of Ti with 1,100 °C nitridatin for 10 h was 1,424.40 ± 123.68 kgf mm^{-2} (11.20 times of the substrate), due to only TiN and Ti_2N formation on its surface. During the nitridation process, there were products deposited on the Ti surface which could protect the surface from the contacting the reactive gas and could delay the underneath Ti from nitridation. As time proceeded, the rate of nitridation slowed down. HV values increased parabolically with an increase of nitridation time. It shows that hardness of the Ti was controlled by the diffusion process in the nitride products, which are solid phases. Therefore, HV values were controlled by temperature and time including a variety of deposited phases.

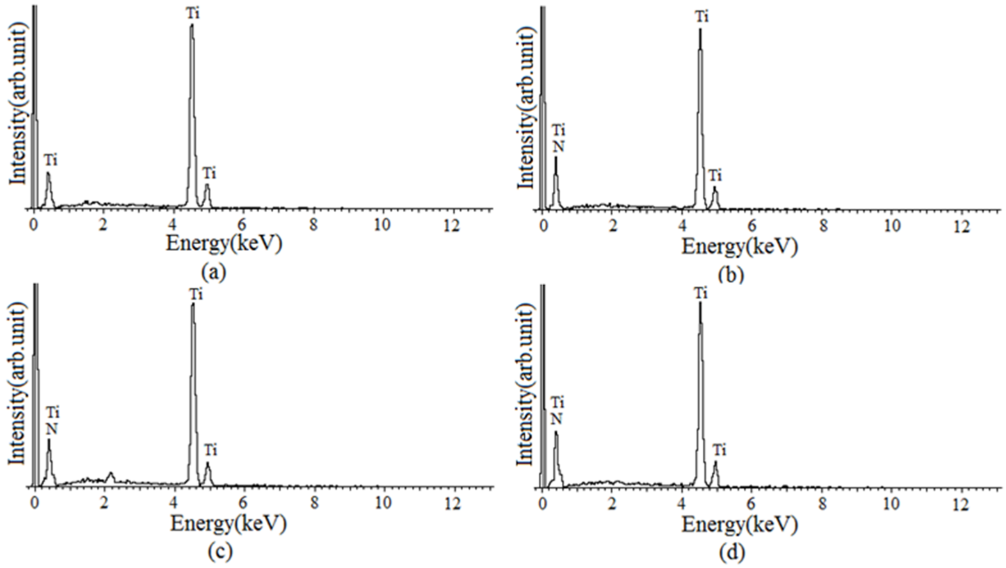

Fig. 4 EDS spectra for (a) Non-nitride (b) nitridation 1,000 °C (c) nitridation 1,050 °C and (d) nitridation 1,100 °C

Energy dispersive x-ray

By using EDX, elemental spectra of the samples before and after processing at 1,000, 1,050 and 1,100 °C for 10 h are shown in Fig. 4. Before processing, only Ti was detected. After processing in NH_3, Ti and N were detected. When N was added to the system, additional N was detected [13]. H is a light element; therefore, it was not detected.

