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EFFECT OF Ti POWDER ADDITION ON THE FABRICATION OF TiO₂ NANOPOWDERS

WPLYW DODATKU NANOPROSZKU Ti NA ZAGĘSZCZANIE I SPIEKANIE NANOPROSZKÓW TiO₂

Sintered samples of Ti added TiO₂ nanopowders were fabricated by combined application of magnetic pulsed compaction (MPC) and sintering. The effect of Ti nano powder on density, shrinkage and hardness of the samples were investigated as part of the study. The optimum processing conditions were found to be around 0.5 GPa MPC pressure and 1450°C sintering temperature, illustrating maximum density, hardness and minimum shrinkage. High pressure compaction using MPC was found to enhance density with increasing MPC pressure up to 0.9 GPa, and significantly reduce the total shrinkage (about 16% in this case) in the sintered bulks compared to other general processes (about 18%). While sintered samples blended with micro Ti showed presence of microstructural cracks, the samples with 1- 2% nano Ti had less or no cracks on them. Overall, the inclusion of nano Ti indicated improvement in mechanical properties of TiO₂ nanopowders sintered preforms as opposed to micro Ti-added TiO₂.

Keywords: TiO₂ nanopowder, magnetic pulsed compaction, densification, sintering

1. Introduction

Nanocrystalline titanium dioxide (TiO₂) is proven to be quite effective for its optical, dielectric and catalytic properties [1]. Nano-sized TiO₂ are also known for exhibiting increased osteoblast adhesion, making TiO₂ a promising biomaterial in the field of orthopedic applications [2]. Therefore nanocrystalline TiO₂-based parts are of considerable interest for a number of applications. With powder metallurgical routes as the preferred fabrication method, the properties of the TiO₂ components are quite dependent on their microstructures, which in turn, are influenced by the processing parameters including sintering time and temperature. Especially, achieving a nearly dense nanostructured bulk is important for various mechanical, electrical, optical, and magnetic applications. Numerous studies on consolidation processes of TiO₂ nanopowders by sintering techniques have been carried out to obtain dense bulk substances [3]. However, the preparation of dense, fine-grained TiO₂ specimen is considered to be quite challenging due to the rapid growth of grains during the later stage of sintering [4]. As sintered microstructure is significantly affected by the initial microstructure and characteristics of the powder, several methods have been used to prepare an agglomeration free, well-compacted nanosized powders in order to fabricate fully dense nanostructured ceramics [5]. Since, it is necessary to achieve the highest density for TiO₂ bulks as required by in-

dustrial applications, a range of economical and cost-effective P/M routes were tested for both compaction and sintering, including classical sintering, hot pressing, sinter-forging and spark plasma sintering (SPS) [6, 7]. It is notable that the aforementioned research was focused on the consolidation of either anatase or a mixture of anatase and rutile (30%<) nanopowders, while only rutile TiO₂ nanopowder was used for consolidation in this study. During the consolidation process, various factors such as pressure, temperature, etc., must all be optimized to retain the initial grain size as well as to simultaneously achieve a higher density, lower shrinkage, and high hardness. In this study, a dynamic compaction method, named *Magnetic Pulse Compaction* (MPC) [4], was employed to prepare Ti added TiO₂ disk for sintering. Later, the effect of added Ti powder (nano or micro) on density, shrinkage, hardness and crack formation of sintered rutile TiO₂ nanopowders was studied.

2. Experimental

Rutile nanocrystalline polygonal TiO₂ nanopowders with an average size of 100~300 nm were used in this study. About 8-grams of raw TiO₂ nanopowder mixed with 2% of Polyvinyl Alcohol (PVA) and 1-2% Ti powders before they were placed into a cylindrical die and punch/pin set of 20 mm inner di-

