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# Residual stresses in $Ti_{41.5}Zr_{41.5}Ni_{17}$ quasi-crystalline ribbons measured by X-ray diffraction

***S.Malykhin***

National Technical University "Kharkiv Polytechnical Institute",
21 Frunse St., 61002 Kharkiv, Ukraine

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Using X-ray diffraction, strain measurement, scanning electron microscopy, and microprobe analysis, structure, composition and stress state were studied in $Ti_{41.5}Zr_{41.5}Ni_{17}$ quasi-crystalline ribbons prepared by one-side melt solidification on the rotating wheel. The macro-stresses have been found to be distributed inhomogeneously across the ribbon section. On the side contacted with cooler, compressive stress up to 130 MPa acts, while the stress sign changes at the opposite side. The total level of residual stresses is defined by the quenching rate from melt. The observed peculiarities of stress distribution along the normal to solidification front are explained by temperature field inhomogeneity across the ribbons as well as by release of the solidification heat.

Методами рентгеновской дифрактометрии и тензометрии, растровой электронной микроскопии и микрозондового анализа исследованы структура, состав и напряженное состояние квазикристаллических лент $Ti_{41.5}Zr_{41.5}Ni_{17}$, полученных методом солидификации из расплава на одностороннем вращающемся диске. Установлено, что макронапряжения неоднородно распределены по сечению образцов. Сжимающие напряжения величиной до 130 МПа действуют в лентах со стороны, контактировавшей с охладителем, а к противоположной поверхности знак напряжений изменяется. Общий уровень остаточных напряжений определяется скоростью закалки из расплава. Выявленные особенности напряженного состояния вдоль нормали к фронту затвердевания объясняются неоднородностью температурного поля по сечению лент и выделением скрытой теплоты затвердевания.

Quasi-crystals (QCs) discovered by D.Shechtman et al. in 1984 [1] form a new class of solids [2, 3]. Their structure cannot be formed by translation rotating the classic Bravais lattices. The most wide-spread quasi-crystals are icosahedral ones. Those include multi-atomic clusters (Bergman or McCay or Tsai types) [4] consisting of icosahedra and dodecahedra inserted into ach other. Such a structure shows the five-fold symmetry. The icosahedral quasi-crystals (i-QCs) grown either as single grains or polycrystals show a highly ordered atomic structure, so, their diffraction patterns consist of sharp and intense discrete peaks. The unusual structure type of QCs causes various unique physical properties as compared to crystalline phases. For instance, the practical interest in stable QCs of Ti–Zr system [2, 5–8] is caused by their ability of accumulating hydrogen in solid solution up to the ratio $H/Me = 2{:}1$ [2, 9]. For Ti–Zr–Ni QCs, the superconductivity transition was found [10, 11] as well as unusual mechanism of plastic strain [12, 13].

It is well known that many properties are defined by structure and substructure perfection as well as by stress state of the samples. Residual stresses exist in materials or pieces in absence of external load. Thus, all the forces and moments should be equilibrated over the whole body. Usually, resid-

ual stresses are due to inhomogeneous distribution of non-elastic size changes introduced under technologic treatment [14–16]. The method of one-side rapid quenching on a wheel implies inhomogeneity both of thermal field and plastic strain across the section of thin ribbons; hence, the formation of residual stresses is possible. An indirect confirmation thereto is the ribbon bending observed by many authors [2, 3]. The samples obtained are as a rule polycrystalline and show a lot of diffraction reflections, thus assuming the possibility of $\sin^2\psi$ method application to QCs. The aim of this work is to prove experimentally the multiple oblique scans method (well-known for crystals) in the study of the 1st kind residual stresses (macro-stresses) in quasi-crystalline samples, and to establish the correlation between Ti–Zr–Ni QCs technological parameters and the structure and stress state thereof.

