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d^0-Ferromagnetism in SHS Titanium Nitride Treated by Ball Milling

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Abstract

In this work, the influence of mechanical treatment (mechanical milling) of the TiN titanium nitride powder produced by self-propagating high-temperature synthesis on the magnetic properties of the milled powders is investigated. The effect of d0-magnetization was observed. The TiN powders were characterized by scanning electron microscopy, X-ray diffraction, vibrating-sample magnetometry, specific surface area measurement, and chemical analysis. The results show that the mechanical treatment of the TiN titanium nitride powder influences the magnetization in a nonmonotonic manner. The conditions of mechanical treatment corresponding to the best value of specific magnetization of milled powders were established. The specific magnetization depended on three measured parameters: specific surface area, coherent scattering region, and average particle size. It was shown that unit cell parameters of milled TiN titanium nitride powders have not been changed with the increasing of duration milling time. The calculated values of CSR of mechanically treated powders decreased with the increasing of duration of milling time. The values of macrostrains were negative. Mechanical treatment of the TiN titanium nitride powders has led to a change in the nitrogen content from 21.4 to 20.0 wt.%. Stoichiometry of the TiN titanium nitride varied from $TiN_{0.903}$-$TiN_{0.886}$; therefore, the observed d^0-magnetization effect is associated with a defective surface structure of mechanically treated powders.

1. Introduction

The effect of "d^0 magnetism" is the subject of theoretical and experimental studies due to the possibility of its use in spin-polarized carrier-based devices [1, 2]. d^0-magnets are a class of materials in which magnetic ions are absent, and in principle these materials should not be ferromagnetic, but actually exhibit room-temperature ferromagnetism (RTFM) [3]. Moreover, it has been suggested that structural defects such as cation and oxygen vacancies, as well as structural heterogeneity, may induce ferromagnetic ordering [4]. RTFM also exists in other inorganic materials with their own surface defects. For example, RTFM occurs in metal nitrides such as NbN, MoN [5], and TiN [6]. Among metal nitrides TiN is of particular interest, as it has many other attractive properties, such as high hardness [7] and favorable optical characteristics [8, 9]. TiN materials combining large specific surface areas with good electrical conductivity should be ideal for use in super-capacitors [10, 11]. Its chemical durability and high melting point make it suitable for use as a carrier in various heterogeneous reactions [12], including as a catalyst for fuel elements of the proton-exchange membrane [13, 14]. Despite many of the above advantages, the observed saturation magnetization at room temperature (RT) of TiN nanoparticles (0.002 emu/g) [6] is not sufficient for real spintronic applications requiring materials with high sensitivity to moderate magnetic fields [15]. The true mechanism leading to the order of ferromagnetism in un-doped oxides, which are diamagnetic or paramagnetic in a bulk form, is the subject of discussion and is not entirely clear. Experimental and theoretical studies have shown that this may be due to internal defects, mainly due

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to metal vacancies or other defects [16–18]. Some researchers have proposed an attractive idea for the implementation of d^0-ferromagnetism by creating structural and chemical heterogeneity in the material by using of appropriate impurities [16]. Since it was observed in highly defective samples, this led to the assumption that magnetism can be a common property of such materials [19]. Consequently, it was obvious that RTFM should be highly dependent on the method of powder production. Recently [20] it was reported that TiN nanoparticles synthesized by a levitation-jet generator demonstrate higher values of the maximum saturation magnetization than nanoparticles obtained by the authors [6]. However, this technique is not large-scale. Therefore, it is necessary to find a more suitable route for the production of TiN powder. Self-propagating high-temperature synthesis (SHS) is a known powerful method for large-scale production of titanium nitride [21–23]. Following [24–27], we used the mechanical milling (MM) for the induction of defects in microsized diamagnetic or paramagnetic powders, suggesting particle size reduction, the creation of defects and deformation of the lattice can be achieved by milling [28]. With increasing milling time or high rotation speed, more defects should be induced into the milled powders and the obtained microsized materials revealed a d^0-ferromagnetic behavior [28].

The aim of this study is to use mechanical milling to induce defects in SHS TiN powders. To the best of our knowledge, the usage of ball milling treatment of nitride compound to induce the d^0-ferromagnetism for the first time is accomplished in this work.

2. Experimental

Ti powder (PTS) with an average particle size of 40 μm and nitrogen gas (99.999 at.%) were used as initial components. The self-propagating high-temperature synthesis of TiN compound was carried out in a reactor at a nitrogen pressure of 30 atm. (described in detailes elsewhere [28]). The obtained cake of sintered powders was subsequently subjected to preliminary mechanical grinding and sieving through a suitable stainless steel sieve (up to 150 μm).

