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The synthesis of titanium nitride whiskers on the surface of graphite by molten salt media

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Abstract

A novel method for synthesis of titanium nitride whiskers on the surface of graphite in NaF–NaCl media at 1100–1400 °C for 3 h in Ar atmosphere was investigated. The formation of TiN whiskers with the diameter of 500–600 nm and variable lengths and morphologies occurs onto graphite by a vapor–liquid–solid (VLS) mechanism. The specific surface area of graphite increases due to the growth of titanium nitride with various morphologies. The excellent oxidation resistance of surface modified graphite could be attributed to growth of TiN whiskers on the surface of graphite, which act as anti-oxidant and prevent the oxidation of graphite substrate.

Keywords: Titanium nitride whiskers; Molten salt; VLS mechanism; Oxidation resistance

1. Introduction

Graphite is used as a raw material in metallurgy, advanced engineering and atomic energy industry because of its low thermal expansion coefficient and good thermal conductivity. One of its major features includes non-wettability which is mostly used in the theme of liquid metal or liquid slag [1]. Also on one hand, the drawback to the use of graphite is low oxidation resistance, greatly increasing porosity after drying and lowering mechanical strength. On the other hand, due to the poor water-wettability of graphite, the resulting castables flow poorly and considerable water content is required [2,3]. Such drawbacks could be overcome by protecting the graphite modified by coating material which acts as antioxidant between environment and the surface graphite.

In the case of coating techniques, the protective coatings on the surface of graphite are prepared by the sol–gel method, chemical vapor deposition (CVD) and carbothermic reduction method [4–8]. For example, Yilmaz et al. [9] used the sol–gel method, to form boehmitic alumina on the surface of graphite, but the treatment initiating materials of the process is complicated. Gadiou et al. [10] produced layered SiC and TiC protective coatings for carbon fibers by the reactive replica process. Chen et al. [4] reported the synthesis of Ti(C,N) powders using TiO_2 and carbon black as raw materials in carbon granules in a sagger at temperatures of 1100–1600 °C. Potassium titanates and gaseous ammonia were used as the starting materials by Bamberger et al. [11]. It has been found that sodium titanate powder can be converted to TiN powder by treatment with gaseous ammonia at 1000 °C. However, most of the methods require complex manipulation procedures, which are expensive and environmentally unfriendly.

So far a low-temperature technique, molten salt synthesis (MSS), has been used to synthesize some complex oxide powders and carbide materials [12,13]. In the present work, TiN whiskers are synthesized on the surface of graphite by molten salt media. The effects of synthesis temperature and ratio of raw materials were investigated.

2. Experimental procedure

Titanium metal powder (≥99% wt% purity, 50–100 μm), graphite (≥97% wt% purity, 200–300 μm), NaF (≥99% wt% purity) and NaCl (≥99% wt% purity) were used as the raw materials. The mole ratios of Ti to graphite were 1:1, 1:2, 1:3 and 1:4, and the weight ratio of NaCl to NaF as 10:1.

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Two kinds of salts with added equal mass of graphite and Ti powders were mixed. The powder mixture was placed in an alumina crucible and heated at 1100–1400 °C for 3 h in nitrogen atmosphere within an alumina-tube furnace. After cooling to room temperature, the solidified mass was repeatedly washed with hot distilled water and filtered several times to remove the residual salt.

Phases in the resultant powders were characterized by X-ray diffraction (XRD, Philips, X'Pert Pro), scanning electron microscope (SEM, FEI, Nova 400 Nano) and a high-resolution transmission electron microscope (HRTEM, JEOL Ltd., JEM-2100F) equipped with energy dispersive X-ray spectroscopy (EDS, EDAX) respectively. The specific surface area of samples was measured by an automatic surface area and pore size analyzer (Quantachrome, Autosorb-1-MP). To elucidate the synthesis and oxidation mechanism of the powders, differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA) were performed at temperatures up to 1200 °C with a heating rate of 10 °C/min in air.

