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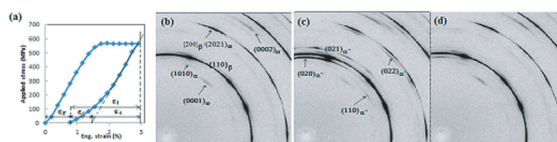
Stress-induced phase transformation in a Ti–17Nb–1Cr alloy

Song Cai^{a*}, Jeremy E. Schaffer^a and Yang Ren^b

^aFort Wayne Metals Research Products Corporation, 9609 Ardmore Ave., Fort Wayne, IN 46809, USA; ^bAdvanced Photon Source, Argonne National Laboratory, 9700 S. Cass Ave., Argonne, IL 60439, USA

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In situ synchrotron X-ray diffraction was used to study the deformation behavior of a Ti–17Nb–1Cr alloy at room temperature. Stress-induced martensite (SIM) transformation increased the total recoverable strain. A maximum of $\sim 3.5\%$ strain recovery was obtained after proper heat treatment. Unlike other alloys with a *bcc* crystal structure, the β -phase has a strong $(210)_\beta$ texture, supporting the previous suggestion that all meta-stable β -Ti alloys may have a similar texture instead of the well-known $(110)_\beta$ texture after axisymmetric deformation. The ω -phase has a $(22\bar{4}3)_\omega$ texture. The $(041)_{\alpha''}$ fiber texture in α'' -phase was formed from the $(210)_\beta$ texture based on their crystal orientation relationship.



Keywords: Synchrotron X-ray, Beta Ti Alloy, Omega Phase, Stress-induced Martensite, Texture

Impact Statement: This manuscript reports the stress-induced phase transformation in a new β -Ti alloy with large recoverable strain and unique textures that are not widely known.

Introduction Scientists have been working on meta-stable β -Ti alloys for many years.[1–3] Most recent work has been focused on improving the super-elastic property associated with the reversible stress-induced martensite (SIM) phase transformation.[3,4] During transformation, the austenitic β -phase (with a *bcc* crystal structure) transforms to the martensitic α'' -phase (with an orthorhombic crystal structure). The strain related to the structure change enables large strain recovery and provides the fundamental possibilities for Ni-free super-elastic alloys to replace NiTi alloys in medical applications where Ni can cause significant allergic reactions.[5] The total recoverable strain of a material depends on microstructural features such as phase fractions, dislocation networks and textures, which are controlled by processing history.[4,6] Further, however, the maximum theoretical strain recovery is determined by lattice parameters of the β - and α'' -phases. For β -Ti

alloys, the maximum strain is along the $\langle 110 \rangle_\beta$ direction and it is controlled by the chemical composition.[4] Kim et al.'s studies on the Ti–Nb system [4] show that the transformation strain increases with decreasing Nb content, and a strain of above 6% can be achieved with less than 17 at.% Nb. This strain level is much higher than that (e.g. 3–4%) routinely obtained in most of the other β -Ti alloys.[4,6,7] One significant problem is that, at this low Nb content, the martensite transformation temperature is much higher than room temperature thus precluding SIM transformation during room temperature deformation. This has been confirmed by our previous study on a Ti–17 at.% Nb alloy, which contains a large amount of α'' and ω -phases at room temperature after annealing.[8] In this study, 1 at.% Cr, a strong β -phase stabilizer,[9] was added to the system to reduce the martensite transformation temperature. The evolution of phase fractions, phase transformation and textures of

*Corresponding author. Email: song_cai@fwmetals.com

each phase during deformation was characterized by *in situ* synchrotron X-ray diffraction. The total strain recovery was tested by loading and unloading in a uniaxial tensile test. Since Ti-17Nb-1Cr is a new alloy, results of this study provide new information and are useful to the titanium community.

Materials and Experiments The material used in this study has chemical compositions of Ti-17Nb-1Cr (at.%). It was arc-melted three times in vacuum and then drop-casted into a $\varnothing 19 \times 140$ mm cold copper mold. After homogenization at 1,000°C for 72 hours in an argon atmosphere, the ingot was extruded at 1,000°C to a diameter of ~ 8 mm, and cold drawn to a diameter of 0.45 mm by the traditional wire drawing and annealing process. The amount of cold work after the last β -recrystallization anneal was 98.1% in area reduction. The cold drawn wire was heat treated at 750°C for 6 seconds in an argon atmosphere and cooled to

room temperature in less than 10 seconds. Differential scanning calorimetry (DSC) testing on this heat treated sample was not able to identify any temperature-induced phase transformation from -100°C to 100°C . To understand the possibility of the stress-induced phase transformation during deformation, *in situ* synchrotron X-ray diffraction tensile testing was carried out at room temperature three weeks after sample production and heat treatment. This experiment was performed on the beam line 11-ID-C at the Advanced Photon Source (APS) at Argonne National Laboratory. The experimental setup is similar to that used previously.[10,11] The X-ray wavelength was $0.11165 \text{ \AA}$ and beam size was $0.5 \times 0.5 \text{ mm}^2$. The specimen gauge length was 20 mm. During the test, the specimen was continuously loaded to an engineering strain of 3%, and then unloaded to zero stress (Figure 1(a)). At selected points, the specimen was held at constant strains for 10 seconds for data collection, where the 2D diffraction images were recorded by a Perkin-Elmer aSi flat panel detector. The