Table 1
The ball milling conditions of SHS TiN powder

Experiment sample/stage		MODE 1			
		M (g) (ball material-corundum, exc.#7)	NG (g)	Duration time (min)	Impact work (a.u.)
#1	origin	0	0	0	0
#2		20	9	5	54
#3		20	9	10	108
#4		18	9	50	540
#5		18	13	70	852
#6		16	20	90	1332
#7		30 (zirconia)	20	110	2052
		MODE 2			
#8		20	20	150	3600
#9		18	20	210	5040
#10		14	20	235	5640
#11		12	20	295	7080
		MODE 3			
#0	origin	0	0	0	0
#01		20	20	5	120
#02		20	20	10	240
#03		18	20	15	360
#04		18	20	35	840
#05		16	20	55	1320
#06		16	20	75	1800
#07		14	20	95	2280

To determine the effect of the degree of grinding on the magnetization of the final product, the initial powder was processed in a FRITSCH Pulverizette 5 planetary mill. The balls and bowls from non-magnetic materials (corundum, zirconium dioxide) were used under the experimental conditions shown in Table 1 (the ratio of the mass of the balls and the mixture was always 1:1). Different modes of treatment were related with a new portion of the starting powder for use. The impact action on the powder was estimated as a proportion of the kinetic energy of the balls, which goes into work of impact. For ease of calculation, an expression was used for such work through the mass of the balls, the acceleration achieved as they move, and the constant distance of the ball when struck (that was included in an impact factor). The number of impact events per second suggests the same for all the regimes (it was included in the impact factor too). This, of course, is not quite true, but such a factor only affects the scale of the phenomenon being studied in time. Therefore, we believe that the mentioned work is expressed as follows:

$$W = kMGt = kmnNgt,$$

where k – impact-factor, M = nm – total ball mass (g), n – number of balls, m – mass of the ball, g – acceleration of gravity (9.8 m/s^2), N – factory gravity factor (9–20), t – duration time of treatment (s).

3. Characterization

The morphology, dimensions and chemical composition were examined using scanning electron microscopes CARL ZEISS ULTRA PLUS/INCA ENERGY 350 and LEO 1450/INCA ENERGY 300. Specific surface area of materials was determined by 4-point nitrogen physical sorption BET measurements using META SORBI-M device. The average particle size was determined by laser particle analyzer MICROSIZER-201C (accuracy of measurements 4–7%).

The phase composition of the samples was determined by X-ray diffraction analysis (XRD) on a DRON-3M diffractometer (CuKα radiation). XRD patterns were recorded in a systematic scanning mode in the interval of angles with a scanning step of 0.02 deg. and time delay of two seconds. The cell parameters of the phases were determined using the internal standard method (reference material – SRM640D silicon). The values of the coherent scattering region (CSR) and microstrains were calculated by two methods: the Williamson-Hall plot and using program "Size and Strain" of diffractometer software.

Chemical analysis for nitrogen content was carried out by Kjeldahl method (accuracy of 0.2%). Magnetic properties of the powders were measured by means of EG&G PARC M4500 vibrating sample magnetometer in applied magnetic fields of up to 13 kOe, which was calibrated using pure Ni standard with a relative accuracy of 1×10^{-4} emu at a room temperature. Sample mass (a few tenths of mg) was determined with a relative accuracy of $\pm5\times10^{-2}$ mg. We subtracted the magnetic moment of samples from the experimental outputs of the diamagnetic contribution associated with a nylon sample container.

4. Results and discussion

Magnetic measurements of milled powders obtained under different modes have shown that the samples #6 (MODE1) had the best values of specific magnetization (0.32 emu/g). Table 2 shows changing in some parameters of titanium nitride powders corresponding to different time of milling.

Table 2
Specific surface area, d-spacing and average particle size of TiN powders (MODE 1)

Time of milling	d-spacing, Å	S, specific surface area, m^2/g	Average particle size (d_{50}), mkm
0	a = 4.24160 (±0.00036)	0.266±0.01	99
5	a = 4.241703 (±0.000162)	0.39±0.02	47
10	a = 4.241843 (±0.000271)	0.48±0.01	44
50	a = 4.241745 (±0.000084)	0.699±0.05	31
70	a = 4.241371 (±0.000192)	1±0.02	9.8
90	a = 4.241638 (±0.00020)	1.35±0.05	5.58
110	a = 4.241901 (±0.000244)	1.8±0.07	3.47

XRD analysis (Fig. 1) established the phase composition of the material was as titanium nitride TiN0.9 (JCPDS PDF2 crystallographic database card #71-0299).