3. Results and discussion

3.1. Effect of heating temperature and ratio of raw materials on synthesis

XRD patterns of samples of Ti/graphite molar ratio of 1:1–1:3 heated at different temperatures for 3 h in NaF–NaCl molten salt are shown in Figs. 1–3. When samples with the molar ratio of Ti/graphite = 1:1 were heated from 1100 to 1400 °C, the main phases of samples consisted of TiN, TiC and graphite. With decreasing Ti/graphite molar ratio to 1:2, the temperature played a key factor on the formation of TiN and TiC. From Fig. 2, it was observed that low temperature was beneficial for the formation of TiC. Nevertheless, when the molar ratio of Ti/graphite was 1:3 (Fig. 3), TiC peaks disappeared, and the intensities of TiN peaks were stronger with increasing temperature to 1400 °C.

Based on above results, it can be deduced that the ratio of raw materials is the dominant factor. When the content

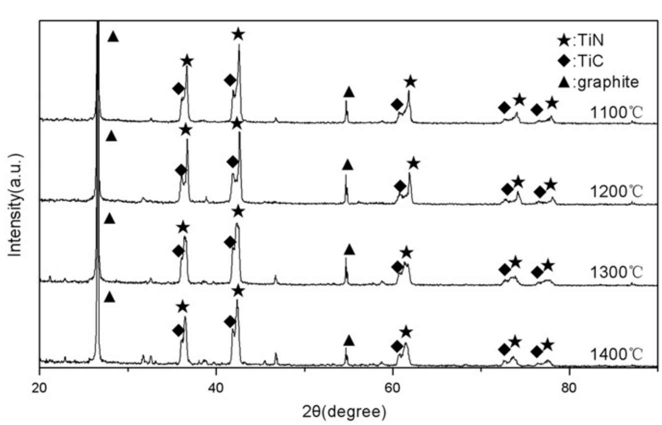

Fig. 1. XRD patterns of samples of Ti/graphite molar ratio 1:1 heated at different temperatures for 3 h.

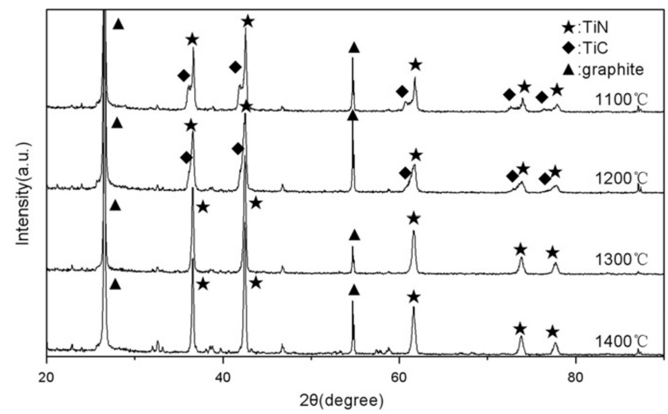

Fig. 2. XRD patterns of samples Ti/graphite molar ratio of 1:2 heated at different temperatures for 3 h.

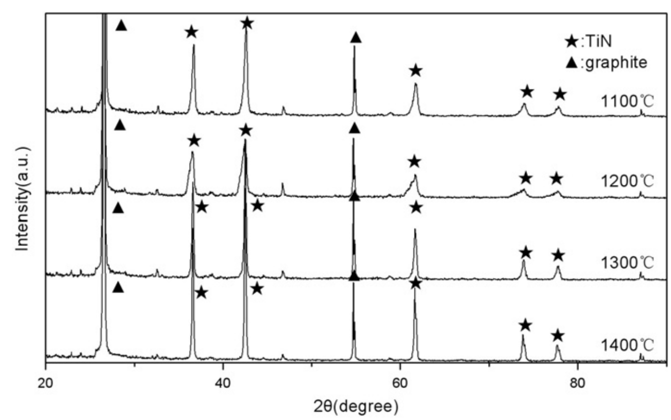

Fig. 3. XRD patterns of samples Ti/graphite molar ratio of 1:3 heated at different temperatures for 3 h.

