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# FEATURES OF STRUCTURE, SUBSTRUCTURE, AND RESIDUAL STRESS OF $Ti_{41.5}Zr_{41.5}Ni_{17}$ QUASICRYSTALS QUENCHED FROM LIQUID STATE

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The structural state, stress, and substructure parameters of ribbons obtained by rapid solidification from the liquid state of the $Ti_{41.5}Zr_{41.5}Ni_{17}$ alloy and powders obtained by deformation were investigated using X-ray diffraction and SEM microscopy methods. The influence of sample preparation parameters such as quenching rate and intensity of deformation, on the content of the $Ti_{41.5}Zr_{41.5}Ni_{17}$ quasicrystalline phase and the crystalline phase of the approximant (*W*-phase), is considered. It is noted that the volume content of the *W*-phase increases with higher deformation intensity and decreases with higher quenching rate. Accumulation of specific defects in the quasicrystalline structure, known as phason defects, occurring during quenching, is observed in ribbon samples. The concentration of phason defects is nonuniform over the cross section of the samples, increasing from the side of the ribbon in contact with the quenching wheel to the free surface. This non-uniformity may be associated with the participation of phason defects at the initial stage of the phase transformation during the formation of the *W*-phase. The concentration of phason defects significantly increases during deformation of ribbons.

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## INTRODUCTION

At present, the thermodynamic stability of various quasicrystal systems has been quite thoroughly studied, and the icosahedral nature of their structure has been confirmed by diffraction patterns [1–3]. However, the perfection of such a structure at the microlevel within the framework of phenomenological description has not been sufficiently explored. In some works, the concept of "coherence length" equivalent to the grain size for polycrystals [1, 4] was introduced in discussions on the width of diffraction peaks. To describe the perfection of the structure, some authors introduce the concept of phasons deformations [5–7]. There is limited literature dedicated to the analysis of the width of X-ray diffraction lines of quasicrystals [4]. In addition, the issue of residual stresses in quasicrystalline samples has not been sufficiently studied.

Therefore, the purpose of this work is to analyze the structural state and physico-mechanical properties of ribbons and powders containing the quasicrystalline phase $Ti_{41.5}Zr_{41.5}Ni_{17}$.

## 1. SAMPLES AND INVESTIGATION TECHNIQUE

Samples of $Ti_{41.5}Zr_{41.5}Ni_{17}$ were obtained using the method of high-speed quenching from the liquid state on the "STRICHKA-3" setup (Institute for Single Crystals, National Academy of Sciences of Ukraine, Kharkiv). The method of rapid solidification from the melt was employed, with components having a purity of at least 99.95%. Quenching occurred on the surface of a copper wheel rotating with a linear velocity (*V*) ranging from 10 to 30 m/s and cooled by flowing water. The thickness of the obtained ribbon samples ranged from 10 to 50 μm. To obtain dispersed powders, the ribbon samples were crushed in a ceramic mortar with an agate pestle in a medium of pure ethanol. Nine ribbon and powder samples were investigated.

The structural characteristics were analysed using XRD methods. X-ray diffraction patterns were obtained on a DRON-type apparatus with filtered Cu-Kα radiation. The spectra were processed using the New_Profile3.5 software package. The identification of the quasicrystalline phase and the determination of its quasicrystallinity parameter ($a_q$) were performed according to Cahn J.W. [8] using an original software package.

Microhardness of the samples was tested by the Vickers diamond pyramid indentation method using a PMT-3M microhardness tester.

## 2. RESULTS AND DISCUSSION

Previously, it has been demonstrated [9, 10] that thin ribbons ($h < 10$ μm) of quasicrystalline samples contain residual macro-stresses. These stresses are balanced within the volume of the samples and are compressive on the side in direct contact with the surface of the quenching disk and tensile on the opposite side.

In samples with a thickness significantly greater than half the thickness of the X-ray absorption layer, the $a_q$-$\sin^2\psi$ plots appear nonlinear (Fig. 1). This non-linearity can be explained by the inhomogeneity of the stress state, composition or structure in the cross section of the samples. Indeed, according to the scanning microscopy data (Fig. 2) and microhardness measurements ($H_\mu$) (Fig. 3), the samples also exhibit inhomogeneity.

As seen in Fig. 3, microhardness varies over the cross section, with the lowest value $H_\mu$ = 350 kg/mm² on the side in contact with the quenching wheel surface. On the free side, microhardness is slightly higher, $H_\mu$ = 450 kg/mm². Over the cross-section, $H_\mu$ changes non-monotonically, reaching its maximum value approximately in the middle of the sample. This

indicates the presence of non-uniformity in the structure and properties over the cross-section of the samples.