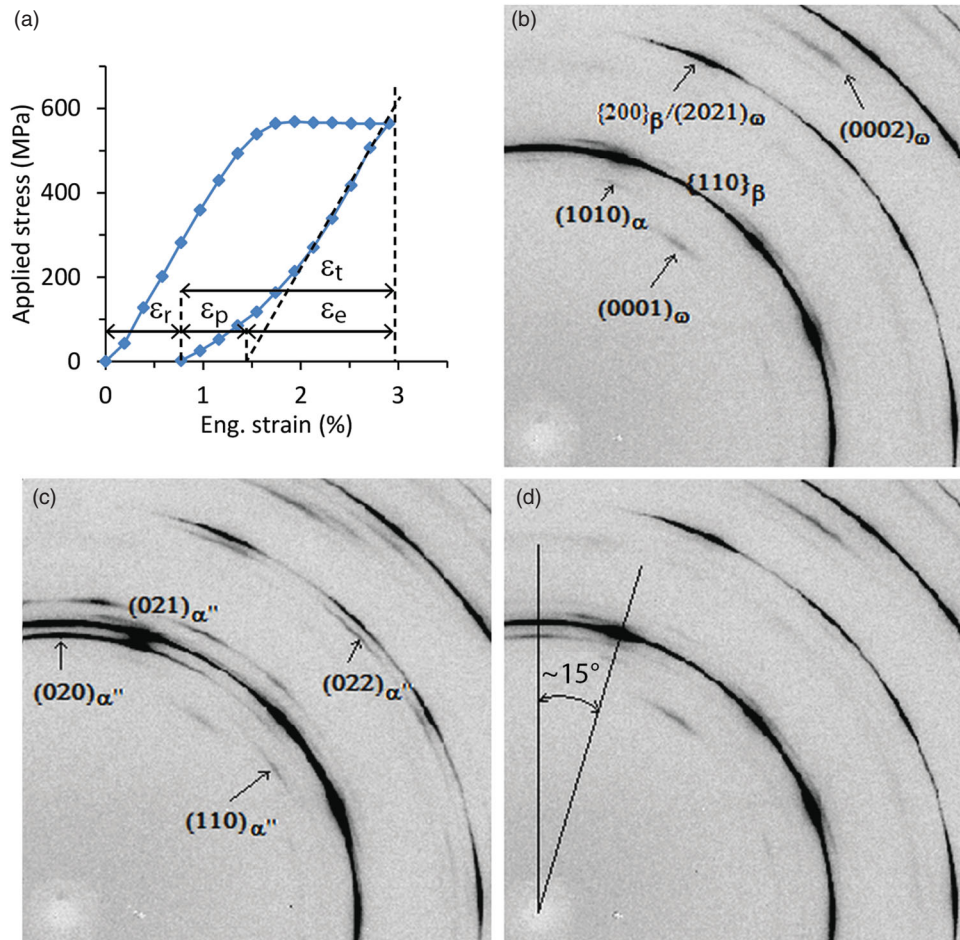


Figure 1. (a) Stress-strain curve of the *in situ* tensile test. ε_t is the total recovery strain, ε_e is the pure elastic strain, ε_p is the phase transformation strain and ε_r is the residual strain. Dots show the frequency of the data collection, (b) X-ray diffraction image before deformation, (c) diffraction image at the strain of 3% and (d) diffraction image after unloading to zero stress. The specimen axial direction in (b–d) is vertical from the beam center.

test was conducted in displacement control at a deformation rate of 0.5×10^{-3} /second. The ‘raw’ data were processed in FIT2D software.[12] Phase fractions and textures were estimated by performing Rietveld refinement [13] embedded in the MAUD software.[14] More details are given in previous similar work.[10,11]

In order to understand the capability of this alloy on strain recovery, the cold drawn wire was heat treated at different temperatures and time. Heat treated samples were immediately tested on an Instron tensile tester. During the test, the sample was continuously loaded to a strain of 4% and unloaded to zero stress; the total recoverable strain, ε_t , was obtained by subtracting the residual strain, ε_r , at zero stress from the deformation strain as illustrated in Figure 1(a).

Experimental Results and Discussion Figure 1(a) shows that, after unloading, the total recovery strain, ε_t , was $\sim 2.2\%$ strain, among which $\sim 1.6\%$, ε_e , was elastic strain and the rest of $\sim 0.6\%$, ε_p , was likely related to SIM reversion. From Figure 1(b), it can be seen that the material consists of β and ω phases as well as a small amount of α -phase before deformation. It is also noticed that the strongest $(110)_\beta$ intensity is located at $\sim 15^\circ$ away from the sample’s axial direction (see Figure 1(d)), suggesting that, unlike other alloys that have a *bcc* crystal structure, this β -Ti wire does not have a $\{110\}_\beta$ texture. During deformation, reflections associated with the SIM were clearly seen as the applied stress reached ~ 500 MPa, and peak intensities increased with increasing strain (Figure 1(c)). After unloading to zero stress, the intensities of the martensite peaks were decreased, but are still higher than those before deformation (Figure 1(d)).

