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The synthesis, microstructure, hardness and thermal properties of bulk nanocrystalline Al produced by in situ consolidation with low-energy ball milling

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ABSTRACT

Bulk nanocrystalline (nc) Al was produced by in situ consolidation of Al powder with low-energy ball milling at room temperature. Microstructure and thermal properties of Al subjected to ball milling were investigated by means of differential scanning calorimeter (DSC), differential thermal analyzer (DTA), transmission electron microscope (TEM), X-ray diffraction (XRD), and scanning electron microscope (SEM). As a result of long time milling, considerable energy has been stored in the powder particles which suffered a repetitive cold welding and fracture mechanism. It was found that the microhardness of Al was increased with the increasing of ball milling time. The highest microhardness (1372 MPa) was observed at room temperature in nanocrystalline Al in the experiment.

1. Introduction

Nanocrystalline materials have been widely studied in the past years [1–3]. The mechanical properties of nanocrystalline materials are still lack of understanding. One of the main reasons is that full density bulk nanocrystalline materials are very difficult to be produced [4,5]. The process of severe plastic deformation (SPD) is one of the desirable processes to produce bulk nanocrystalline materials, so that the severe plastic deformation (SPD) has attracted the interest of people in producing of nanocrystalline materials [6]. Ball milling is a more convenient process to produce nanocrystalline powder. The most widespread equipment of high-energy ball milling which could produce nanocrystalline powder is Spex 8000 [7]. Now it is known that the evolution of nanostructure of metal milled is controlled by the temperature and milling intensity [8,9]. Comparing to high-energy ball milling, low-energy ball milling causes negligible heating by impact, and the equipment of low-energy ball milling is cheaper and simpler than that of SPD and high energy Spex 8000. Additionally, the traditional ball milling is only used for producing nanocrystalline powder. Not only nanocrystalline powder but also bulk nanocrystalline materials are produced by the simple roller mill made by ourselves (low-energy ball milling). The goal of our research is to produce in situ consolidated bulk nanocrystalline Al by ball milling. The research of bulk nanocrystalline materials produced by ball milling is rarely reported by authors [5,10,11]. This technique can produce spheres samples (2–3 mm diameter) with nearly full density, which microhardness test can be measured. If the process can be further improved, the larger ball could be produced, and many other mechanical properties can be tested, e.g. tensile tests can be done. In this paper the ball milling process was described and the microhardness, microstructure and thermal properties of nanocrystalline Al were investigated.

2. Experimental

The raw powder was prepared from Al powder which is made by Strem Chemicals with a purity 99.8% and average particle size of 50 μm. Stainless steel balls (4.0 mm and 9.5 mm diameter) were used with a ball-to-powder ratio of 100:1 (weight). The ratio of the weight of large ball (9.5 mm diameter) to small ball (4.0 mm diameter) is 1:1 (the method abbreviated: BM) and 3:1 (the method abbreviated: B1M) respectively. Then the raw powders and stainless steel balls were mixed and put into a tool steel vial. The ball milling was carried out in a roller mill made by ourselves at room temperature. Nanocrystalline Al spheres (maximum 2 mm in diameter) were formed after ball milling over 20 h at room temperature. The surface of Al spheres was observed by scanning electron microscopy (SEM) which is carried out in a LEO 1450VP & 1450VP-02-02. These balls were ground and polished into disks whose microhardness was measured on a Buehler Micromet 2100 Series Microhardness Testers using a load of 50 g. The average hardness value and standard deviation were obtained by measuring 10 hardnesses in each sample. For transmission electron microscopy (TEM) sample preparation, the Al spheres were compacted into 0.2 mm thick disks. The small disks were thinned by