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ameters for compaction. The die and pins were sprayed with high-temperature Boron Nitride release agent to facilitate ejection of powder preform and prevent powders from sticking to the pins. For compaction of the TiO₂ nanopowders, a magnetic pulsed compaction (MPC) process was applied, which translates the pulsed electric power into mechanical units, channeling them into the compaction area. The duration of the compaction process was about 0.3 seconds. In this experiment, TiO₂ bulks have been fabricated by the combined application of the magnetic pulsed compaction and subsequent sintering process. The pressure during the magnetic pulsed compaction varied from 0.5 to 0.9 GPa. The green compacts were then transferred into a resistance heating furnace and sintered in air at atmospheric pressure. Two batches of sintered samples were prepared. Once the temperature inside the furnace reached 800°C, all samples were held isothermally for two hours at this temperature. The first batch of samples were then taken out of the furnace and cooled naturally to room temperature. Once the first batch of samples were taken out, the furnace temperature was then raised to 1450°C for the second batch to sinter. The holding time at 1450°C was 2 hours. The heating rate was 4°C/min, while natural cooling was applied to the samples after they were sintered. The densities of the disks, both after compaction and sintering, were measured using the Archimedes method. The shrinkage observed in the samples was also measured using a Vernier caliper with ±0.01 mm precision. Hardness tests were carried out on a Vickers Hardness tester (Wilson Instron Series 2000). A minimum of 10 indentation results were averaged for each sintered specimen. Microstructural analysis was carried out using a FE-SEM (TESCAN MIRA LMH). For crack length analysis, several cracks initiating from the edges of the indentation marks were considered and measured, and the values were then averaged. The percentage of error within this set of data did not exceed 5%.

3. Results and Discussion

In this study, a number of specimens were compacted by Magnetic Pulsed Compaction (MPC) at different pressures,

and then sintered for two hours, at both 800°C and 1450°C, in order to investigate the changes in density, shrinkage, hardness, and crack formation. Table 1 summarizes the different mixing arrangements of PVA, water, Ti and TiO₂ powders, the pressures applied during the compaction process, and the result of visual inspection regarding the formation and types of cracks in the sintered samples. Edge cracks were observed in the sintered samples where compaction pressure exceeded 0.5 GPa. The formation of edge cracks may be attributed to the much higher applied pressure as well as rapid rate of applied stress than conventional pressing. This, on top of the low amount of binder present in the specimen, can be thought of as reasons for the presence of edge cracks occurring in the sintered samples. Although there is a possibility that both face crack and wall crack can form in the preforms, the latter was not seen to be present in the sintered samples in this study.

The study started with observing the nature of the Ti particles. While nano Ti and TiO₂ powders illustrate almost spherical shape particles, micro Ti powders on the other hand are of irregular shape, and quite coarse in nature. The changes in density of the green discs/preforms with increasing compaction pressure and varied Ti content and size are delineated in Figure 1 (a). It can be seen that for all three different Ti additions, density seemed to have increased gradually with increasing pressure from 0.5 to 0.9 GPa, and reached a maximum of nearly 60% for the sample with 1% nano Ti and at 0.9 GPa compaction pressure. The fact that the sample with 1% nano Ti illustrated higher density compared to the one with 2% nano Ti could be due to a higher degree of agglomeration of Ti particles at higher concentration. When micron size Ti particles were used, the issue of agglomeration may have still existed, but not to an extent that samples with 2% nano-Ti particles exhibited. Another reason for these TiO₂ + 2% Micron Ti samples displaying higher density than TiO₂ + 2% Nano Ti could be attributed to the shape of the micron-size Ti particles as opposed to the shape of the nano particles. Also, no cracks were found on the surface or along the edges of the MPC-ed discs.

TABLE 1

Mixing conditions and relative appearances of the sintered bulks

No.	GPa	PVA (wt%)	Water (wt%)	TiO ₂ (wt%)	Ti in wt% added to (PVA+W+TiO ₂)	Crack Formation (800/1450°C)	Note
1	0.5	2	18	80	1	Non/Non	Nano Ti
2	0.5	2	18	80	2	Non/Non	Nano Ti
3	0.5	2	18	80	2	Non/Non	Micro Ti
4	0.7	2	18	80	1	Non/Crack	Nano Ti
5	0.7	2	18	80	2	Crack/Crack	Nano Ti
6	0.7	2	18	80	2	-/Non	Micro Ti
7	0.9	2	18	80	1	Non/Crack	Nano Ti
8	0.9	2	18	80	2	Crack/Crack	Nano Ti
9	0.9	2	18	80	2	-/Crack	Micro Ti