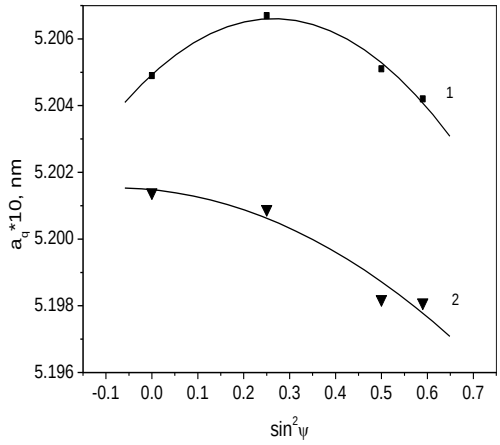


*Fig. 1. $a_q$-$\sin^2\psi$ plots constructed from the results of scanning the side in contact with the surface of the quenching wheel; samples were prepared at the wheel linear velocity V = 25 (1) and 15 m/s (2)*

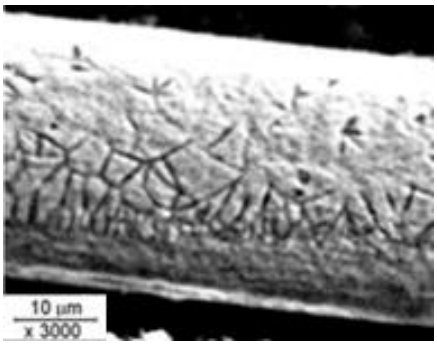


*Fig. 2. SEM image of the cross section of the ribbon prepared at the wheel linear velocity V = 15 m/s*

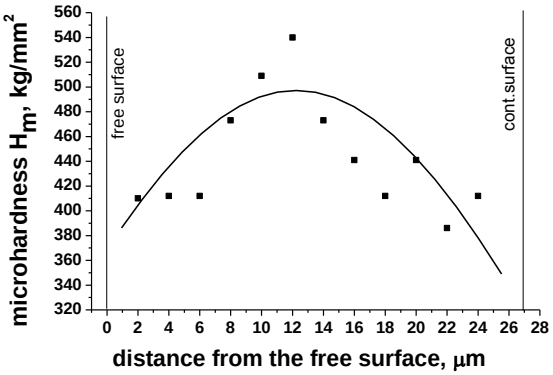


*Fig. 3. Distribution of microhardness over the cross section of the ribbon prepared at the wheel linear velocity V = 15 m/s*

The reason for this heterogeneity should be investigated through phase analysis. However, since the thickness of the ribbon exceeds half the thickness of the X-ray absorption layer (Cu-Kα), it was decided to grind the ribbons and study them in the form of powdered samples. This approach is expected to allow the study of internal layers.

Fig. 4 shows X-ray diffraction patterns of the best ribbon sample and the powder sample obtained from it. It can be seen that all reflections of the ribbon sample are identified as belonging to the icosahedral quasicrystalline phase. The diffraction pattern of the powder sample (see Fig. 4,b) shows a larger number of diffraction peaks, many of which do not belong to the quasicrystal. Reflections from the known impurity phase are marked on the diffraction pattern with arrows.

The reflections of the impurity phase were identified by computer modeling of the theoretical scattering spectrum using the PowderCell 2.1 program [11] and the basis of the possible *W*-phase (1/1 crystal-approximant) presented in [12]. The comparison of experimental diffraction patterns with theoretical ones for several powder samples allows us to state that the powder contains an icosahedral quasicrystalline phase with a quasicrystallinity parameter $a_q$ = 0.52069 nm and its crystalline approximant 1/1 with a lattice period $a_{1/1}$ = 1.43773 nm. The parameters $a_q$ and $a_{1/1}$ are related by a strict expression [1, 6]:

$$a_{q/p} = \frac{2(p+q\cdot\tau)}{\sqrt{2+\tau}} \cdot a_q \ ,$$

where *q/p* is the rank of the approximant and τ=1.618... is the golden ratio. The verification showed that this ratio is indeed accurately fulfilled.

A quantitative estimation of the phase composition can be carried out based on the assumption that the structures of the both phases, as well as their atomic-crystalline composition are similar. This allows us to assume that the diffraction properties of the phases are approximately the same. Thus, from the intensity ratio (see Fig. 4) of the reflection (20,32) of the quasicrystalline phase and (620) of the *W*-phase, we can concluded that the amount of the *W*-phase is approximately 30 vol.%. Calculation according to the Scherrer equation shows that the average crystallite size in both phases is about 15 nm.

