

THE EFFECT OF TiC ADDITION ON MAGNETIC PROPERTIES OF ATOMISED NDFEB PERMANENT MAGNETIC POWDER

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ABSTRACT

NdFeB permanent magnetic materials with and without TiC addition were prepared by inert gas atomization. The powders produced were characterized using particle size analyzer, scanning electron microscope (SEM), X-ray diffraction (XRD) and optical microscope. The magnetic properties such as remanence (Br), coercivity (Hc) and maximum energy product (BH max) of the powders were obtained using vibratory sample magnetometer (VSM). It was found that the gas atomization process produced spherical powder for both materials. However the NdFeB powder with TiC addition has smaller grain size compared to the powder without TiC. It was also found that the magnetic properties of the powder containing TiC is higher compared to the powder without TiC. The reasons for the difference in properties for both powders were discussed.

INTRODUCTION

Bonded magnets are made from compacted high coercivity powders that are held together by non-magnetic binders such as epoxy, nylon and polyamides. The big advantages of bonded magnets include the cost effective net-shape manufacturing process, which can be held to tight tolerances. Energy products of bonded magnets increased from 5 MGOe for injection molded and to 12 MGOe for compression molded. The flexibility of bonded magnets in the processing, shape and magnetic properties contributes to their success in the market.

At present bonded magnet was manufactured by compaction of melt-spun ribbons produced by melt spinning process. This flake (ribbon) type material is widely used for metal injection molding (MIM) but it requires higher shear forces to deliver the equivalent amount of material into the die. Spherical powder having similar properties as the ribbon is preferable because it can solve some of the problems encountered in using melt spun ribbons. However spherical powder cannot be used as bonded magnet because it has low magnetic properties compared to melt-spun ribbon due to the lower cooling rate in the former. Inert gas atomization (IGA) offers the potential to produce isotropic powder with a spherical shape, suitable for many powder-processing

operations. IGA has distinct advantage that it is well suited for scaling up, with commercial plant available that can produce many tons of powders per day. While atomization techniques have been explored for many years, this process has yet to prove to be successful as a source for isotropic powders for bonded magnet instead of being restricted to sintered magnet application. Magnequench International has announced the first spherical powder available commercially by the trade name of MQP-S 9-8 [1] and followed by MQP-S-11-9 recently. However the technique used to produced the powders is not a conventional gas atomization but by spinning-cup atomization.

The magnetic properties of the gas atomized powder is believed to be further increased by the addition of titanium carbide (TiC) in the NdFeB alloy. TiC inhibits the formation of free iron, reduces the cooling rate required to obtain the optimal microstructure and increases the glass forming ability [2]. Thus, the objective of the present work is to produce the spherical powder by IGA with and without TiC addition and to study the effect of its effect on microstructure and magnetic properties of the powders.

EXPERIMENTAL

The master alloy for this study was prepared from commercial grade materials by vacuum induction melting. The compositions were checked by inductive coupled plasma (ICP). The spherical powders were prepared from master alloy by IGA using PSI atomizer with a close-coupled annular nozzle using argon gas at the pressure of 40 bar. The Nd-Fe-B powder were sieved to <20 μm , 20 to 60 μm and 63 to 106 μm and used in this study. The as-atomized NdFeB and NdFeB-TiC powders were mounted in epoxy for magnetic properties measurement.

Magnetic hysteresis loops were measured by DMS vibrating sample magnetometer (VSM), with a maximum applied field of 2.7 Tesla. No demagnetization corrections were applied. For scanning electron microscopy (SEM) observation, some of the atomized powders were cold mounted, polished and etched with 3% nital to reveal the cross section microstructure and then coated with gold. Leo 1525 Field Emission Scanning Electron Microscope (FESEM) equipped with Energy Dispersive Spectrometer (EDS) was used for imaging and analysis. The as-atomized powders were observed by SEM to study their morphologies. X-ray diffraction (XRD) was employed to identify the phases present in the powders. Dry particle size analyzer was used to determine the size distribution of the atomized powders.