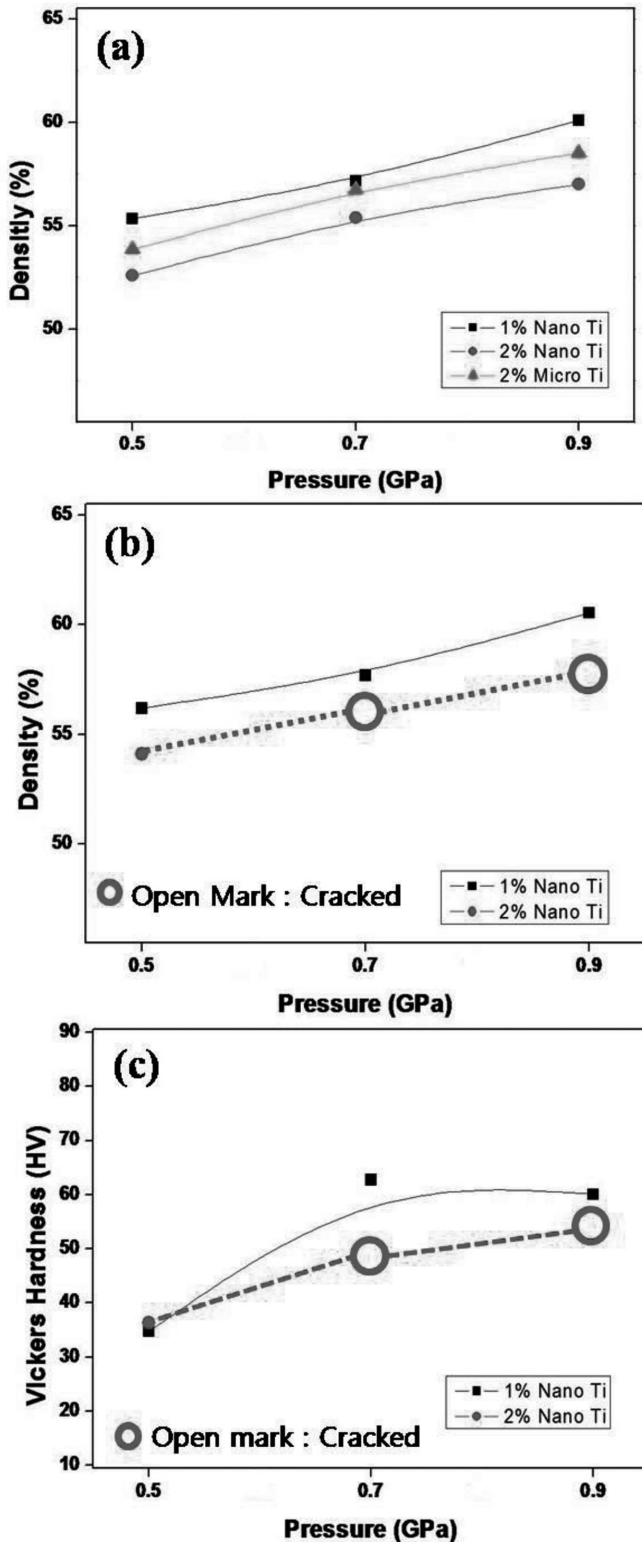


Fig. 1. Changes in (a) Density after MPC process, (b) Density of MPC-ed discs sintered at 800°C and (c) Hardness of MPC-ed discs sintered at 800°C

The magnetic pulse compaction process that was employed in this study is quite critical because of its unconventional nature. During compaction, powders go through several stages, namely packing, elastic and plastic deformation at contact points, which essentially translate to cold working for ductile materials or fragmentation for brittle materials like ceramics. During the initial stage where powder is placed inside

of a die, particles tend to lightly join together due to friction amongst the particles; a phenomenon known as 'bridging'. Next, the particles tend to move closer to each other when the piston goes down, and presses the particles. This continues, even against mild and severe friction until the particles start to deform. At this stage, the particles are joined only due to rigid friction and possibly, cold working. When particles experience an increase in pressure, they tend to slide between themselves, which is also referred to as elastic compression. This elastic compression between particles, usually at contact points, results in increased density without having the powders to permanently deform or break. Densification at this stage is thought to be nearly complete, as further increase in pressure can permanently crush or flatten the contact zones of the particles. At maximum compaction pressure, extreme resistance against further densification is observed, specifically due to strain hardening of materials [8-10]. One of the areas where this dynamic compaction can effectively contribute is through making the compaction process faster. With the use of MPC, it is possible to apply several GPa of pressure on powder samples within fraction of a second. The nature of the compaction can offer different pressing and joining mechanisms for different types of powders. Although this process is generally carried out at room temperature, powders can be preheated and then compacted to take advantage of the short duration consolidation process. For materials that have a low melting point, preheating followed by MPC can yield interesting insights for compaction.