There is a theoretical assumption that the phase transition from the quasicrystalline phase to the approximant phase occurs due to the accumulation and merging of specific defects in the quasicrystalline structure, known as phasons [13]. They enter the volume of the quasicrystalline phase as a result of mechanical processing or quenching. Indeed, we observe an increase in the amount of the approximant phase relative to the quasicrystalline phase with intensified grinding. The quenching rate is changed by varying the linear velocity on the surface of the quenching wheel.

According to the results of data processing, two phases are present in the ribbon manufactured at a velocity *v*=25 m/s: the main phase is the icosahedral quasicrystalline phase and the crystalline *W*-phase. The quasicrystallinity parameter is 0.52064 nm, and the lattice period of the crystal-approximant is 1.1432 nm. The estimated content of the *W*-phase is approximately 11 vol.%. The dependence of the amount of crystalline phase on the linear velocity of the quenching wheel is shown in Fig. 5.

From the figure, it can be seen that the higher the quenching speed, the smaller the fraction of the crystalline phase. The lower the *W*-phase content, the higher the perfection of the quasicrystalline phase structure (see Fig. 5). This is due to the fact that more material goes into the quasicrystalline phase. This conclusion is in accordance with existing literature data.

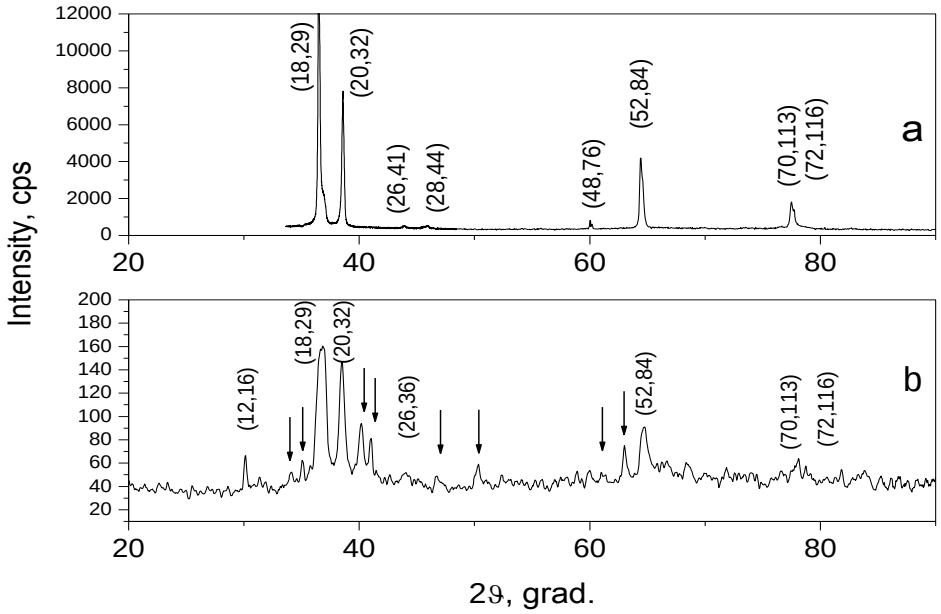


*Fig. 4. X-ray diffraction patterns for the ribbon sample (a) and powder sample obtained by grinding (b)*

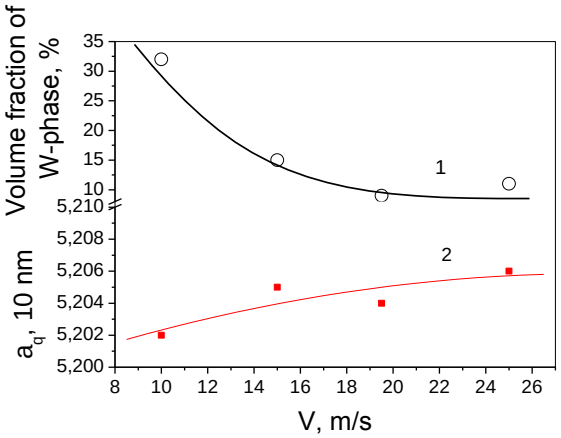


*Fig. 5. Variation in the content of the crystalline W-phase (1) [9] and the quasicrystallinity parameter (2) depending on the linear velocity of the quenching wheel*

According to literature data, the formation of phason defects or phason deformations is characteristic of icosahedral quasicrystal structures. These defects introduce local chemical and structural disorder into the ideal structure. X-ray analysis makes it possible to identify these defects by shifting and broadening of diffraction peaks.Typically, such defects may be absent only in samples that have been subjected to very long annealing.