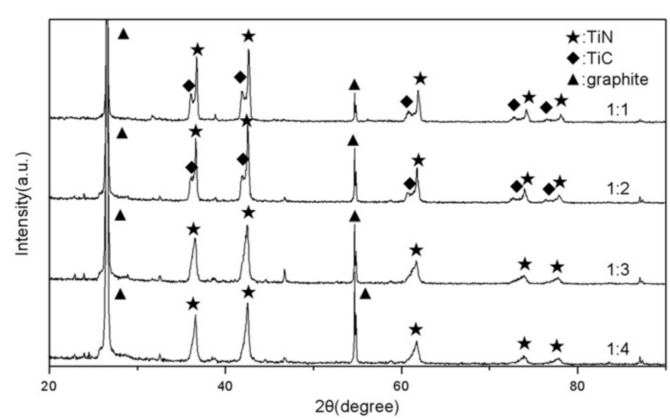

Fig. 4. XRD patterns of samples at different ratios heated at 1200 °C for 3 h.

of Ti is higher, parts of metal ions dissolved in the molten salt which affected the spread of ions at high temperature and the metal ions are distributed in a very small region. If they did not contact with the region of airflow, Ti ions would react with graphite and resulted in TiC. While if the content of Ti was lower, the metal ions would spread rapidly, which would easily contact with nitrogen and be beneficial to the formation of TiN.

For comparing with each other, Figs. 4 and 5 show XRD patterns of samples at different ratios heated at 1200 °C and 1300 °C for 3 h, respectively. At the same temperature, increasing ratio of Ti/graphite, as well as the content of titanium, was beneficial for the generation of titanium carbide. However, on decreasing ratio of Ti/graphite, the TiC peaks disappeared. At 1300 °C, it is obvious from these results that higher temperatures and lower Ti/graphite ratio were favorable for the synthesis of TiN. The results are consistent with former discussion.

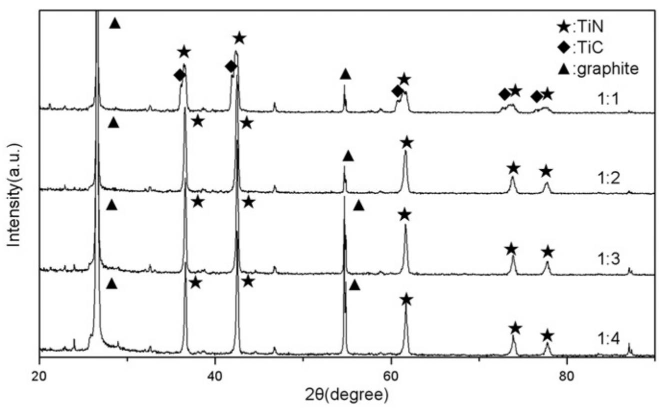

Fig. 5. XRD patterns of samples at different ratios heated at 1300 °C for 3 h.

3.2. Microstructure analysis

SEM micrographs of powder products were taken from samples prepared under the conditions of different temperatures and different ratios of raw materials. Fig. 6 shows SEM images of as-prepared TiN whiskers at Ti/graphite molar ratio of 1:3 heated at 1200 °C for 3 h. From Fig. 6(a), it is evident that the TiN product mainly consists of straight and crystalline rod-like structures, with length 5–10 μm and diameter 500–600 nm. Fig. 6(b) shows the higher magnification SEM image of the marked local in Fig. 6(a); it is obviously observed that the rod-like shape is cylindrical. The surface of whisker was rough and some particles had accumulated on the surface, which indicated that the formation of TiN whiskers caused deposition and growth in liquid phase environment of molten salt.

Fig. 7 shows conical TiN whiskers generated, and globular particles from liquid phase have been found on the top of whisker. In vapor–liquid–solid environment, there existed certain amount of titanium ions in the top liquid drop, and with the growth of crystal, the concentration of metal ion in liquid drop reduced gradually until globular drops disappeared and then crystal stopped growing. The whisker roots were surrounded by the graphite. As the mass transfer in such a solid phase may be very slow, it is hard to consider that the growth of

