A structure formation in Ti-Ni powder after high-energy mechanical treatment

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Abstract. In this work a structure formation in Ti-Ni powder after high-energy mechanical treatment in a planetary ball mill with an acceleration of 60g are presented. Mechanical treatment time of powder was 5-300 seconds. It was shown the powder in initial state consists of phase mixture TiN (B2, B19’), Ti2Ni (E93) and TiNi3 (D024). The lattice parameters of powders not significantly change at mechanical treatment and correspond in good agreement with literature data. The quasi-amorphous phase is formed after mechanical treatment and the relative content of phases change so that the relative content of quasi-amorphous phase increases steeply from 0 % to 45 % in first 10 second of treatment mechanical treatment and not significantly changes at more prolong milling. The full widths at half maximum of peaks not significantly change to 10 second mechanical treatment, but the more prolong milling leads to them increasing due to forming of dislocation in all phases, wherein the value of the dislocation density of Ti2Ni phase is more than of TiNi and Ni3Ti phases and corresponds to 10^{13} cm^{-2} at 60 second of mechanical treatment.

1. Introduction
Plastic deformation of metals leads to structural changes that it is reflected on properties of the material; the example could appear lattice stresses and generate stacking faults and dislocations [1]. However, the final state depends on many parameters, the example, chemical composition of materials, crystal structure, rate of deformation and other [2, 3].

Ti–Ni alloy of near-equatomic composition is interesting material for investigation of plastic deformation of different phases existing in it and these phases - TiNi (B2, B19’), Ti2Ni phase (E93) and TiNi3 phase (D024) will obtain a new data for understanding deformation in multiphase material [4, 5]. Such studies possible to investigate only in the powdered state by using a high-energy mechanical activation [6]. Moreover a similar treatment often leads to amorphization [7-10], formation of new quasicrystalline phases [11], supersaturated solid solutions and nanostructures [12-14].

It is well known that in cold-worked metals for example in aluminium, the dislocation density may up to 10^{10} cm^{-2} [15], the dislocation density in equiatomic alloy Ti50Ni50 is 10^{11} cm^{-2} after 8 cycles of the equal channel angular pressing (ECAP). For copper powder after treatment in ball mill for 8 hour a dislocation density before and after milling changes from 10^{10} cm^{-2} to 10^{12} cm^{-2} [16].

However, the information on mutual influence of different phases in multiphase alloys of TiNi at mechanical treatment in the literature is limited. In this work it has been studied a structure formation in Ti-Ni powder after high-energy mechanical treatment.
2. Material and methods
Near equiatomic Ti_{0.45}Ni_{0.55} powder was used as starting materials (Polema plant), the average particle size of 11.1 µm with 7.5 µm of standard deviation.

A high-energy AGO-2 planetary ball mill with steel vial and steel balls were used for mechanical treatment. The rotation speed of planetary disk of 1820 rpm; acceleration during treatments was 60 g. Phase composition of the powder were characterized by X-ray diffraction (XRD) on a X-ray diffractometer using Cu Kα radiation. The coherently diffracting domain (CDD) of the powder was measured by X-ray line-broadening technique using Scherrer equation [17] on the first line of X-ray spectra. To evaluate of the relative content of crystalline phases and quasi-amorphous phase were used quantitative calculations of integral intensities. The total milling energy was calculated according to [11, 18]. The dislocation density was calculated according to [15] using the first line of X-ray spectra for all phases.

3. Results
The total energy of milling were calculated according to [11, 18] and corresponded 0.19 Joule for one second and has a linear dependence with milling time. On Fig. 1 a are shown XRD patterns of TiNi powders before and after mechanical treatment at 300 second and on Fig. 1 b – a relative content of crystalline and quasi-amorphous phases. As one can see (Fig. 1, a) the powder in initial state 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. In the process of mechanical treatment, widths of the peaks increase and after 300 s XRD pattern of powder looks like belongs to quasi-amorphous state of material. Mechanical treatment results in a non-monotonous change in the relative content of phases (Fig. 1, b), so that the relative content of crystalline phases decreases steeply from 100 % to 55 % after 10 seconds mechanical treatment and more slowly decreases from 55 % to 45 % after 300 seconds mechanical treatment, while the content of the quasi-amorphous phase increases in the same way. As one can see, the changes between phases stopped after first 10 sec of treatment, therefore, we can conclude that total energy is spend not only for formation quasi-amorphous phase but for particle aggregation, stiction of particles to the walls of vial, heating balls, powder, walls of vial and decreasing number of collisions between balls and powder/walls of vial, because the relative content of quasi-amorphous phase not significantly change.

The lattice parameters are in good agreement with the literature data [19-22]. The lattice parameters of TiNi (B2) phase decreases from 0.30074±0.00005 nm to 0.29968±0.00005 nm after...
30 seconds mechanical treatment. The lattice parameter $a$ of TiNi$_3$ phase not significantly changes and it is $0.509\pm0.005$ nm, while the lattice parameters $c$ and $c/a$ decrease from $0.832\pm0.005$ nm to $0.826\pm0.005$ nm ($c$) and from $1.635\pm0.005$ to $1.625\pm0.005$ ($c/a$) after 30 seconds mechanical treatment. The lattice parameters of Ti$_2$Ni phase decreases from $1.13332\pm0.00005$ nm to $1.12709\pm0.00005$ nm after 60 seconds mechanical treatment.