RESULTS AND DISCUSSION

Table 1: Chemical composition of the atomized powder.

| Sample | Concentration (wt.%) | | | | | | | |
|-----------|----------------------|------|-------|------|------|------|------|------|
| | Nd | B | Fe | Dy | Pr | Co | O | TiC |
| NdFeB-TiC | 26.38 | 0.72 | 70.33 | 1.40 | N.D. | 0.43 | 0.24 | 0.50 |
| NdFeB | 27.88 | 0.65 | 69.40 | 1.41 | N.D. | 0.44 | 0.22 | - |

The chemical compositions of the atomized powders is shown in Table 1. Figure 1 shows the scanning electron micrographs of the as-atomized powders before sieving. The atomized powders produced are spherical with very fine particles attached to larger particles and have a wide particle size distribution. Most particles exhibited no sign of collisions during solidification, either with solid (such as faceted surfaces, from interactions with previous solidified particles or with chamber walls) or molten droplets (resulting in 'capped particle'). The particle size distribution for NdFeB measured by laser particle size analyzer showed the trimodal type distribution with the mean particle sizes (d_{50}) of 20 μm , 40 μm and 80 μm . The particle size distribution for the NdFeB-TiC showed the unimodal distribution with the mean particle size of 45 μm . EDS analysis showed no severe oxidation on the surface of the powders. This analysis is not reliable because the x-ray collected by the EDS detector is not coming from the surface but from a few micrometers beneath the surface. EDS is not suitable for surface analysis. Sellers et al. [3] showed that by using Auger Microscope, it is possible to determine the oxide layer on the surface. The Nd₂O₃ layer of approximately 150 \AA was observed and this layer was stable at room temperature.

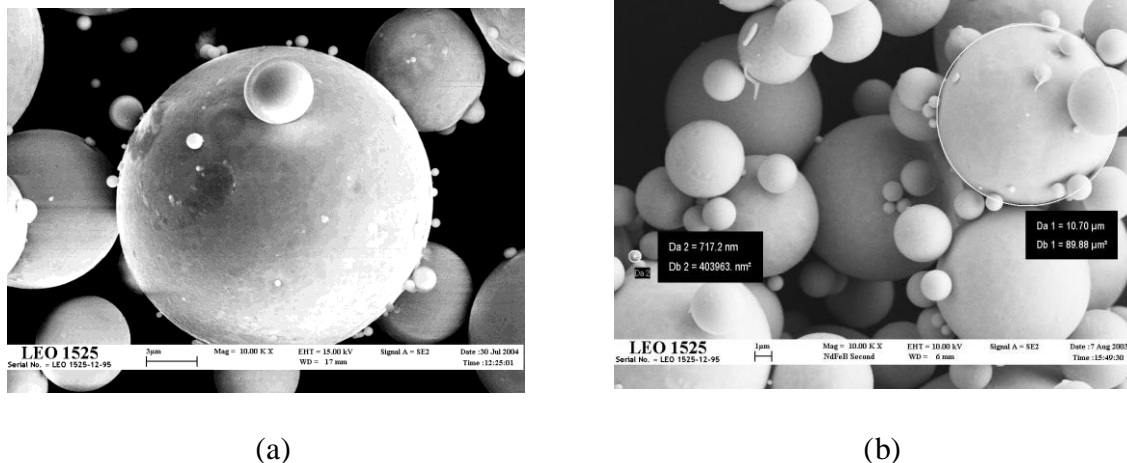


Figure 1: SEM Image of a) atomized NdFeB-TiC powder and b) atomized NdFeB powder.

Figure 2a shows the optical micrographs of the cross section of the powder having particle size of 20 to 63 μm . The powder was etched with 3% nital to reveal the microstructure. As can be seen from Figure 2a), the microstructure of NdFeB powder produced by atomization is dendritic. There are few centers of crystallization observed in the powder. Figure 2 b shows the optical micrograph of NdFeB-TiC powder showing much finer structure compared to NdFeB powder. The grains are more equiaxed. The amorphous shell observed by Vasilyeva et al. [5] was not seen in this study. This is because the material used in this work is different. It is believed that the additions of alloying elements such as Tb, Ti and Mo in Vasilyeva et al. [5] study has contributed to the formation of the amorphous shell.