The samples were made of $Ti_{41.5}Zr_{41.5}Ni_{17}$ alloy prepared by arc-melting the nominal proportions of iodide Ti, Zr (99.9 mass. % purity), and Ni after electron-beam re-melting (99.9 mass. % purity) in purified argon atmosphere under $10^{-5}$ Pa with multiple tumbling the melt to provide the homogeneity of the whole melt. Then, the ribbons of 15 to 100 μm thickness were obtained by rapid quenching of homogenized melt on the cooled copper wheel. The quenching regimes were set by varying the wheel rotation linear velocity $V$ from 10 to 25 $m \cdot s^{-1}$. The structure and stress state were studied by X-ray diffraction (XRD) using $Cu–K_\alpha$ radiation. The crystalline phases were identified using JCPDS card index [17], and QC phase, using the technique described in [2, 18–20]. According to the scheme by J.W.Cahn et al. [19], the indices ($N$, $M$) were ascribed to the reflections of i-QC phase. The quasi-crystallinity parameter characterizing the QC structure perfection, $a_q$, was defined as

$$a_q = \lambda / 4\sin\theta \cdot \sqrt{\frac{N + M\tau}{1 + \tau^2}} = \frac{d}{2}\sqrt{\frac{N + M\tau}{1 + \tau^2}}, \quad (1)$$

with $\tau = 1.618$, that is "the golden mean"; $\theta$, diffraction angle; $d$, the measured interplanar spacing. To study the residual stresses, the standard $\sin^2\psi$ method was applied [14, 15]. A series of scans at different tilt angles $\psi$ of the sample was made in $\theta - 2\theta$ scheme. Then, interplanar spacings $d$ were calculated from the Bragg angles; quasi-

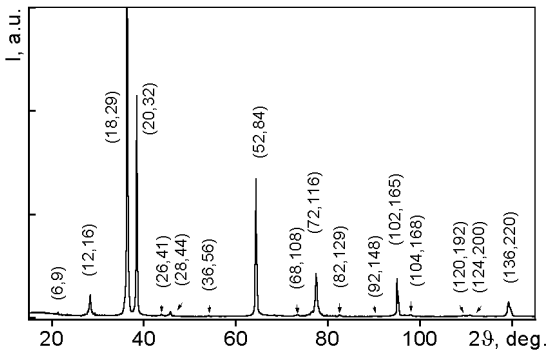


Fig. 1. A typical X-ray diffraction pattern. The reflections are identified by two Cahn indices ($N$, $M$).

crystallinity parameters $a_q$ were calculated from (1); and the plots $a_q$ *vs* $\sin^2\psi$ were constructed. In order to estimate the variations in structure and stress state across the ribbon thickness, the samples were analyzed on both sides: on the side contacted with quenching wheel (CS), and on the free side (FS). Ribbon thickness was more than 30 μm, i.e. exceeded by a factor of 4 the X-ray half-absorption thickness for all the samples studied. Thus, superposition of the results measured on CS and FS was excluded. The X-ray studies were accompanied by microstructure observations using scanning electron microscopy (SEM) and by microhardness measurements.

According to XRD and SEM data, the samples studied were polycrystalline. The grain sizes varied from 20 μm to 1 μm and less, moreover, on CS, the grain size was less than on FS. Increased quenching rate resulted in smaller grains. Elemental composition attestations using X-ray fluorescence and micro-probe analyses have shown the component average distribution being practically homogeneous both over the sample surface and across its thickness, and the composition corresponded to the formula to within 0.5 at.%.

XRD patterns for all the ribbons were practically the same, a typical pattern is shown in Fig. 1. Phase analysis has shown the presence of the only quasi-crystalline icosahedral phase with primitive lattice. The reflections from i-QC phase are observed up to diffraction angles $2\theta$ about 120 to 140° that provides a precise determination of the quasi-crystallinity parameter $a_q$. To study the stress state, the reflection with Cahn indices (136, 220) was chosen.

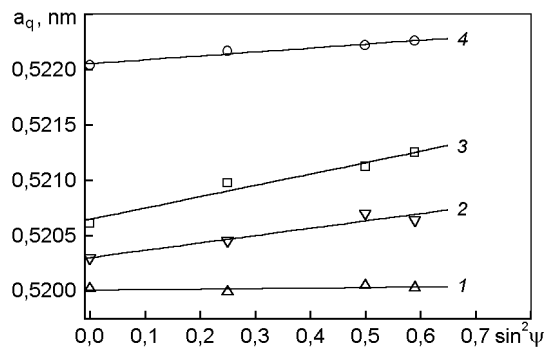


Fig. 2. $a_q$–$\sin^2\psi$ Plots constructed using the scanning results for the free surfaces of the samples prepared at the wheel linear velocity (m/s): 10 (*1*), 15 (*2*), 19.5 (*3*) and 25 (*4*).