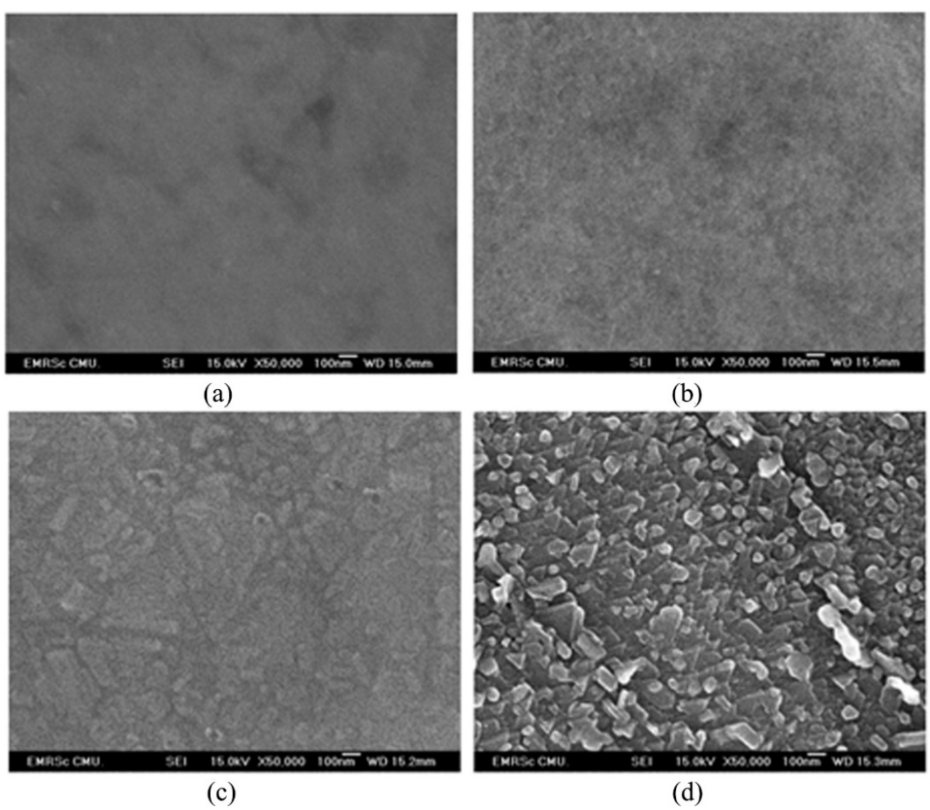

Fig. 5 SEM micrographs of (a) Non-nitride (b) nitridation 1,000 °C (c) nitridation 1,050 °C and (d) nitridation 1,100 °C.

Scanning electron microscope

SEM micrographs for non-nitride and nitride samples at 1,000, 1,050 and 1,100 °C for 10 h are shown in Fig. 5(a) – Fig. 5(d). The micrographs show the difference between a plain surface of non-nitride and a rough surface of nitride samples which the resulting from the formation of TiN and Ti_2N. The layers are irregular showing that the reactive gases reacted with titanium. The reaction leads to surface roughness which reflects their tribological properties. It is worth noting that surface roughness was increased with the increase in the temperature. For 1,100 °C, show surface roughness more than at 1,050 and 1,000 °C with increase of Ti_2N. At this stage, more products were deposited on the substrates.

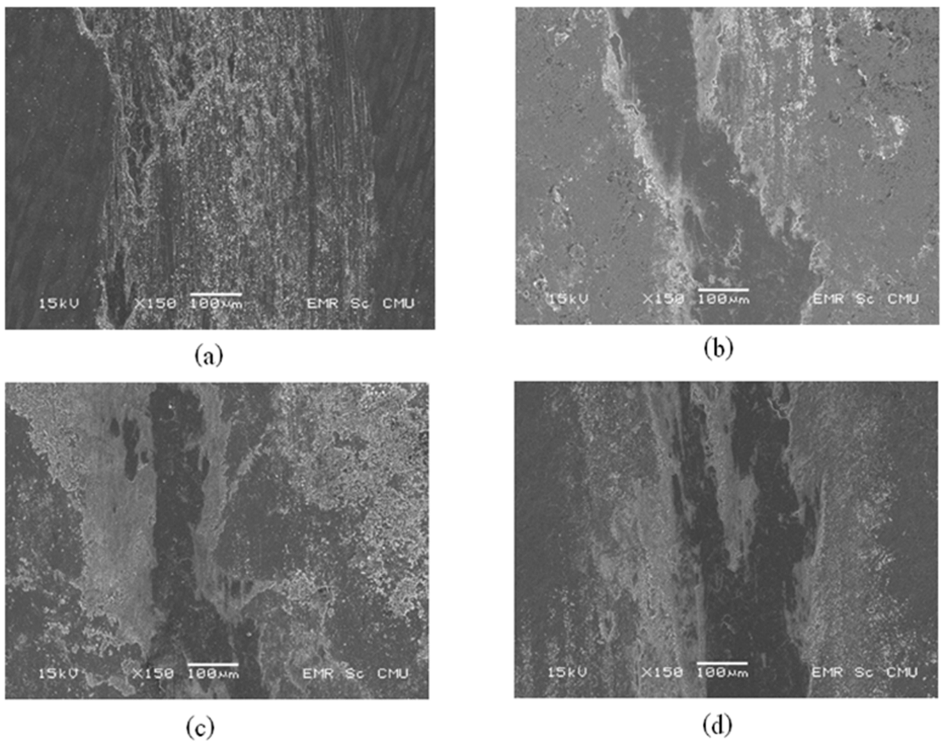

Fig. 6 SEM images of wear track of (a) non-nitride (b) nitride at 1,000 °C (c) nitride at 1,050 °C and (d) nitride at 1,100 °C.

Tribological properties

After wear testing, external morphologies of wear tracks on the samples were examined using an SEM images are shown in Fig. 6. Wear track morphology of non-nitrided samples is obviously different from the nitride samples. Wear tracks of the non-nitrided show the characteristics of ductile metals and appears to be sharp and uniform with fine abrasions. Wear track of the nitrided samples appears to be rough and nonuniform, especially at the wear track boundary, e.g., the wear track of the sample nitride at 1,100; which was similar to that of 1,000 °C and 1,050 °C; shown in the figure. Nonuniform wear track reflected high roughness of coating layer.