The variation in density and hardness of the bulks at 800°C sintering temperature and increasing MPC pressure can be visualized from the graphical presentation of Fig. 1(b) and 1(c), respectively. In addition, it is also possible to conceive the differences between sintered samples with 1% and 2% nano Ti. For both density and hardness, samples with 1% nano Ti, sintered at 800°C, illustrated better performance compared with the ones with 2% nano Ti. Density and hardness both seem to have gradually increased with increasing MPC pressure, and reached a maximum for the samples that went through 0.9 GPa MPC pressure and 800°C sintering temperature. The appearance of these sintered bulks was whitish yellow and did not demonstrate rapid or drastic color change. The color distribution was homogeneous along the entire surface of the discs. In addition, no cracks were seen on the surface or along the edges of the sintered samples with 1% nano Ti. However, the samples with 2% nano Ti showed presence of fairly irregular edge cracks at elevated MPC pressure, which explains the comparative drop in density and hardness in these samples that contain 2% nano Ti powder, as opposed to the ones with 1% nano Ti. Although incorporation of nano particles in these samples play an important role in terms of enhancing certain mechanical properties, it is quite difficult to optimize the amount in the composition. We have mentioned earlier that these nano particles are quite spherical in shape, which may be beneficial for their bonding properties and nature. However, due to the possibilities of agglomeration in these nano particles, addition of these nano materials is limited beyond certain extent, depending on the properties or the microstructural characteristics of the samples.

The changes in density, shrinkage, and hardness in the MPC-ed samples sintered at 1450°C, for both compositions

(1% and 2% nano Ti) with varying MPC pressure are shown in Figure 2 (a), (b) and (c), respectively. Evidently, in the case of the 1450°C sintering temperature materials, the porosity is usually low, or sometimes interconnected, resulting in high density and hardness. Also, continuous grain boundary network is a general feature in the samples at this sintering temperature, where most of the pores are found to be along the grain boundaries. The decrease in porosity at 1450°C, as opposed to the microstructure at 800°C is possibly due to the bridging of fine crystallites and formation of closed pores.