To analyze the presence of phason defects, ribbons obtained at a quenching wheel velocity $v = 19.5$ m/s were selected. Theoretically, the reflections with a large magnitude of the diffraction vector in the perpendicular space $Q_\perp$ are sensitive to the presence of phason defects. Therefore, the dependence of shifts of diffraction reflections on $Q_\perp$ values was analyzed. To characterize the shift of the reflections, the parameter $\Delta a_q$ (N, M) was calculated as the difference between quasicrystallinity parameters for a given reflection with indices (N, M) and for the reflection (136,220) located at a large angle 2ϑ and having the smallest $Q_\perp$. The diffraction vector in the perpendicular space $Q_\perp$ is determined as

$$Q_\perp = \frac{1}{2a_q} \cdot \sqrt{\frac{\tau(N\tau - M)}{2+\tau}}.$$

Figs. 6–9 illustrate the dependencies $\Delta a_q$ (N, M) on $Q_\perp$. The graph in Fig. 6 shows the relationship for two ribbon samples, the diffraction patterns of which were recorded from the "free" side of the samples. Circles and squares correspond to different samples, but, as you can see, almost the same dependence is obtained. Fig. 7 shows a similar dependence for measurements from the side in contact with the surface of the quenching wheel. In both cases, a linear dependence is observed, but the slope of the second graph is relatively less. The obtained dependence indicates the presence of phason defects in the structure of the ribbons. They most likely have a quenching nature, and their number increases in the direction of the "free" surface of the ribbon.

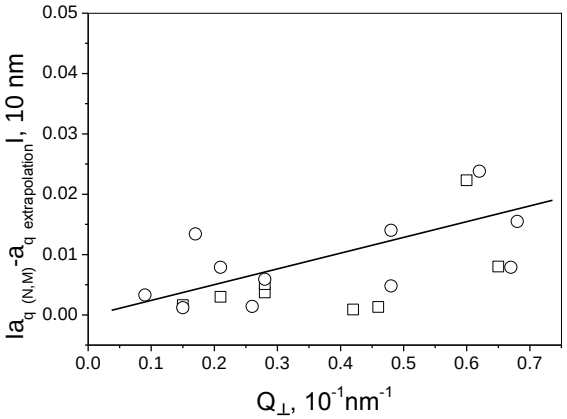


*Fig. 6. Dependence of the difference $\Delta a_q$(N,M) on the magnitude of the diffraction vector in perpendicular space $Q_\perp$ for the free surface of the ribbon sample prepared at the wheel linear velocity V = 19.5 m/s*

Figs. 8 and 9 illustrate the dependence of $\Delta a_q$ (N,M) on $Q_\perp$ for powder samples for powder samples of different degrees of refinement. It can be noted that for

these samples, the dependence is more pronounced than for the ribbon samples. It can be concluded that phason defects accumulate intensively in the structure of a quasicrystal during deformation, and this accumulation is greater the higher the degree of refinement.

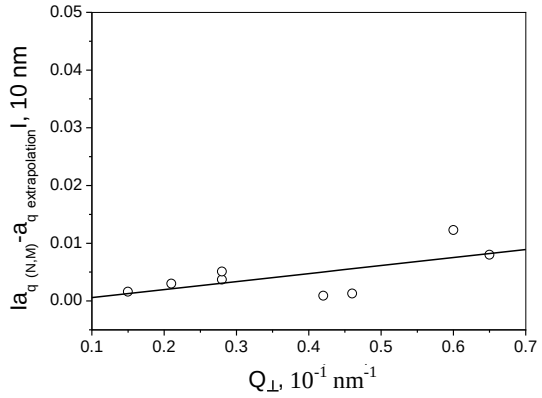


*Fig. 7. Dependence of the difference $\Delta a_q$ (N,M) on the magnitude of the diffraction vector in perpendicular space $Q_\perp$ for the contact surface of the ribbon sample prepared at the wheel linear velocity V = 19.5 m/s*

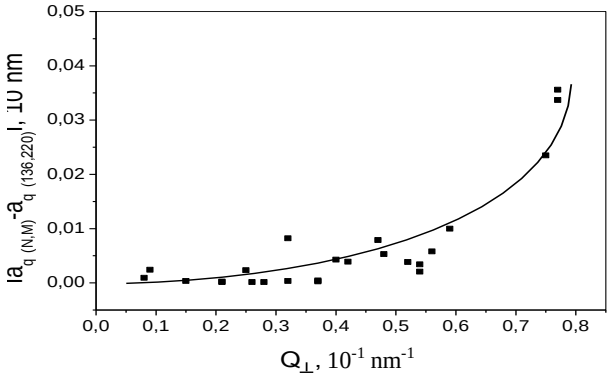


*Fig. 8. Dependence of the difference $\Delta a_q$ (N,M) on the magnitude of the diffraction vector in perpendicular space $Q_\perp$ for a powder sample obtained by "gentle" grinding*