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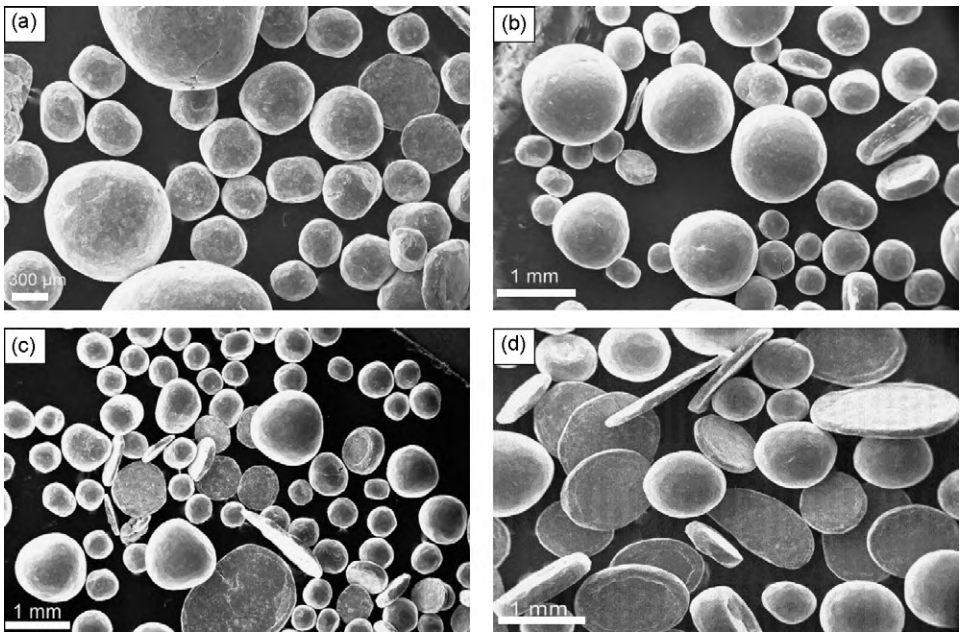

Fig. 1. Al sphere samples at B1M process for different ball milling times: (a) 24 h; (b) 35 h; (c) 50 h; (d) 72 h.

polishing with mechanical methods, then were thinned by an ion polished system. The microstructures of samples were analyzed by TEM, which was performed in a microscope operating at 120 kV.

The grain sizes were calculated with Scherrer formula [7]. The samples were analyzed by a Rigaku Ru-300 Rotating Anode X-ray Generator. The diffractometer was operated using Cu-radiation $\lambda = 0.154$ nm and a graphite monochrometer at 50 step per degree and a count time of 10 s/step. The most intensive four peaks were used to calculate the grain size.

The milling sample was submitted to a thermal analysis by means of a differential scanning calorimeter (DSC) and a differential thermal analyzer (DTA), which are the Perkin Elmer DSC-7 respectively. The two kinds of equipments were used because the highest temperature of DSC-7 is 600 °C in our laboratory and the sample of DTA-7 is too few to measure the thermal change of the sample milled in heating. The samples were about 50 mg and 5 mg used for DSC and DTA respectively. The heating rate was 20 °C/min in a continuous flux of Ar atmosphere.

3. Results and discussion

3.1. Effect of ball milling time on Al powder particle size

Pure Al powders have been ball milled up to 72 h at room temperature. The samples ball milled less than 20 h (B1M24 and BM20 respectively) are in the form of powders. All other samples ball milled more than 20 h are in the form of spheres. Fig. 1 shows the Al spheres produced by ball milling are about 1–2 mm in diameter. In B1M process, the sphere diameter increased as the ball milling time increased after ball milling 24 h (B1M24), and eventually greatest diameter is about 2 mm at ball milling time of 40 h. With the ball milling time 72 h, the spheres were changed into flake partially as