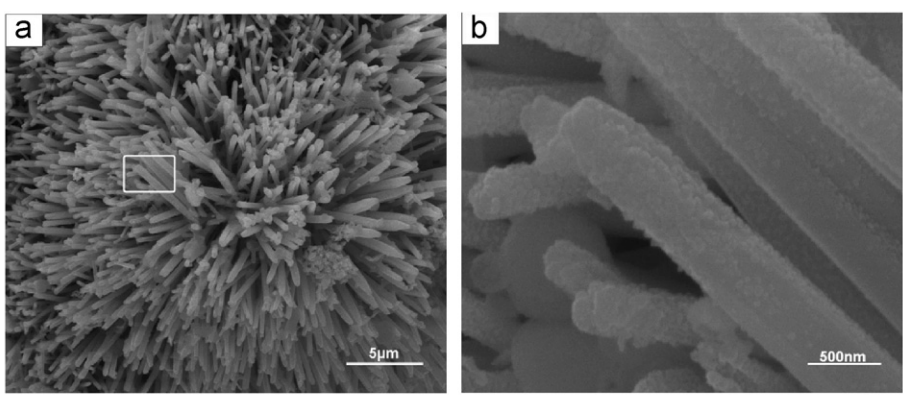

Fig. 6. SEM micrograph of TiN whiskers at Ti/graphite molar ratio of 1:3 heated at 1200 °C for 3 h: (a) typical image showing the tip of the whiskers and (b) magnified image showing the surface of the whiskers.

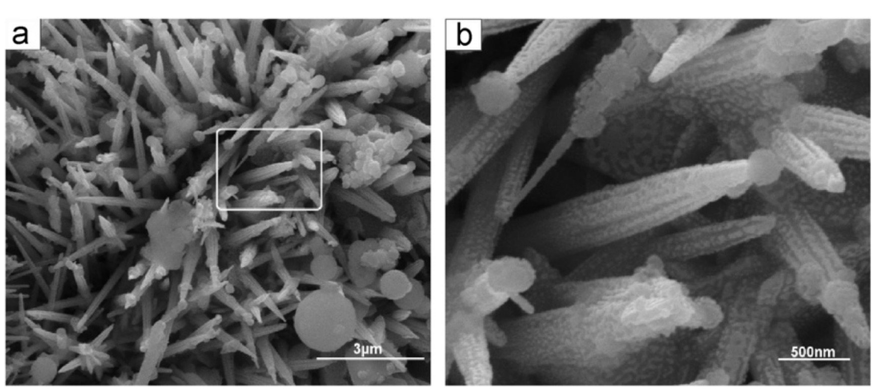

Fig. 7. SEM micrograph of TiN whiskers at Ti/graphite molar ratio of 1:2 by heated at 1300 °C for 3 h: (a) typical image showing the tip of the whiskers and (b) Magnified image showing the surface of the whiskers.

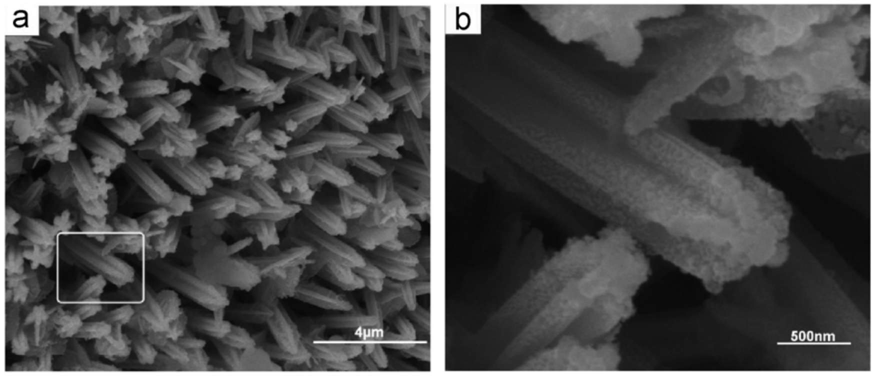

Fig. 8. SEM micrograph of TiN whiskers at Ti/graphite molar ratio of 1:3 by heated at 1300 °C for 3 h: (a) typical image showing the tip of the whiskers and (b) magnified image showing the surface of the whiskers.

