The effect of mechanical treatment of TiNi powder on structure and phase composition

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Abstract. In this work, the study of the effect of mechanical treatment of TiNi powder on structure and phase composition is presented. The powder was processed in high-energy planetary ball mill for different time. It has been shown that the average particle size measured by scanning electron microscopy changes not monotonous after mechanical treatment, but form of particles changes. The coherently diffracting domain size decreases from 43 nm to 5 nm with increasing of mechanical treatment time that significantly less than the average particle size measured by laser diffraction method and the average particle size calculated from the obtained values of the specific surface. That is to say, the powder particles consist of several crystallites. The width of all peaks changes after 10 s of mechanical treatment that can correspond to an increasing of the defect density. The lattices parameters of all phases change not more than 0.8 % after mechanical treatment. Two processes compete during mechanical treatment, characterizing either brittleness or plasticity. Many defects appear during mechanical treatment stipulate a quasi-amorphous state with increasing of mechanical treatment time.

1. Introduction

The creation of new materials is actual task for the development of new technologies used in Siberia and the Arctic region.

As it well known that amorphous phase, metastable crystalline and quasicrystalline phases, supersaturated solid solutions and nanostructures can formed in result mechanical treatment and properties of materials can change [4, 5]. Mechanical treatment allows creating active states in a solid that can leads to accelerating of chemical reactions. It is crucial in use in different areas, for example, for the storage of hydrogen. Among hydride forming system which applied in this area, special emphasis should be placed on the intermetallic compound Ti- at near-equatomic composition which as a rule has a complex phase content consisting with TiNi (B2), (B19’), Ti2Ni (E93) and TiNi3 (D024) [6, 7]. Therefore, the study of structure, phase composition after mechanical treatment of multicomponent mixtures is actual question.

In this work it has been studied the effect of mechanical treatment of Ti-Ni at near-equatomic composition of powder on structure and phase composition.

2. Material and methods
Near equiatomic Ti$_{0.45}$Ni$_{0.55}$ powder (produced by the «Polema» plant) with average particle size of 11.1 μm with 7.5 μm of standard deviation is used for studies.

The mechanical treatment was performed in an AGO-2 high-energy planetary ball mill using the container and stainless steel balls with 6…10 mm diameter. The powder mixture was treated at a rotation speed of 1820 rpm; acceleration during treatments was 60g. The ratio of the mass of balls and powder was 5:1. The mechanical treatment was carried out for different time 5 – 300 second.

The morphologies of powders were observed by scanning electron microscopy (SEM) TESCAN VEGA 3SBH. The measurements of particle size distribution of powders by means of laser diffraction (LD) method were performed with SALD-7101.

Analysis of the phase and structural transformations was carried out with diffractometers with CuK$_\alpha$ radiation using step-by-step registration and counting time for obtaining statistical accuracy better 3 %. XRD line profile analysis was used to determine the coherently diffracting domain (CDD), which calculated by the Scherrer equation [8] for the first spectra line. The lattice parameters were determined using an application package for X-ray analysis.

The powders specific surface areas (SSA) were measured with a Sorbi$^{\text{TM}}$ series instrument measurement device. From the obtained values of the specific surface, it has been calculated the average particle size assuming their spheroids shapes.

3. Results

SEM images showing morphology of powders after mechanical treatment after 30 s (a); 300 s (b) are shown in Fig. 1. One can see it decreases of size particles from 11.1 to 7.8 μm after 30 s of mechanical treatment due to the fracture of particles, and then it increases of size particles to 33.2 μm after mechanical treatment 300 s due to agglomeration. The form of particles changes from angular to spherical one. These results correspond to measured powder apparent density, when it increases from 1.96 to 2.56 g/cm$^3$ and then decreases to 2.38 g/cm$^3$ after 30 and 300 s mechanical treatment, respectively.

![Figure 1](image1.png)

(a)

![Figure 1](image2.png)

(b)

**Figure 1.** SEM images showing morphology of powders after mechanical treatment: 30 s (a) and 300 s (b)

In Fig. 2 shows the dependence of the average particle size measurement different methods and CDD at different time of mechanical treatment. The average particle size measured by method laser diffraction decreases from 8.0 to 0.5 μm with increasing of mechanical treatment time. The average
The average particle size calculated from the obtained values of the specific surface do not significantly change: 3.9 μm – 1.7 μm. The CDD size decreases from 43 nm to 5 nm after mechanical treatment, that is significantly less than the average particle size measured by methods SEM, LD and BET. That is to say, particles consist of several crystallites, so number of crystallites increases from $5 \times 10^4$ to $13 \times 10^6$ with increasing time of mechanical treatment.