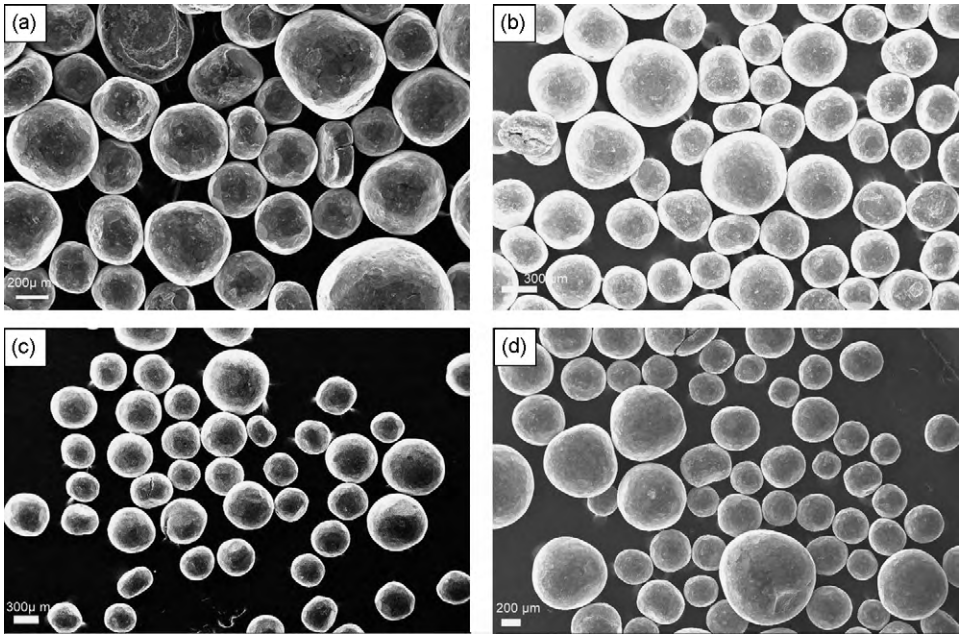

Fig. 2. Al sphere samples at BM process for different ball milling times: (a) 36 h; (b) 40 h; (c) 50 h; (d) 60 h.

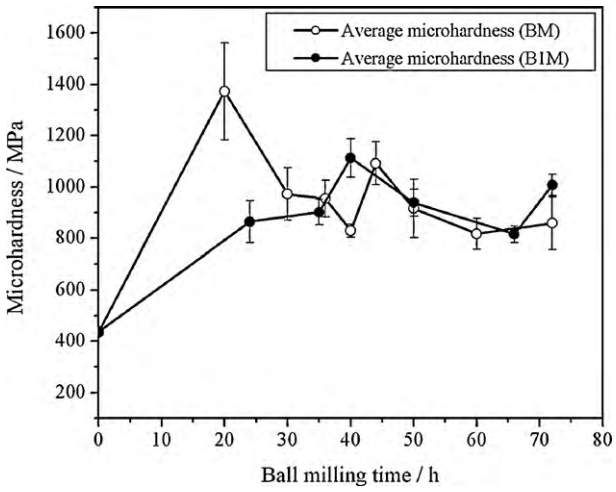

Fig. 3. Variation in hardness with ball milling time for B1M and BM process.

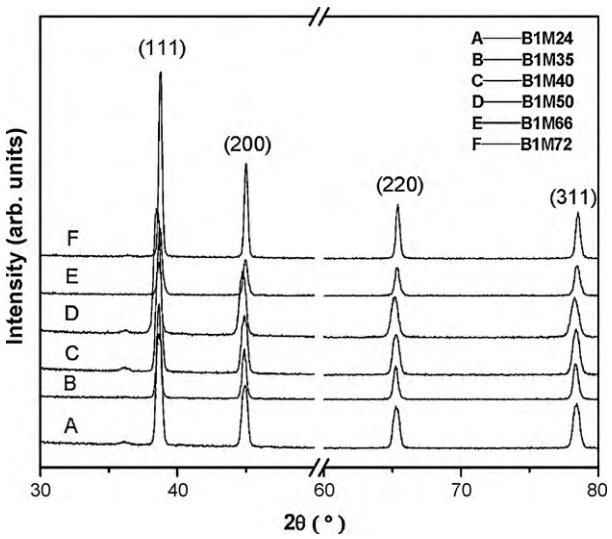

Fig. 4. Al phase with considerable peaks broadening after ball milling (B1M).

shown in Fig. 1(d), which is because steel ball continue to impact Al spheres leads to the result. This result is similar to that of BM process (Fig. 2). The sizes of bulk Al spheres produced by B1M process are greater than those of bulk Al spheres produced by BM process after same hours because the bigger diameter of steel balls is used and energy of balls is higher so that the process of B1M is easier to produce the bulk nanocrystalline Al.

The changes of powder particle size milled have been explained in the paper [7]. During milling the powder particles are repeatedly cold welded, fractured and rewelded. The work hardening and fracture of the powder particles are produced by force of the impact plastically deforms. The powder particles are also cold welded together to become spheres during ball milling. As continued deformation, the particles get work hardened and fracture by a fatigue failure mechanism. When the tendency of particles cold welded is greater than that of particles fractured after milling for a certain length of time, the Al spheres size will be increased. Steady-state equilibrium is obtained when a balance is achieved between the rate of welding, which tends to increase the average particle size, and the rate of fracturing, which tends to decrease the average composite particle size. The appearance of these Al spheres becomes more smooth-faced and uniform for longer milling time. A relative higher density of bulk Al spheres has been observed by SEM in Fig. 1. If the process of low-energy ball milling can be further improved, the larger ball could be produced so tensile property will be tested. The tensile property of metal milled has been measured [5,11].