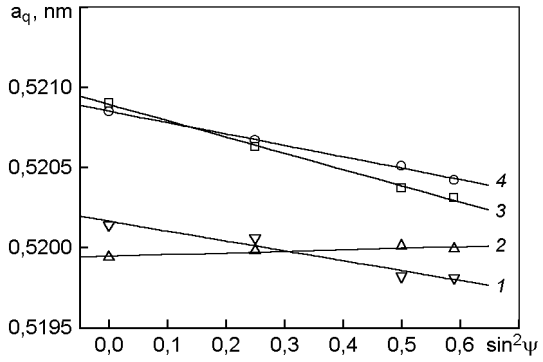


Fig. 3. $a_q$–$\sin^2\psi$ Plots constructed using the scanning results for the contact surfaces of the samples prepared at the wheel linear velocity (m/s): 10 (*1*), 15 (*2*), 19.5 (*3*) and 25 (*4*).

For this reflection, the component of diffraction vector in perpendicular space is small enough, thus, according to [21, 22], the additional shift of diffraction maximum due to QC specific defects (phasons) is practically absent.

The $a_q$ – $\sin^2\psi$ plots are shown in Figs. 2 and 3. For all the samples measured, a linear dependence $a_q$ *vs* $\sin^2\psi$ is observed. Such a behavior indicates stress homogeneity within the range of X-ray absorption layer. The positive slope of the plots in Fig. 2 shows the presence of residual tensile strains at the FS of the ribbons. On the ribbon opposite side (CS), the $a_q$ – $\sin^2\psi$ plots demonstrate negative slope indicating the presence of compressive strains (see Fig.3). For the sample obtained at the lowest cooling wheel velocity of 10 $m \cdot s^{-1}$ (see plots *1* in Figs. 2, 3), the slope of $a_q$ – $\sin^2\psi$-plots is almost zero, i.e. no residual stresses are absent.

The residual stresses were estimated in arbitrary azimuth direction φ using approximation of biaxial stress state according to the expression

$$\sigma_\varphi = \frac{E}{1+\nu} \cdot \frac{a_{q,\parallel} - a_{q,\perp}}{a_{q,0}}, \qquad (2)$$

where $a_{q,\parallel}$ and $a_{q,\perp}$are quasi-crystallinity parameters for $\psi = 90°$ and $\psi = 0°$, respectively, calculated from linear dependence $a_q$ *vs* $\sin^2\psi$ obtained using least square method. The $a_{q0}$ value was found from the equation $\sin^2\psi_0 = 2\nu/(1+\nu)$. The Poisson coefficient $\nu = 0.3$ was taken as typical of metallic alloys, while Young modulus was measured previously using nano-indentation method [12]. In Fig. 4, the calculated resid-

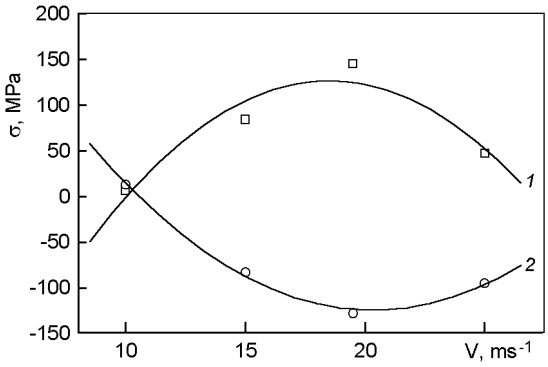


Fig. 4. Dependences of the residual macrostress value on the quenching rate for the free (*1*) and contacting (*2*) sample surfaces.

ual macro-stresses at CS and FS are plotted vs quenching wheel rotation linear velocity $V$. It is seen that residual stresses, first, vary across the sample section and are equilibrated in the bulk, and, second, their values depend on linear velocity $V$ of the quenching wheel surface.