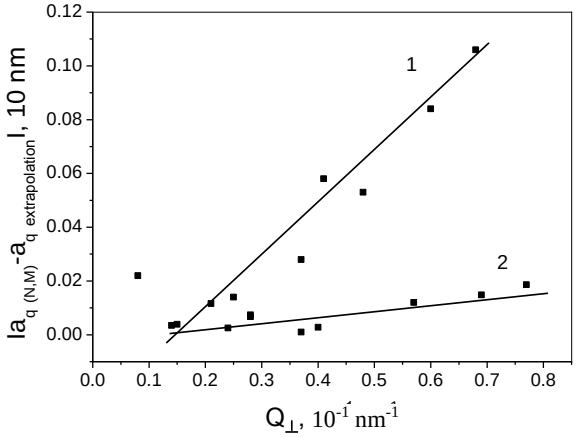


*Fig. 9. Dependence of the difference $\Delta a_q$(N,M) on the magnitude of the diffraction vector in perpendicular space $Q_\perp$ for a powder sample obtained by "intensive" grinding:*
*1 – "reflections from the 5th order symmetry plane";*
*2 – "reflections from the 2nd order symmetry plane"*

According to the literature [5], phasons accumulate in the structure of quasicrystals under mechanical loading due to the movement of dislocations. Dislocations and dislocation dipoles in the icosahedral structure of quasicrystals are predominantly located in planes perpendicular to the axis of fifth-order symmetry [14, 15]. Therefore, for reflections obtained from planes normal to the fifth-order axis, the shift of the diffraction maxima should be the largest. Fig. 9 shows the highest $\Delta a_q$ (N,M) values corresponding to the line 1, precisely for such reflections. The smallest shift of diffraction maxima is characteristic of reflections formed from planes normal to the axis of the second order (line 2).

## CONCLUSIONS

The methods of XRD, SEM, and microhardness measurements were used to establish the heterogeneity of the grain structure, structural state, substructure, phase composition, and residual stresses throughout the volume of $Ti_{41.5}Zr_{41.5}Ni_{17}$ ribbon samples obtained by melt solidification.

It has been shown that the main phases in ribbon and powder samples are quasicrystalline $Ti_{41.5}Zr_{41.5}Ni_{17}$ and the crystalline 1/1-approximant phase (*W*-phase), and their volumetric content depends on the rotation velocity of the quenching wheel and the degree of fragmentation. The volumetric content of the *W*-phase increases with increasing deformation degree and lower quenching speed.

It has been established that phason defects specific to the quasicrystalline structure accumulate in ribbon samples. They have a quenching nature. Ultimately, there are more of them on the free side than on the contacting side. This is due to the fact that they participate in the formation of the approximant phase.

Deformation of the ribbons leads to a significant increase in the number of phason defects.

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## ОСОБЛИВОСТІ СТРУКТУРИ, СУБСТРУКТУРИ ТА ЗАЛИШКОВИХ НАПРУЖЕНЬ У КВАЗІКРИСТАЛАХ $Ti_{41,5}Zr_{41,5}Ni_{17}$, ЩО ЗАГАРТОВАНІ З РІДКОГО СТАНУ

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Методами рентгенівської дифрактометрії та SEM-мікроскопії досліджені структурний стан, напруження та параметри субструктури стрічок, що отримані швидкісним загартуванням з рідкого стану сплаву $Ti_{41,5}Zr_{41,5}Ni_{17}$ та порошків, які отримані деформуванням. Розглядається вплив параметрів отримання зразків, таких як швидкість загартування та інтенсивність деформації на вміст квазікристалічної фази $Ti_{41,5}Zr_{41,5}Ni_{17}$ та кристалічної фази апроксиманта (*W*-фази). Відзначено, що об'ємний вміст *W*-фази зростає при більш високій інтенсивності деформації та зменшується при більш високій швидкості загартування. У стрічкових зразках виявлено накопичення специфічних дефектів квазікристалічної структури – фазонних дефектів, які виникають при гартуванні. Концентрація фазонних дефектів неоднорідна у поперечному перерізі зразків: вона збільшується від сторони стрічки, яка контактувала з гартівним барабаном, у напрямку до вільної поверхні. Така неоднорідність пов’язується з можливою участю фазонних дефектів у початковій стадії фазового перетворення при утворенні *W*-фази. Концентрація фазонних дефектів значно збільшується при деформації стрічок.