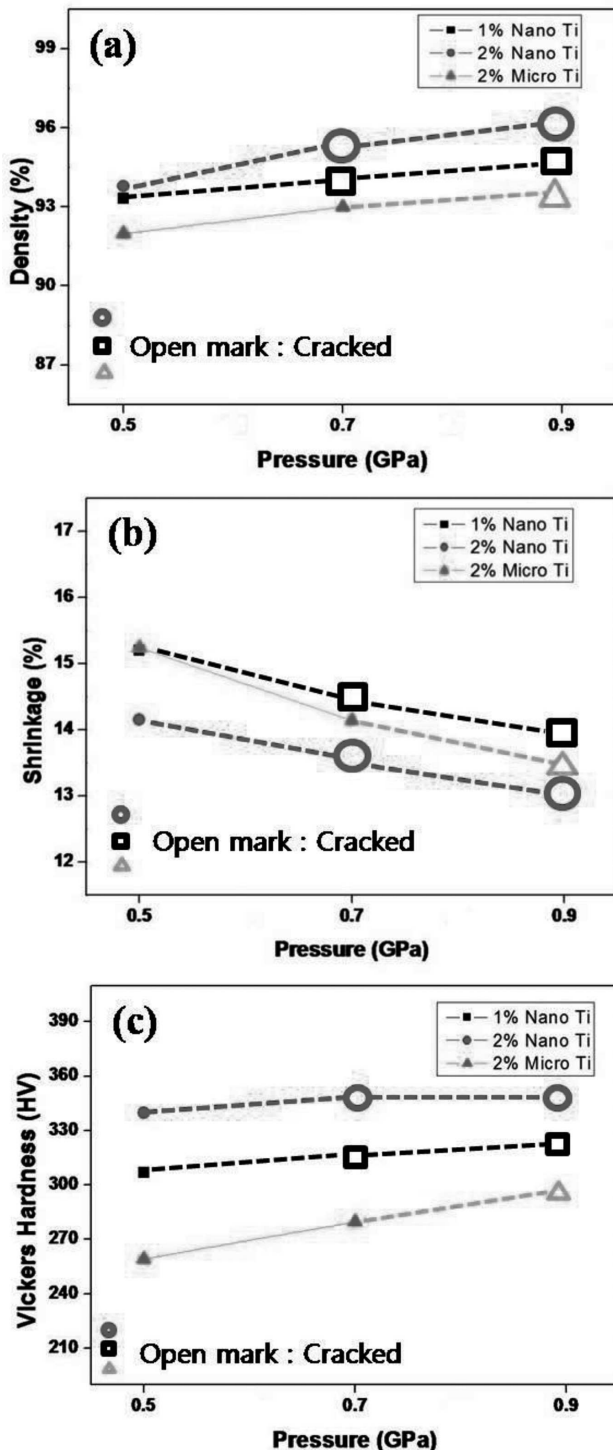


Fig. 2. Changes in (a) Density (b) Shrinkage and (c) Hardness of MPC-ed discs sintered at 1450°

There is no apparent secondary phase(s) present within the grain or along the grain boundaries [11]. Our result suggests that a maximum of 96% density can be achieved in samples with presence of 1 or 2% nano Ti particles, where the shrinkage could be as low as 15-16%, which is quite improved, compared with the conventional shrinkage (total) of nearly 18%. It appears that the sintering mechanism suggests that density increases and varies with the increase of sintering temperature and the change of mixture respectively. Higher sintering temperature causes a greater diffusion of atoms and molecules between the contact points of particles, which substantially reduces the amount of pores. Such kind of thermodynamic phenomenon motivates the sintered bulks to gain a superior density [12]. However, the increase in MPC pressure beyond certain limit can have adverse effect on the sintered bodies. Here in our experiments, several sintered samples that had gone through MPC pressing beyond 0.5 GPa, were found to have edge cracks. Not only does this affect the final density, but also affects the hardness of these brittle materials. Unlike ductile materials, when MPC is applied on brittle materials with high pressure, initiation of necking behavior between particles do not occur during sintering, which may induce greater amount of pores or defects in the final sintered bodies, eventually leading to low hardness [13, 14].

Fig. 3 (a, b) shows a comparative analysis on how sintered samples with micro Ti behave against sintered samples with nano Ti, in terms of crack length or presence of cracks. While it shows that samples with micro Ti illustrate presence of cracks, samples with nano Ti don't have cracks present along the edges of the indentation marks. These cracks were generated along the edges of the indentation mark, as a result of the Vickers hardness test, when 10 kgf load was employed on all of the samples with 15 s of dwell time. Cracks were not seen in all four edges of the indentations. However, secondary cracking was absent in the microstructure, suggesting a homogeneous distribution and strong binding mechanism at the same time. Internal stresses were produced within the sample as a result of the thermal expansion mismatch of the constituents. Therefore, the residual stresses may be the reason for the micro cracking, and reasonable and diminishing crack propagation [15].

The reason why this study is crucial and difficult at the same time is because of the probabilities of having crack in the surface or along the edges of the samples, due to the inherent nature of these brittle materials [16-18]. It is quite obvious from this study that when 1% micro Ti samples were used, with uneven shaped particles, consolidation through MPC, and later sintering, could not have the full advantage in terms of optimized pressing and pore reduction. Due to the uneven nature of the particle size and particle breaking, although reasonably high density and hardness were achieved, cracks also evolved in some samples, where MPC pressure of more than 0.5 GPa was employed.