Friction coefficient of Ti without and with 1,000, 1,050 and 1,100 °C nitridation for 10 h versus sliding distance are shown in Fig. 7. During wear testing, coefficient of friction varied with sliding distance that the WC pin moved. The coefficient of friction of without nitridation rapidly increased from zero to about 0.89 within the first 50 m. Then, they continued to fluctuate around this value unit the completion of the test. The coefficient of friction of Ti with 1,000, 1,050 and 1,100 °C nitridation for 10 h a constant value between 0.40 and 0.60. The change in the friction coefficient was irregular due to TiN and Ti_2N phases formed on the surface at different temperatures and the vibration of the WC pin. Comparing the samples of without and with 1,000, 1,050 and 1,100 °C nitridation for 10 h, the coefficient of friction of the sample without nitridation showed more fluctuation than that of the samples with nitridation. The minimum friction coefficient value of Ti with 1,100 °C nitridation for 10 h was about between 0.35 – 0.55. The different of friction coefficient caused scratch weight effect to different of the color line.

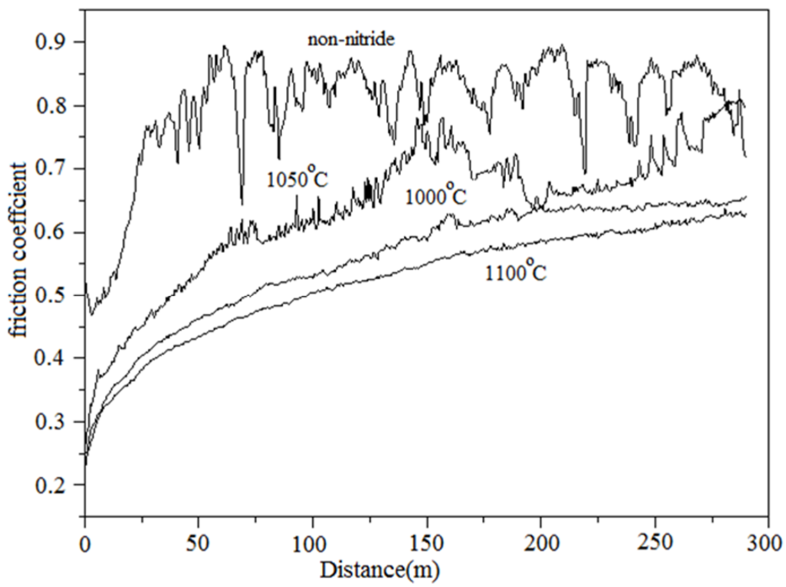

Fig. 7 Friction coefficient of non-nitride and nitride at 1,000, 1,050 and 1,100 °C for 10 h.

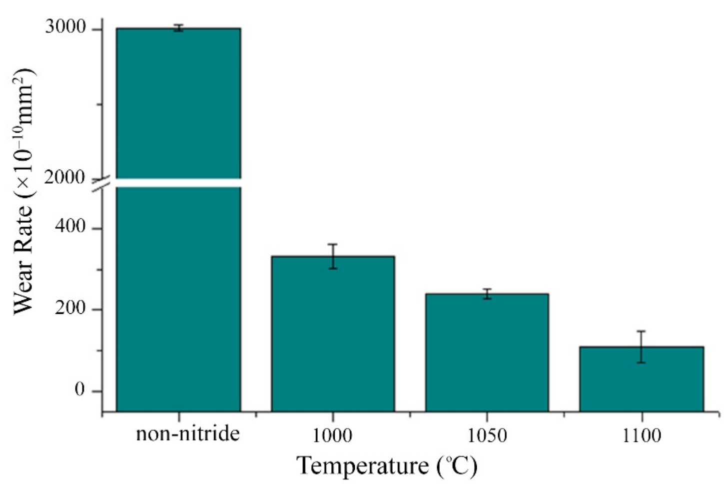

Fig. 8 Wear rate of non-nitride and nitride at 1,000, 1,050 and 1,100 °C for 10 h.

Wear rates of the disks are shown in Fig. 8. It is obvious that the wear rate of non-nitrided was about 3 orders of magnitude higher than nitrided at 1,100 °C reflecting the wear rate of HCP Ti is superior to that of orderd tetragonal Ti_2N. It shows that hardness and wear resistance have the same tendency. Wear resistance of nitride is less than that of non-nitride. The 1,000 – 1,100 °C nitridation process can improve both hardness and wear resistance. At different nitridation temperature, wear rates of the samples were irregular due to the irregularity of wear tracks. The irregularity could be the width, the depth or the shape of the wear tracks. The results are in agreement with those for the friction coefficient of the corresponding alloys, as previously explained. The nitridation temperature could play a role in the formation of different phases and compositions which reflect the irregularity of wear resistance as well.

4. Conclusion

Tribological properties of Ti were improved after titanium was subjected to DMGN due to formation of TiN and Ti_2N phases. Coating of these nitride could improve surface hardness and reduce friction coefficient of the samples. The maximum HV value of the sample was 11.20 times of the substrate, when it was nitrided at 1,100 °C for 10 h. HV values were increased with the increase of nitride temperature and time. SEM micrographs show that their surfaces are covered with the deposited phases of nitride, nitirdes reflecting the surface properties.

5. Acknowledgement

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