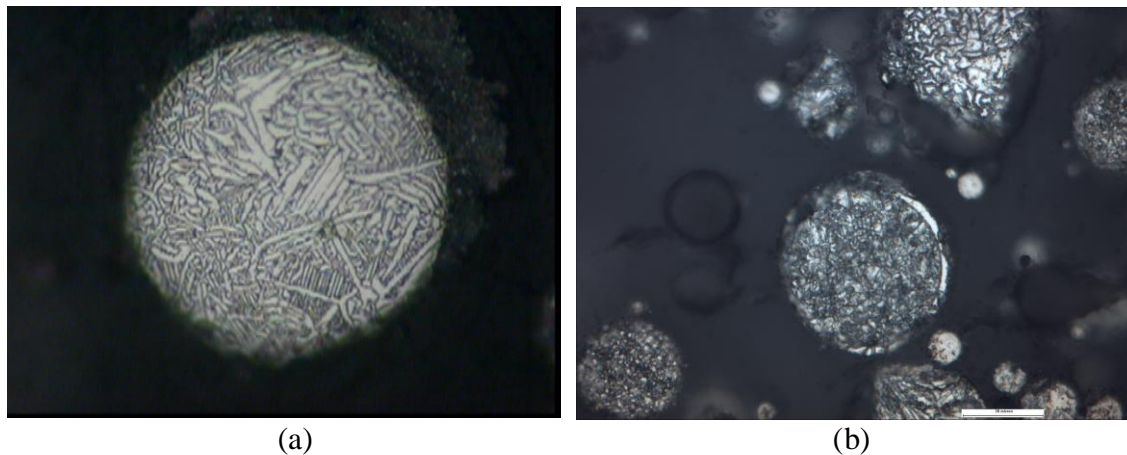


Figure 2: Optical micrograph of a) NdFeB powder b) NdFeB-TiC powder. (Mag 500X)

SEM images taken on the cross section of the NdFeB and NdFeB-TiC powder are shown in Figure 3. The NdFeB powder consisted of an underquenched dendrite-like structure with the majority of the phases are $\text{Nd}_2\text{Fe}_{14}\text{B}$ and a fine network of RE rich phase at the grain boundaries which were identified by EDS. In NdFeB-TiC powder, the grain size is finer than NdFeB powder. Ti and C were observed within the grain and at grain boundaries of $\text{Nd}_2\text{Fe}_{14}\text{B}$ phase. However it was not possible to quantify boron in $\text{Nd}_2\text{Fe}_{14}\text{B}$ as its concentration is about 1 wt.%. The existence of boron in $\text{Nd}_2\text{Fe}_{14}\text{B}$ phase was based on the qualitative and not quantitative analysis. No free iron phase observed in the atomized powder for both powders. XRD analysis on the NdFeB and NdFeB-TiC powders, also confirm that the majority of the phase is crystalline $\text{Nd}_2\text{Fe}_{14}\text{B}$. No significant amorphous phase is found in any size fraction of the powder studied, although the smaller particles exhibited peak broadening. It is expected that in NdFeB-TiC powder, very fine particles are at least partially amorphous, but they could not be easily separated for measurement.

Figure 3a shows the microstructure of the powders at different particle size. As can be seen from this figure, the NdFeB powder with bigger particle size has dendritic structure. However, for the smaller particle powder the grain size is smaller and more

equiaxed. As for NdFeB-TiC, more equiaxed structure is observed as compared to NdFeB even at much bigger particle sizes.

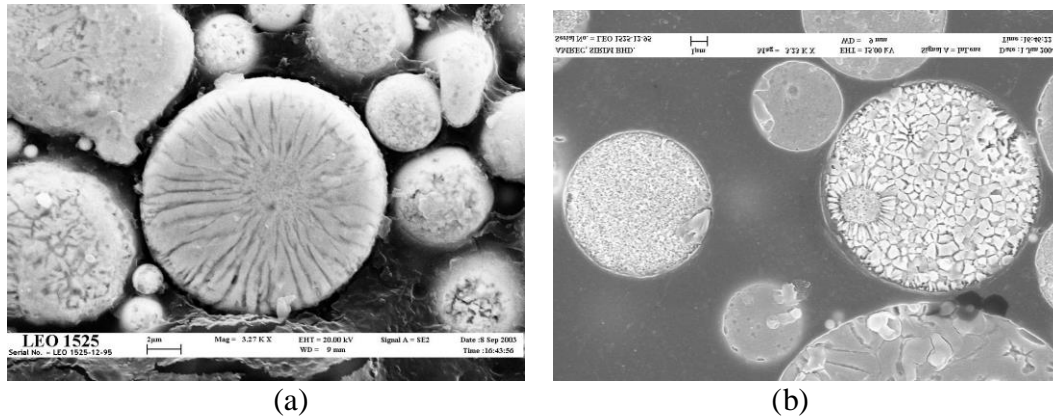


Figure 3: SEM image of a) X-section of the NdFeB powder b) X-section of NdFeB-TiC powder.