The full widths at half maximum (FWHM) of peaks presented in Fig. 2 are obtained at different mechanical treatment time. One can see the FWHM changes insignificantly until 10 seconds of treatment and increasing of FWHM of peaks after this time can be directly related to strains produced by dislocations within these domains [23-25].

![Figure 2](image)

**Figure 2.** The dependence of the width (FWHM) of peaks on mechanical treatment time

The dislocation densities calculated like in [15] are shown in Table 1 for different phases and time of treatment. As one can see the dislocation density increases quicker in the Ni$_3$Ti phase than in the TiNi and Ti$_2$Ni phase up to 30 s of treatment, however value of the dislocation density at 60 second mechanical treatment for Ti$_2$Ni phase is more when 4 time higher than for TiNi phase and in ~17 time than for Ni$_3$Ti phase. These results well correlate with literature data [16] for Cu powder and dislocation density before and after ball milling changes from $\rho=2.3\cdot10^{10}$ cm$^{-2}$ to $\rho=6.0\cdot10^{11}$ cm$^{-2}$, accordingly.

| Mechanical treatment time (s) | TiNi | Ni$_3$Ti | Ti$_2$Ni |
|------------------------------|------|----------|----------|
| ini                          | 3.4  | 0.3      | 20.2     |
| 5                            | 4.7  | 0.8      | 26.2     |
| 10                           | 4.8  | 2.2      | 27.7     |
| 30                           | 11.4 | 2.5      | 41.5     |
| 50                           | 13.0 | -        | 71.0     |
| 60                           | 25.2 | -        | 78.0     |
| 200                          | 86.2 | -        | -        |
| 300                          | 124.9| -        | -        |
4. Conclusion
It has been shown that powder in initial state consists of TiN (B2, B19′), Ti2Ni (E93) and TiNi3 (D024) phases and the lattices parameters of this phases does not significantly change after mechanical treatment and are in good agreement with the literature data. It has been shown that relative content of these phases in crystalline state significantly decreases in a first 10 second of mechanical treatment and in system appeared quasi-amorphous phase, after this the phase content does not changes, this means that energy of mechanical activation introduced to a system is spend not only for formation quasi-amorphous phase but for particle aggregation, stiction of particles to the walls of vial and other for processes.

It has been shown that widths of peaks significantly increase after 10 second mechanical treatment due to increasing of dislocation densities which increase for a prolonged milling time and can reached up $10^{13}$ cm$^{-2}$, these value is in good agreement with the literature data.

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References
[1] Chalmers B Physical Metallurgy 1962 (New York: John Wiley & Sons) p 468
[2] Cottrell A H Dislocations and Plastic Flow in Crystals 1958 (London:Oxford University Press) p 17.
[3] Mohamed F A 2014 Int. Mater. Rev. 59, 394–416.
[4] Tang W, Sundman B, Sandström R et. al. 1999 Acta Metall. 47, 3457–3468.
[5] Otsuka K, Ren X 2005 Prog. Mater Sci. 50, 511–678.
[6] Gattia D M, Gizer G and Montone A 2014 Int. J. Hydrogen Energ. 39, 9924–9930.
[7] Murty B S, Ranganathan S, Mohan M R 1992 Mater. Sci. Engng. A 149, 231-240.
[8] Abdulmenova E V and Kulkov S N 2019 IOP Conf. Series: Materials Science and Engineering 696 012018.
[9] Coccol G, Soletta I, Enzo S 1990 et al. Colloa. Phys. 51, C 4-181.
[10] Murty B S, Mohan M R, Ranganathan 1990 S. Scripta metall. mater. 24, 1819.
[11] Burgio N, Iasonna A, Magini M 1991 IL Nuovo Cimento D 13(4), 459–476.
[12] Zadorozhnyi V Yu, Milovzorov G S., Skakov Yu A, 2008 MitOM 8, 46–52.
[13] SkakovYu A 2004 MitOM 4, 3–12.
[14] Schwarz R B, Koch C C 1986 Appl. Phys. Lett. 49(3), 146–148.
[15] Williamson G K, Smallman R E 1956 Philosophical Magazine 1(1), 34–46.
[16] Islamgaliyev R K, Nesterov K M, Valiyev R Z 2013 Vestnik UGATU 17 81–89 (Russia)
[17] Scherrer P 1918 Göttinger Nachrichten Gesellschaft 2, 98–101.
[18] Hodaei A, Ataie A, Mostafavi E 2015 J. Alloys Compd. 640, 162–168.
[19] Laves F, Wallbaum H J 1939 Kristallogr Z, 101, 78.
[20] Stuwe H.-P, Shimomura Y Z., 1960 Metallkd 51, 180.
[21] Sinclair M G 1981 Acta Crystallogr.Sec. E 37, 1803.
[22] Mueller M H, Knott H W 1963 Trans. Met. Soc. AIME 227, 674.
[23] Yao X, Wu C, Du A et al. 2007 Chem. Soc. 129 15650 – 15654.
[24] Bratanich T I, Getman O I et al. 2006 Powder Metall. Metal Ceram. 45 11 – 12
[25] Shan X, Payer J H and Jennings W D 2009 Int. J. Hydrog. Energy 34 363-369.