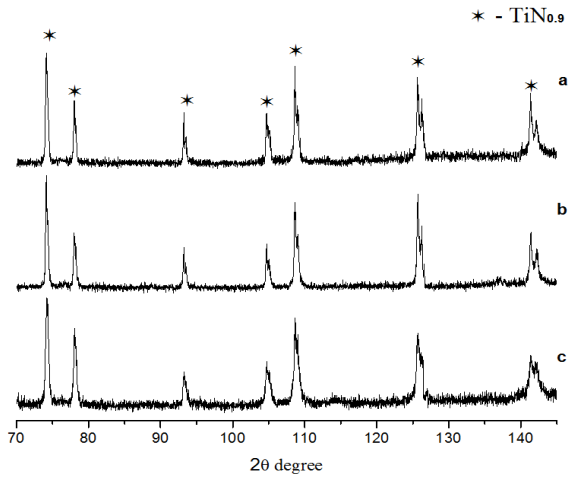

Fig. 1. XRD patterns of the initial powder (a) and MM-treated materials: (b) – treated during 70 min, (c) – treated during 110 min.

Unit cell parameters calculated for each sample showed actually no changing in d-spacing, but as it can be seen from XRD patterns there is some broadening of the peaks with increasing of milling time. The values of the coherent scattering region (CSR) and macrostrains were calculated by two methods: the Williamson-Hall plot and using program "Size and Strain" of diffractometer software. The results of both methods showed the similar values for (CSR) and that the values of macrostrains were negative. This means that there is no contribution to the broadening of the peaks from the macrostrain. Figure 2 shows CSR decreases with the MM duration time.

As mentioned above, grinding the powder was considered as a factor that can change the state of the surface of the TiN particles. It was expected that it would lead to an increase in the defectiveness of the material structure and, accordingly, to an increase in its d⁰-magnetization. To assess the effect of contamination of the initial TiN powder with ferromagnetic impurities, its chemical analysis was carried out using the volumetric method. The results of the analysis indicate the presence of metallic iron for 0.8 weight percentage. The calculation of the parasitic contribution from this metallic iron (the magnetization of the bulk iron is equal 218 emu/g) to the total magnetization of the powder gives a value of about 180 memu/g. In this case, we assume that in the initial sample there are an insignificant number of defect places.

Figure 3 shows a cumulative graph of the dependences of the magnetization of TiN powders on the impact work during its grinding, where the contribution from the impurity metallic iron (originated from preliminary stage of grinding) was previously subtracted from the total magnetization. In addition, the graph shows the values of the specific surface of the powders, measured at the corresponding stages of the study. Analysis of Figs. 3 and 4 suggest that the observed consistent decrease in magnetization at the initial stages of machining may be due to a temporary decrease in the density of initial defects on the surface of large powder particles when it is destroyed by the defects already present in the sample particles. To establish the nature of defects we use the chemical elemental analyses. In the sample #1, such analyses discovered $TiN_{0.903}$ (21.4 wt.% of nitrogen) compound, and in sample #5 – $TiN_{0.886}$ compound (20 wt.% of nitrogen). Decrease in nitrogen content leads to formation of point defects – atomic vacancies that is one of the common factors of defect mechanism for d⁰-ferromagnetism.

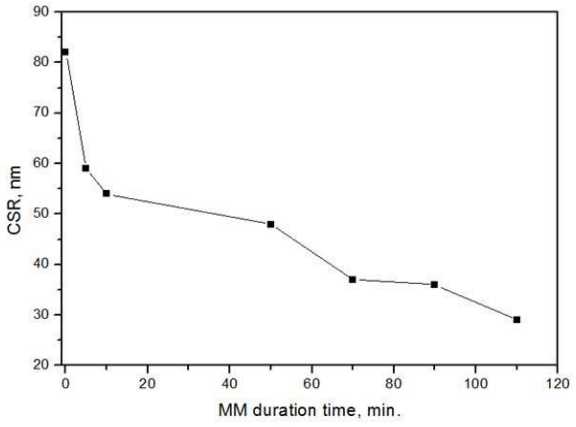

Fig. 2. Coherent scattering region (CSR) vs the time of MM of the powdered samples (MODE 1).