The dendritic structured powder is not suitable for the isotropic magnet and its application is limited to sintered magnet. The dendritic structure formed during atomization in NdFeB powder was due to underquenching of the melt. The formation of dendrite can be avoided if the higher cooling rate during atomization is applied. However it is very difficult to increase the cooling rate during atomization because the cooling mechanism for the atomization is by convection (due to the interface between the gas and the melt). Unlike melt spinning whereby the cooling mechanism is by conduction (the melt has the direct contact with the copper roller) the cooling rate in atomization is lower than in melt spinning. The cooling rates in atomization and melt spinning are 10^4 - 10^5 K/s and 10^5 - 10^7 K/s respectively. From the present result it is believed that TiC addition in NdFeB powder has reduced the critical cooling rate as such that the smaller grain size can be formed at much slower cooling rate. However this cooling rate is not fast enough to form the amorphous powder and the present NdFeB-TiC powder produced is believed to have the mixed structure of amorphous and fine grains.

The effects of particle size (i.e. grain size) on the magnetic properties of NdFeB and NdFeB-TiC powder are shown in Figure 4 (a), 4 (b) and 4 (c). From this Figure, it is observed that the magnetic properties of the NdFeB-TiC are higher than NdFeB powder without TiC addition. As shown in Figure 4 (a) in NdFeB-TiC, coercivity (H_c) decreases as the particle size increases. However in NdFeB powder the H_c is almost constant regardless of the particle size. This is because even though the particle size is small the grain size is big and dendritic in nature. Annealing is needed in order to increase the H_c in NdFeB powder. In general, H_c of NdFeB-TiC is higher than NdFeB powder in all particle sizes range studied. However the differences in the value are more pronounced in the smaller particle size than in bigger particle size. As discussed earlier TiC addition reduces critical cooling rates and produces smaller grain during atomization. The small grains increased the grain boundaries and hence increased the H_c of the powder.