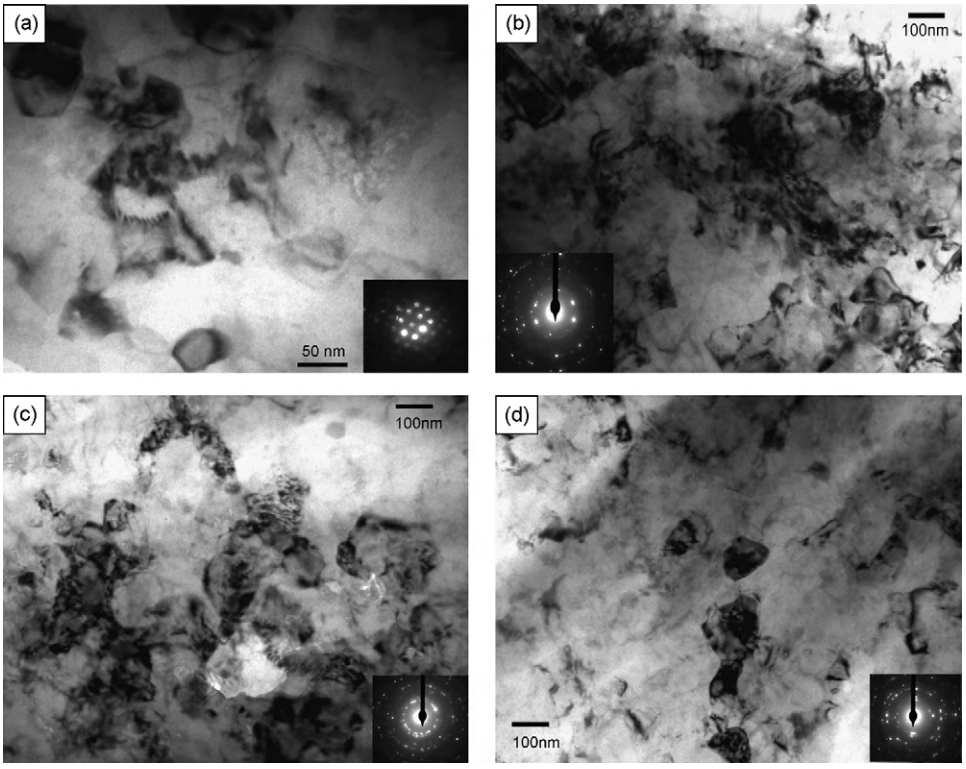

Fig. 5. TEM bright field images of nc Al (B1M) after different milling times: (a) 72 h; (b) 66 h; (c) 50 h; (d) 40 h.

Table 1
The grain size and ball milling times.

Milling time (h)	B1M	BM	
	Average grain size (nm)		Average grain size (nm)
	By X-ray	By TEM	By X-ray
24	88	–	–
35	82	–	103
40	84	89	108
50	75	87	95
66	71	87	–
72	70	82	–

3.2. Effect of ball milling time on the hardness of nc Al

As seen in Fig. 3, the hardness of nc Al produced by ball milling (B1M and BM) was found to increase to 882–1372 MPa. The highest average hardness of nc Al is 1372 MPa. With the increasing of milling time, the hardness of nc Al increased. But the hardness increases slowly after ball milling time over 30 h. It is important to note that due to relatively long milling time, a small amount of impurities were inevitably introduced into the samples during low-energy ball milling process, the microhardness of nc Al prepared in our experiment is higher than that prepared through other methods [12], and the impurity will absolutely affect the microhardness of nc Al.

The microhardnesses of bulk Al spheres produced by B1M process are higher than those of bulk Al spheres produced by BM process after ball milling of 40 h because the bigger diameter of steel balls is used and impact force of balls is higher. The process of B1M is easier to produce the bulk nc Al.