In Fig. 3 shows XRD patterns of TiNi powders before and after mechanical treatment. As one can see the powder before mechanical treatment consists of a mixture of phases such as TiNi (B2 and 19′), Ti$_2$Ni (E9$_3$) and Ni$_3$Ti, vertical lines are indicated them the angular positions. The lattice parameters calculated from diffraction lines are in good agreement with the literature data [9-12], TiNi (B2) the parameter is 0.30074 nm, TiNi (B19′): $a = 0.26902$ nm, $b = 0.45698$ nm, $c = 0.41215$ nm, $\beta = 87.412^\circ$; Ti$_2$Ni $a=1.13332$ nm, TiNi$_3$ $a = 0.50989$ nm, $c = 0.83077$ nm. From the measured angular positions of the lines with increase mechanical treatment time it has been calculated lattice parameters which decreases by 0.3 % for TiNi, TiNi$_3$ parameters decrease not more by 0.8 %, for Ti$_2$Ni this change was 0.5 %.

The dependence of the width of peaks with mechanical treatment time is shown in Fig. 4. As one can see, there are two stages during treatment: on the first step up to 10 s the width of all peaks doesn’t significantly change, but on the second step after 10 s the width of all peaks increases for mechanical treatment, it can be connected to an increase in the defects density in the crystal lattice which according to literature data [13].

As one can see from Fig.5 after mechanical treatment quasi-amorphous phases during treatments appears on x-ray patterns and its content increase for an increasing of milling time. This result is shown in inset in Fig.5, the arrows indicate X-ray lines that correspond to the quasi-amorphous phase. The relative content of the quasi-amorphous phase increases to 55 % with increasing mechanical treatment time, while the content of the crystalline phases decreases.
The grinding process can evaluate using the equation according to [14], characterizing the kinetics of the fine-milling process (Eq. (1)):

\[ R = R_0 e^{-kt^m} \]  

where \( R \) is particles content in coarse fraction after milling for time \( \tau \), \( R_0 \) is particles content in coarse fraction in the initial material, \( k \) – kinetic coefficient of the milling; \( m \) – grinding mechanism constant. In [14] it has been shown that more brittle materials have higher grinding rates \( k/m \).

Therefore, from the dependence of the average volume particle size on the time of mechanical treatment (Fig. 6.) can calculate \( k \) and \( m \). It was shown that \( k \) is 3.22, \( m \) is 0.05, and so \( k \) is more than \( m \) by 64 times, that mean the particles are brittle and quickly grinding by balls with an increase mechanical treatment time. However, on the SEM results (Fig. 1, a and b) can see that form of particles change that mean he plasticity of the powder. Thus, two processes compete during mechanical treatment, characterizing eitherbrittleness or plasticity. Many defects appear during mechanical treatment stipulates a quasi-amorphous state with increase of mechanical treatment time, that can be seen in Fig. 5.

### 4. Conclusion

It was shown that the average particle size measured by scanning electron microscopy changes not-monotonous after mechanical treatment due to destruction and subsequent agglomeration particles. A state with a very small coherently diffracting domain size (5 nm) is formed after mechanical treatment 300 s, which corresponds to quasi-amorphous state of material. The relative content of quasi-amorphous phase increases to 55 %. The coherently diffracting domain size is significantly less than average particle size measured by laser diffraction and the average particle size calculated from the obtained values of the specific surface. Therefore, the powder particles consist of several crystallites, the number of which increases from \( 5 \times 10^4 \) to \( 13 \times 10^6 \) with mechanical treatment time. Two stages during treatment can be detected, on the first step up to 10 s the widths does not change, on the second
step up after 10 s the widths changes in result of increasing the defect density. The lattices parameters of all phases decrease after mechanical treatment, in particular, the lattice parameter TiNi decreases by 0.3 %, TiNi₂ parameters decrease by not more than 0.8 %, for Ti₂Ni this change is 0.5 %.

Thus, one can identify two processes competing, characterizing either by fragility (changing the average particle size) or by plasticity (changing geometric form of particle and formation quasi-amorphous phase) during mechanical treatment.

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References
[1] Skakov Yu A 2004 MitOM 4, 3–12.
[2] Zadorozhnyi V Yu, Milovzorov G S., Skakov Yu A, 2008 MitOM 8, 46–52.
[3] Schwarz R B, Koch C C 1986 Appl. Phys. Lett. 49(3), 146–148.
[4] Boldyrev V V. 1986 Proc. Indian natn. Sci. Acad. 52, 400–417.
[5] Smetkin A A, Pimenova N V et. al. 2004 Poroshkovaya metallurgiya 27, 61–64.
[6] Otsuka K, Ren X 2005 Prog. Mater Sci. 50, 511–678.
[7] Tang W, Sundman B, Sandström R et. al. 1999 Acta Metall. 47, 3457–3468.
[8] Scherrer P. 1918 Göttinger Nachrichten Gesellschaft. 2 98–101.
[9] Stuewe H-P, Shimomura Y Z 1960 Metallkd 51, 180.
[10] Sinclair M G 1981 Acta Crystallogr. Sec. E 37, 1803.
[11] Laves F, Wallbaum H J 1939 Z. Kristallogr 101, 78.
[12] Mueller M H, Knott H W 1963 Trans. Met. Soc. AIME 227, 674.
[13] Gattia D M, Gizer G, Montone A 2014 Int. J. Hydrog. Energy. 39, 9924–9930.
[14] Tadzhiev F Kh, Ismatova R I, Shamuratova Sh M 1991 Glass Ceram. 48(6), 255–257.