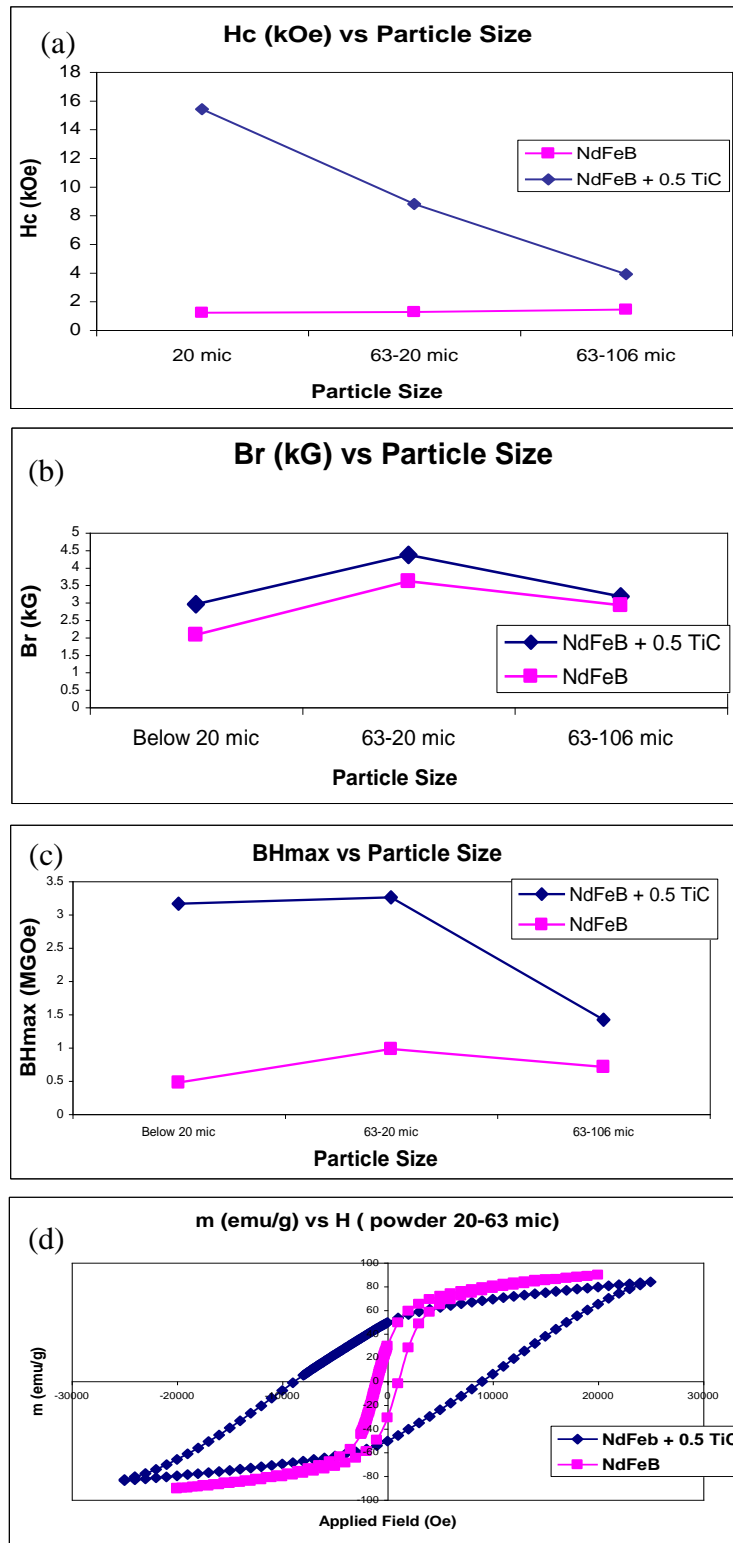


Figure 4: Magnetic properties of the powder at various particle sizes.

As shown in Figure 4 (b) the remanence (Br) increases as the particle size is increased and then reduced in both NdFeB and NdFeB-TiC powders. Br in NdFeB-TiC is higher than NdFeB. This finding is rather surprising. This is because NdFeB-TiC should have lower Br value due to the presence of additional phase (TiC) in Nd₂Fe₁₄B phase. The possible explanation for this is that the TiC is so fine and well distributed in the powder as such that its effect as a second phase on Br is not significant. The TiC particle size used in this study is 5 μm.

The Maximum energy product (BH_{max}) for the NdFeB powder and NdFeB-TiC increase as the particle size is increased to the range of 20 to 60 μm and reduces as the particle size is further increased to the range of 63-100 μm. The highest values of BH_{max} for NdFeB and NdFeB-TiC powder obtained at the range of 20 to 60 μm are 0.98 and 3.25 MGOe respectively. Regardless of the particle size, the BH_{max} of the NdFeB-TiC powder is higher than NdFeB powder. The lower magnetic properties in the NdFeB spherical powder compared to NdFeB-TiC powder is related to the differences in the microstructure between them. The NdFeB atomized powder having dendritic structure shows lower magnetic properties compared to NdFeB-TiC with smaller equiaxed grains. However the magnetic properties of NdFeB-TiC powder is rather low compared to melt spun ribbon, which is commonly used for bonded magnet.

In both NdFeB and NdFeB-TiC alloy, atomization process using argon gas could not produce the amorphous structure, which is needed to form nanocrystalline after further annealing. In contrary, melt-spinning process produced amorphous structure, which could be further annealed to form nanocrystalline structure. This nanocrystalline structure increases the magnetic properties of the ribbon. Addition of TiC in NdFeB has reduced the grain size to some degree, however it is not sufficient to form the amorphous structure. It is concluded that for the present alloys studied, the amorphous powder could not be produced by argon gas atomization due to the low cooling rate during solidification. In order to increase the cooling rate helium gas has to be used for atomization.

Figure 4 (d) shows the example of the hysteresis loop (M-H) of the NdFeB and NdFeB-TiC powder of the range between 20 to 63 μm.

CONCLUSION

In the present work it is observed that the magnetic properties of the NdFeB-TiC powder is higher than in the NdFeB without TiC addition. The optimum magnetic properties for both materials are obtained in particle size of 20 to 63 μm. The increased magnetic properties are believed to be due to the finer grain size obtained in the NdFeB-TiC powder as compared to NdFeB powder. The addition of TiC in NdFeB alloy has reduced the critical cooling rates of the alloy as such that the small grain structure can be obtained at much lower cooling rates.

However the magnetic properties obtained in NdFeB-TiC are lower than the annealed melt spun ribbon. The differences in the properties are due to the different microstructure for both materials. The poor properties of the as-atomized NdFeB

powder are due to bigger grain sizes and the formation of dendritic structure of $\text{Nd}_2\text{Fe}_{14}\text{B}$.

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