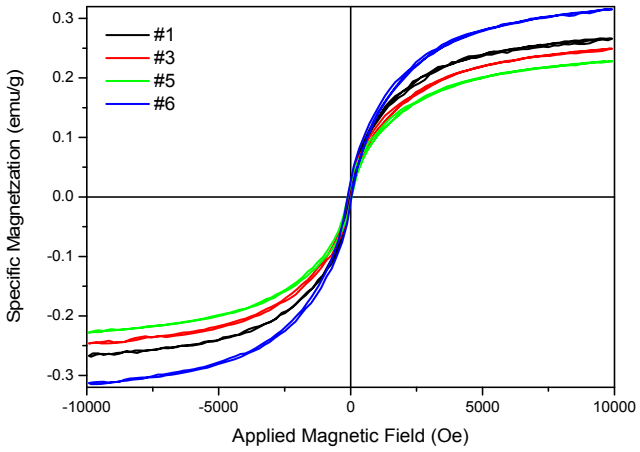

Fig. 3. Magnetization vs. magnetic field of some TiN powders after the MM-treatment. The numbers correspond to the samples after certain stages of treatment, which are listed in Table 1.

During subsequent MM, increased surface magnetism was discovered (Fig. 4).

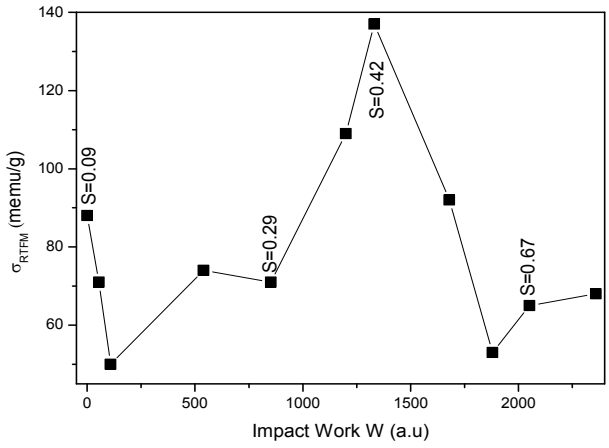

Fig. 4. The dependence of magnetization on the impact work during the grinding of TiN powder. The numbers near experimental points correspond to the values of the specific surface area of the corresponding material.

At the final stages of processing (#8 – #9), with the maximum shock treatment of the particles surface used in this work, they can cause some particles to stick together into larger formations with a partial decrease of the defective surface. For d^0-magnetism, so the special surface area of the sample, generally, increases due to the sufficiently good permeability of such agglomerates for the carrier gas during the BET measurements. This behavior of the material helps to reduce the total magnetization of the sample. Thus, the boundaries of the application area of grinding for this material

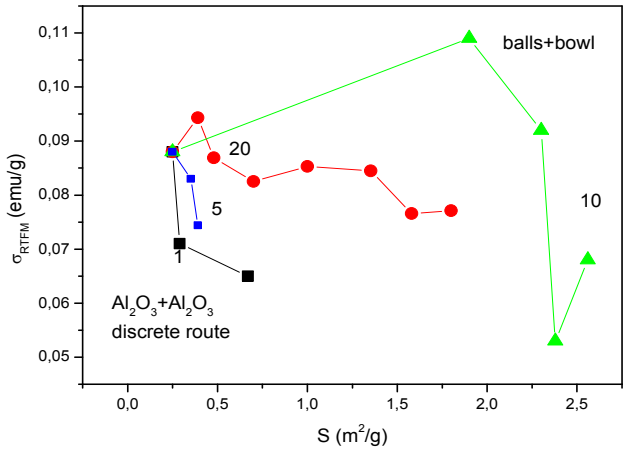

Fig. 5. The dependence of magnetization on the specific surface area of TiN powder after grinding at different processing modes (numbers on the plot pointed to the started quantity of grinding bowls).

are established, at which it is possible to achieve a noticeable magnitude of magnetization for d^0-magnetism. Some dependencies of σ_{max} (RTFM) vs S is shown in Fig. 5.

5. Conclusions

It was shown that mechanical grinding of SHS titanium nitride powder increases its magnetization in a non-monotonic manner. Mechanical milling is an effective and simple technique to prepare defect-induced ferromagnetism in ultrafine powders. Several milling parameters can be used to increase the defect density in the initial powder such as milling time, rotation speed, and ball-to-powder mass ratio. However, the starting powder with high purity and non-magnetic milling tools should be used in order to avoid any contamination with magnetic impurities that misled to the appearance of ferromagnetic behavior.

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