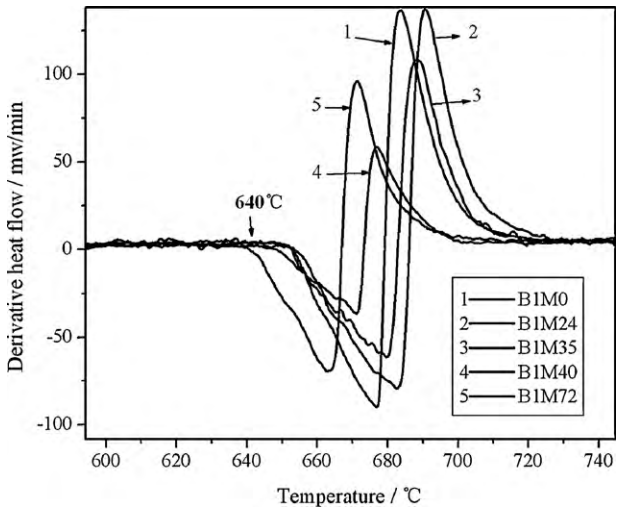

Fig. 7. The DTA curves between derivative heat flow and temperature during heating Al spheres obtained for different times at a heating rate of 20 °C/min.

3.3. Effect of ball milling time on the grain size of nc Al

Fig. 4 shows diffraction patterns of Al in different milling times. Repeatable four most intense peaks were accurately measured by special experiment method of XRD, and were used to calculate the nc grain size shown in Table 1. The grain sizes of nc Al measured by XRD were confirmed by TEM images (Fig. 5) observing 144 grains in B1M72 in Table 1 and Fig. 6. This experiment of XRD has good agreement with that of TEM.

The grain sizes decrease as milling time increases and approach a steady state after long milling time. The average grain size is about

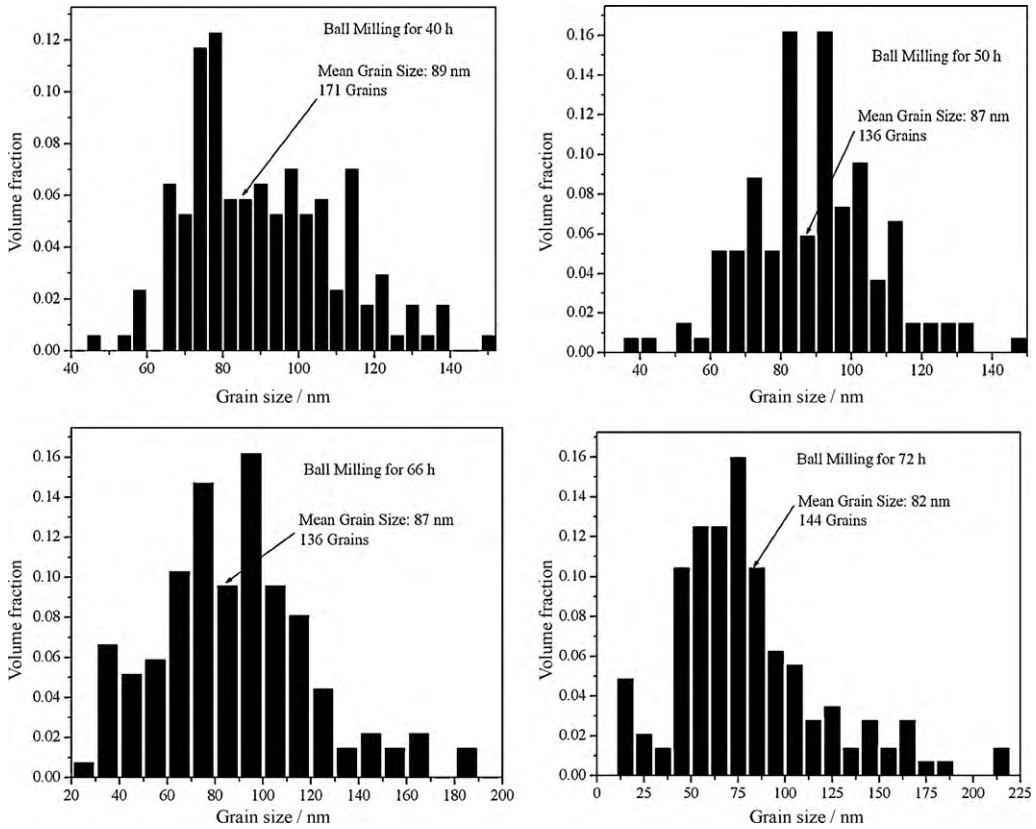

Fig. 6. Histogram showing grain size distribution in the nc Al samples in TEM images.