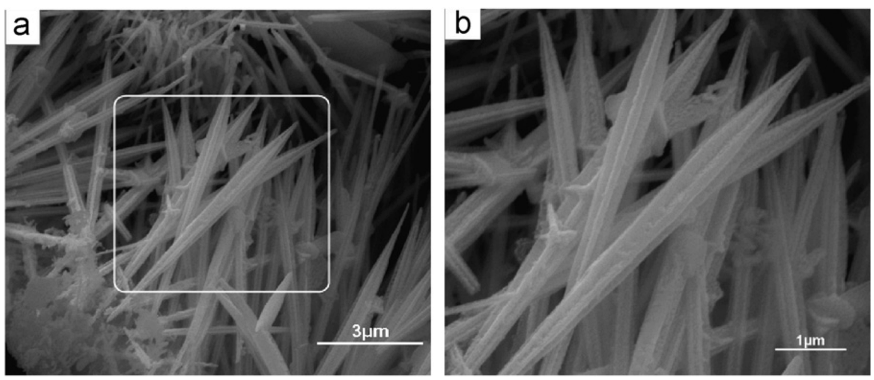

Fig. 9. SEM micrograph of TiN whiskers at Ti/graphite molar ratio of 1:3 by heated at 1400 °C for 3 h: (a) typical image showing the tip of the whiskers and (b) magnified image showing the surface of the whiskers.

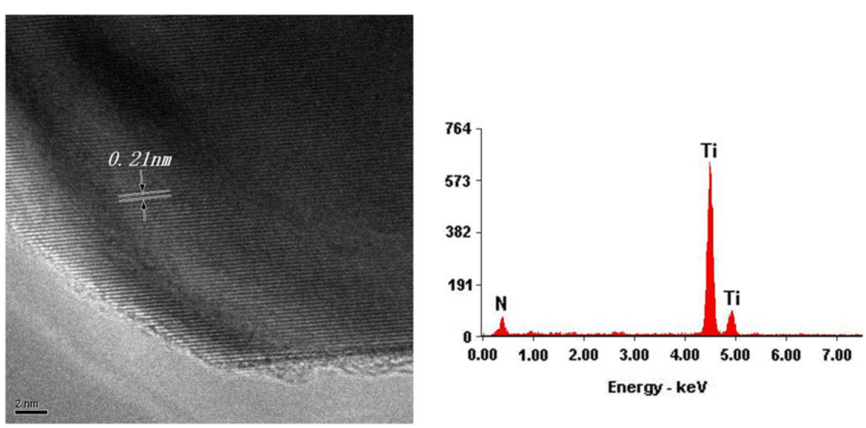

Fig. 10. HRTEM image of titanium nitride whisker at Ti/graphite molar ratio of 1:2 heated at 1300 °C and its corresponding EDS spectra.

whiskers occurs at the root. It may also be concluded from the facts that the present whiskers to grow at the tip [14]. With the continuous supply of gas source, the whiskers grew continuously to raise the small droplets until they stop growing. At last, small droplets were left on the top of the whiskers. In the growth of the TiN whiskers, small globes were observed on the tips, and it is considered that the VLS mechanism has been proposed for the growths. A lot of papers reported similar morphology characteristics of whiskers by VLS mechanism [15–21]. Compared with the morphology in Fig. 6, TiN whiskers grew further with increasing Ti content and temperature; as seen from Fig. 7, there were still some metal droplets that had not been run out completely.

SEM micrographs of TiN whiskers synthesized at Ti/graphite molar ratio of 1:3 are shown in Figs. 8 and 9. TiN whiskers with large star-shaped cross-section appear at Ti/graphite molar ratio of 1:3 heated at 1300 °C for 3 h.

With temperature increasing, TiN whiskers on longer grow up with the shape of a cylinder in length direction, but grow with the shape of a star in radial direction (Fig. 8(b)). As the temperature increases to 1400 °C, TiN whiskers have changed to a structure with thin at each end and thick at the center shown in Fig. 9(h).

Further evidence for the formation of TiN whiskers at Ti/graphite molar ratio of 1:2 and heated at 1300 °C for 3 h could be found in HRTEM image and its corresponding EDS spectra shown in Fig. 10. This HRTEM image clearly shows the lattice fringes which are consistent throughout the crystal. The spacing between adjacent lattice planes is 0.21 nm, corresponding to (200) plane of titanium nitride, which indicates that the preferred growth direction of whiskers is perpendicular to (200). However, the morphology of TiN crystal would be affected by the temperature and the proportion of raw material, which would show out different morphologies of growth.

3.3. Specific surface area determination by N_2 gas adsorption

The specific surface area of samples chart at different ratios heated for 3 h at 1200 °C is reported in Fig. 11. It was shown that the specific surface area of sample was larger than that of graphite after processing; especially at 1:2, the specific surface area was 3 $m^2\,g^{-1}$. As can be seen from the SEM photograph, the morphology of the surface of graphite has been changed by the rod shaped TiN whiskers generated in the sample, so the specific surface area of samples has been increased.