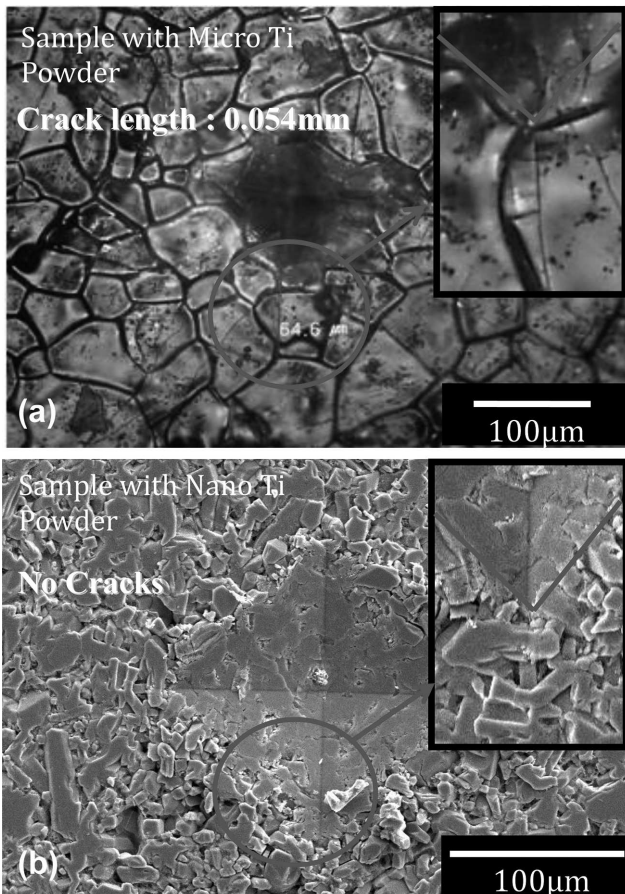


Fig. 3. Micrographs showing crack length in (a) micro and (b) nano Ti samples

4. Conclusion

Highly dense TiO_2 composites were successfully obtained by combined application of magnetic pulsed compaction and subsequent sintering, at 1450°C , where compositions were varied with incorporation of 1~2% nano Ti and micro Ti. The application of magnetic pulsed compaction for consolidation of TiO_2 nanopowders was critical in this study in providing an understanding of how dynamic compaction can effectively work on nanopowders, while successfully illustrating an ultra-fine microstructure. The optimum processing conditions in order to find the maximum density, hardness and minimum shrinkage were found to be 0.5 GPa MPC pressure and 1450°C sintering temperature, mostly for samples with 1 or 2% nano

Ti. The obtained density of the MPC-ed and sintered bulk increased with the increasing MPC pressure from 0.5 to 0.9 GPa, although cracks started to form along the edges of the samples beyond 0.5 GPa. Due to the uneven nature of the particle size and particle breaking in the samples with micro Ti, although reasonably high density and hardness were achieved, cracks were seen, where pressure exceeded 0.5 GPa during MPC.

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REFERENCES

- [1] P.T. Hsiao, K.P. Wang, C.W. Cheng, H. Teng, J. Photochem. Photobiol. A: Chem. **188**, 19 (2007).
- [2] T.J. Webster, R.W. Siegel, R. Bizios, Biomater. **20**, 1221 (1999).
- [3] H. Hahn, J. Logas, R. Averbach, J. Mater. Res. **5**, 609 (1990).
- [4] Y.A. Kotov, V. Osipov, M. Ivanov, O. Samatov, V. Platonov, E. Azarkevich, A. Murzakaev, A. Medvedev, Tech. Phys. **47**, 1420 (2002).
- [5] D. Lee, S. Yang, M. Choi, Appl. Phys. Lett. **79**, 2459 (2001).
- [6] K. Vanmeensel, A. Laptev, J. Hennicke, J. Vleugels, O. Van der Biest, Acta Mater. **53**, 4379 (2005).
- [7] M. Omori, Mater. Sci. Eng. A **287**, 183 (2000).
- [8] B. Azhdar, B. Stenberg, L. Kari, Polym. Testing **24**, 909 (2005).
- [9] H.F. Fischmeister, Proceedings of the Institution of Mechanical Engineers **196**, 105 (1982).
- [10] J. Wang, X. Qu, H. Yin, M. Yi, X. Yuan, Powder Tech. **192**, 131 (2009).
- [11] S.J. Kalita, S. Qiu, S. Verma, Mater. Chem. Phys. **109**, 392 (2008).
- [12] A. Yamada, S. Gaudio, C. Lesher, J. Phys. Conference Series, IOP Publishing, Bristol (2010).
- [13] J.H. Kim, R.M. Raihanuzzaman, C.K. Rhee, J.G. Lee, M.K. Lee, S.J. Hong, Mater. Trans. **52**, 1156 (2011).
- [14] R.M. Raihanuzzaman, J.W. Song, S.J. Hong, J. Alloy. Compd. **536**, S211 (2012).
- [15] A. Newman, S. Sampath, H. Herman, Mater. Sci. Eng. A **261**, 252 (1999).
- [16] J.W. Song, H.S. Kim, S.S. Kim, J.M. Koo, S.J. Hong, J. Kor. Powd. Met. Inst. **17**, 242 (2010).
- [17] J.S. Park, H.S. Kim, K.S. Lee, J.G. Lee, C.K. Rhee, S.J. Hong, J. Kor. Powd. Met. Inst. **16**, 223 (2009).
- [18] J.W. Song, H.S. Kim, H.M. Kim, T.S. Kim, S.J. Hong, J. Kor. Powd. Met. Inst. **17**, 302 (2010).