It is well known that at the quasi-crystalline phase synthesis by solidification, it is just the velocity $V$ as well as temperature conductivity and overcooling degree that define the quenching rate. The observed dependence of residual stresses on quenching rate implies that the stresses may be caused by temperature gradient $\Delta T$ across the section due to heat removal differences at the opposite sides of the sample. As the solidification front moves, the solidification rate changes, and the structure is formed inhomogeneous along the normal to surface direction. This is indicated by the observed differences (see Fig. 5) between both quasi-

crystallinity parameters $a_{q0}$ and specific volumes. At CS, the quasi-crystallinity parameter is found to be rather low and depends weakly on the quenching rate $V$, while at FS, it becomes higher and increases steeper with $V$. Microhardness measurements on both sample sides give different values as well, and those vary as $V$ increases.

As neither Laves phase, nor α–Ti(Zr) one stable over the peritectoid transition temperature [8] were observed in diffraction patterns, we believe the temperature gradient $\Delta T$ hardly exceeded 600°C. It is more reasonable to assume the temperature gradient between FS and CS being 200 to 300°C. Then, taking into consideration the temperature origin of the residual stresses, the values thereof indicate the linear thermal expansion coefficient being (7 to 10)·$10^{-6}$ $K^{-1}$ that is a quite reasonable value.

Thus, the residual stresses were studied in spinning-produced poly-quasi-crystalline $Ti_{41.5}Zr_{41.5}Ni_{17}$ ribbons with thickness ≤40 μm by the strain measurement technique using X-ray diffraction. The residual stresses have different signs at the opposite sides of the ribbons being compressive at the side contacted with cooling wheel, but tensile at the free side. Across the sample section, the stresses equilibrate. It was shown that the quenching wheel surface linear velocity increase from 10 to 19.5 m·$s^{-1}$ results in residual stress rising from 0 to 120 MPa. A further velocity increase leads to a little drop of residual stresses. A possible cause of residual stresses is assumed to consist in the inhomogeneous variation of the specific volume due to heat field inhomogeneity across the ribbon section at the sample preparation.

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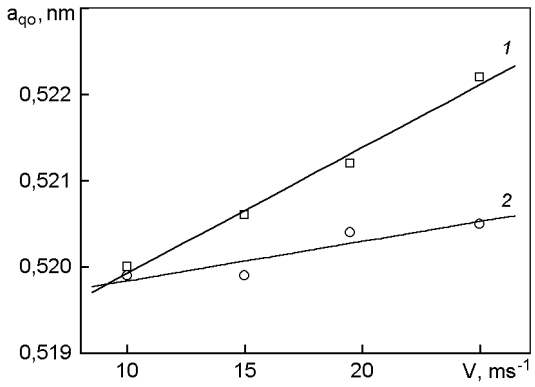


Fig. 5. Dependences of the quasi-crystallinity on the quenching rate for the free (*1*) and contacting (*2*) sample surfaces.

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# Залишкові напруження у $Ti_{41,5}Zr_{41,5}Ni_{17}$ квазікристалічних стрічках, отриманих солідифікацією із розплаву

***С.В.Малихін***

Методами рентгенівської дифрактометрії та тензометрії, растрової електронної мікроскопії та мікрозондового аналізу досліджено структуру, фазовий склад і напружений стан квазікристалічних стрічок $Ti_{41,5}Zr_{41,5}Ni_{17}$, отриманих методом солідифікації з розплаву на односторонньому диску, що обертається. Встановлено, що макронапруження неоднорідно розподілені за перетином зразків. Стискуючі напруження величиною до 130 МПа діють в стрічках із сторони, що контактує з охолоджувачем, а до протилежної поверхні знак напружень змінюється. Загальний рівень залишкових напружень визначається швидкістю загартування з розплаву. Виявлені особливості напруженого стану уздовж нормалі до фронту затвердіння пояснюються неоднорідністю температурного поля за перетином стрічок і виділенням прихованої теплоти затвердіння.