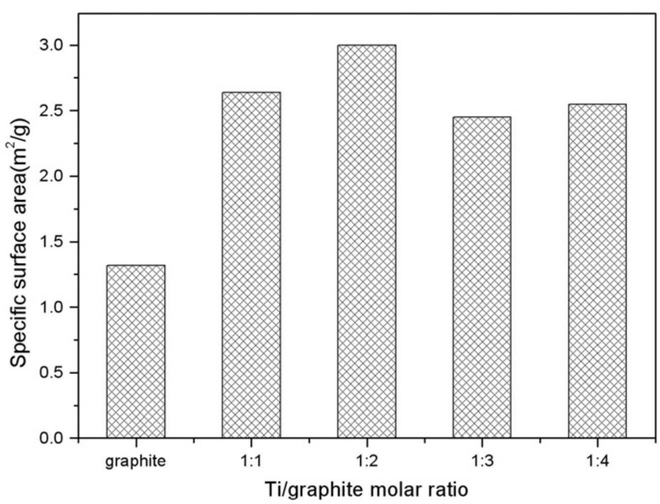

Fig. 11. Specific surface area of samples at different ratio heated at 1200 °C for 3 h.

3.4. Oxidation resistance of TiN whiskers

The oxidation resistance of all the samples including as-received ones was evaluated by DSC/TG measurement (Fig. 12). According to the DSC curves, it can be found that there were obvious exothermic peaks of the treated sample from 450 °C to 650 °C, and flake graphite began to oxidize at about 650 °C, then a high exothermic peak appeared from 650 °C to 1000 °C. As for the treated samples, some results can be seen correspondingly from TG figure curves that TiN was oxidized at first [22], and the TiO_2 from oxidization increased with certain mass, and the graphite in treated samples began to oxidize at 650 °C with the mass reducing gradually, while the untreated graphite was fully oxidized. Because a small amount of TiC was generated of the treated samples at 1100 °C and 1200 °C, the exothermic peak had little migration. It can be seen from the experiment that TiN whiskers formed on the surface of graphite acted as anti-oxidant to a certain extent, the TiO_2 formed on the graphite surface in the process of oxidation had reduced the oxidation rate of graphite, and with increasing quantity, it further prevented the inner graphite from oxidation.

4. Conclusions

Titanium nitride whiskers were formed between 1100 °C and 1400 °C on the surface of graphite by NaF–NaCl media. The results showed that the VLS mechanisms existed in the process of whiskers growth. TiN whiskers were about 500–600 nm in diameter with variable lengths and morphology, which was determined by Ti/graphite molar ratio and heating temperature. The specific surface area of graphite increases due to the growth of titanium nitride with various morphologies. TiN whiskers formed

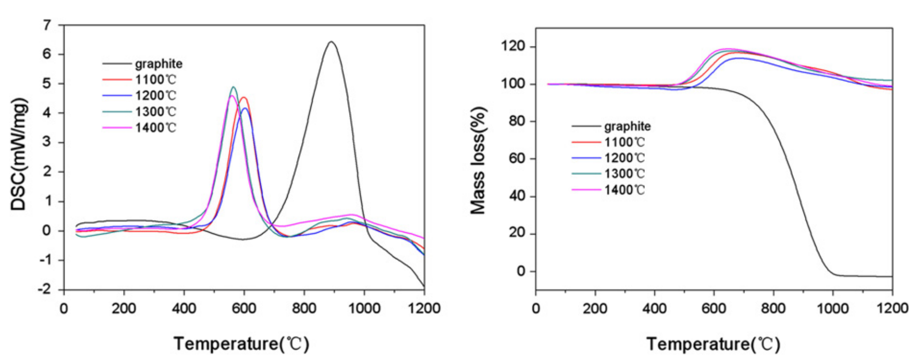

Fig. 12. DSC and TG curves of samples with Ti/graphite molar ratio of 1:2 heated at different temperatures for 3 h.

on the graphite surface could act as anti-oxidant to a certain extent and prevent oxidation of graphite substrate.

Acknowledgments

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