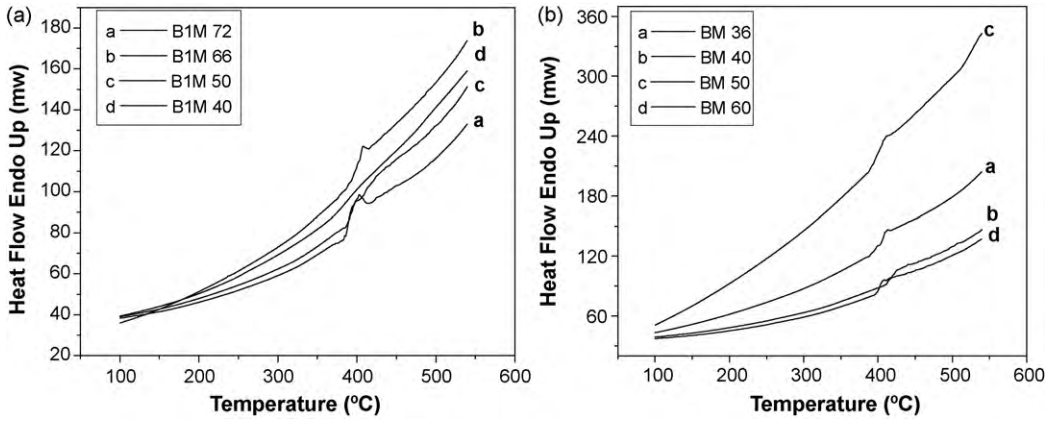

Fig. 8. The DSC curves during heating Al spheres obtained for different times at a heating rate of 20 °C/min: (a) B1M; (b) BM.

82 nm after milling for 72 h, while some grains in excess of 100 nm are also present. During low-energy ball milling for long time, the cold weld compact exerts large force and lead to nc Al. Although high-energy milling has higher efficiency to obtain nc Al, long time milling causes moderate heating to a vial temperature of about 60 °C. Low-energy ball milling for long time have not affected the evolution of microstructure of Al changed by the temperature.

3.4. The thermal properties of nc Al

The thermal properties of nc Al were measured by DSC, DTA and TMA. Fig. 7 shows the DTA curves between derivative heat flow (mw/min) and temperature during heating Al spheres obtained for different times at a heating rate of 20 °C/min. The melt points of Al milled for different times decrease with increasing of the ball milling time. When Al powder was milled for 72 h and 40 h respectively, nc Al starts to melt about less than 660 °C and nc Al milled for 72 h starts to melt at 640 °C. It is worthy to notice that the melt point of Al decreases excessively. Many experimental studies have been carried out on the size dependence of the melting point of various metallic particles, including Sn, Bi, Ag, Cu, Au, Al, Na and CdS [13–17]. Although those metals are in the form of particle, the results in this experiment are similar to that of melting point depression in particle because there is few paper to deal with the research on the change of melt point in bulk nanocrystalline. The author [18] thinks it is because there exists an Al_2O_3 amorphous oxide film on the surface of the nc Al so that the bulk sample does not melt macroscopically at 700 °C, which also explain that the nc Al milled is free of contamination.

Fig. 8 indicates the DSC curves during heating Al spheres obtained for different times at a heating rate of 20 °C/min. The curve shows a small endothermic peak between 380 °C and 420 °C. The endothermic processes could be explained with grain reorganization and lattice expansion [19]. The result of DSC of nc Al in this paper does not agree with those of papers [20–22], which will need further investigation in detail in future.

4. Conclusions

Bulk nc Al was produced by in situ consolidation of Al elemental powders using low-energy ball milling at room temperature. It was found that the microhardness of Al increases with the increasing of ball milling time. The highest microhardness (1372 MPa) was observed at room temperature in nc Al in the experiment. The average grain size of Al (B1M70) is about 82 nm measured by TEM. When Al powder was milled for 72 h and 40 h respectively, nc Al starts to melt about less than 660 °C and nc Al milled for 72 h starts to melt at 640 °C. The small endothermic peak between 380 °C and 420 °C was observed in nc Al heated at a heating rate of 20 °C/min in DSC.

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