Figure 2 shows the comparison between the measured diffraction spectra and those fitted by Rietveld refinement before (Figure 2(a)) and during deformation (Figure 2(b)). Each image consists of 72 diffraction spectra, corresponding to intensities integrated at 5 degrees interval along the 360 degree azimuthal angle.[10,11] It can be seen that Rietveld refinement was able to capture the experimental observations in detail. Based on the overall goodness-of-fit between the experimental and modeling results, the evolution of phase fractions and textures during deformation were evaluated. According to the Rietveld refinement, the material had $\sim 59 \pm 1$ mass% β -phase, $\sim 38 \pm 0.4$ mass% ω -phase and $\sim 3 \pm 0.1$ mass% α -phase before deformation. Compared to the Ti–17Nb alloy,[8] the large amount of β -phase in this alloy shows the strong β -phase stabilizing effect of the Cr. The lattice parameters of different phases are listed in Table 1. At the strain of $\sim 1.4\%$ (or the stress of ~ 493 MPa), $\sim 1\%$ SIM was transformed from the β -phase. Lattice parameters of each phase at this point are also listed in Table 1. Based

on these numbers, the maximum phase transformation strain, which is from the $\langle 110 \rangle_\beta \rightarrow [010]_{\alpha''}$ transformation, is 4.9% using Kim et al.’s equation.[4] This number is $\sim 17\%$ less than that predicted by Kim et al. on the Ti–17Nb binary alloy,[4] suggesting the negative effect of Cr on transformation strain. More SIM was formed as deformation continued (Figure 2(c)). At 3% strain, $\sim 17 \pm 2\%$ SIM phase was formed, while the fraction of the β - and ω -phase was dropped to $\sim 45 \pm 1\%$ and $35 \pm 0.4\%$, respectively. The amount of the α -phase stayed unchanged. After unloading to zero stress, the residual martensite was $\sim 1 \pm 0.04\%$ in the X-ray-irradiated volume.

Figure 3 shows the texture change in different phases during deformation. Similar to those in other β -Ti alloys,[15,16] the β -phase in this material had a strong $\{210\}_\beta$ texture, while the ω -phase had a strong texture component in the vicinity of the $\{11\bar{2}2\}_\omega$ to $\{2243\}_\omega$ planes. The strong $\{210\}_\beta$ texture in this alloy provides one more evidence to support our previous hypothesis that all meta-stable β -Ti alloys have a tendency to form a $\{210\}_\beta$ texture instead of the well-known $\{110\}_\beta$ texture after cold-drawing.[15] The texture of the ω -phase was previously reported as the $\{11\bar{2}2\}_\omega$ fiber, but close comparisons in this study suggest that it is more towards the $\{2243\}_\omega$ texture. These texture patterns were maintained during deformation. At 3% strain, the strength of the $\{210\}_\beta$ texture was slightly decreased, while the texture strength of the ω -phase was unchanged. The SIM had a very strong $(041)_{\alpha''}$ texture. Textures in different phases are likely related to each other following their lattice orientation relationship. For example, based on the orientation relationship between the β - and ω -phases,[8] the $\langle 210 \rangle_\beta$ direction is parallel to the $[11\bar{2}]_\omega$ (i.e. $[11\bar{2}6]_\omega$) direction, which is very close to the $(2243)_\omega$ plane normal. Therefore, a strong $\{210\}_\beta$ texture could result in a strong $\{2243\}_\omega$ texture after phase transformation. Similarly, the $\langle 210 \rangle_\beta$ direction should be converted to the $[031]_{\alpha''}$ direction during SIM transformation (e.g. $[012]_\beta \rightarrow [031]_{\alpha''}$) based on their crystal orientation relationship,[4] which is only ~ 6 degree from the $(041)_{\alpha''}$ plane normal. Therefore, the strong $(041)_{\alpha''}$ fiber texture was directly formed from the strong $\{210\}_\beta$ texture. The reason that the $\{210\}_\beta$ grains did not choose other α'' directions is that the $[012]_\beta \rightarrow [031]_{\alpha''}$ transition gives the largest transformation strain (i.e. $\sim 4.5\%$), and thus most effectively accommodated the tensile deformation strain.

The influences of the heat treating temperature and time on recoverable strain are illustrated in Figure 4. Although samples heat treated at the relatively lower temperature (e.g. 550°C) or shorter time (3 seconds at 600°C) showed a very good strain recovery (e.g. $\varepsilon_t > 3\%$), most of it was contributed by the pure elastic deformation, ε_e , due to the high material

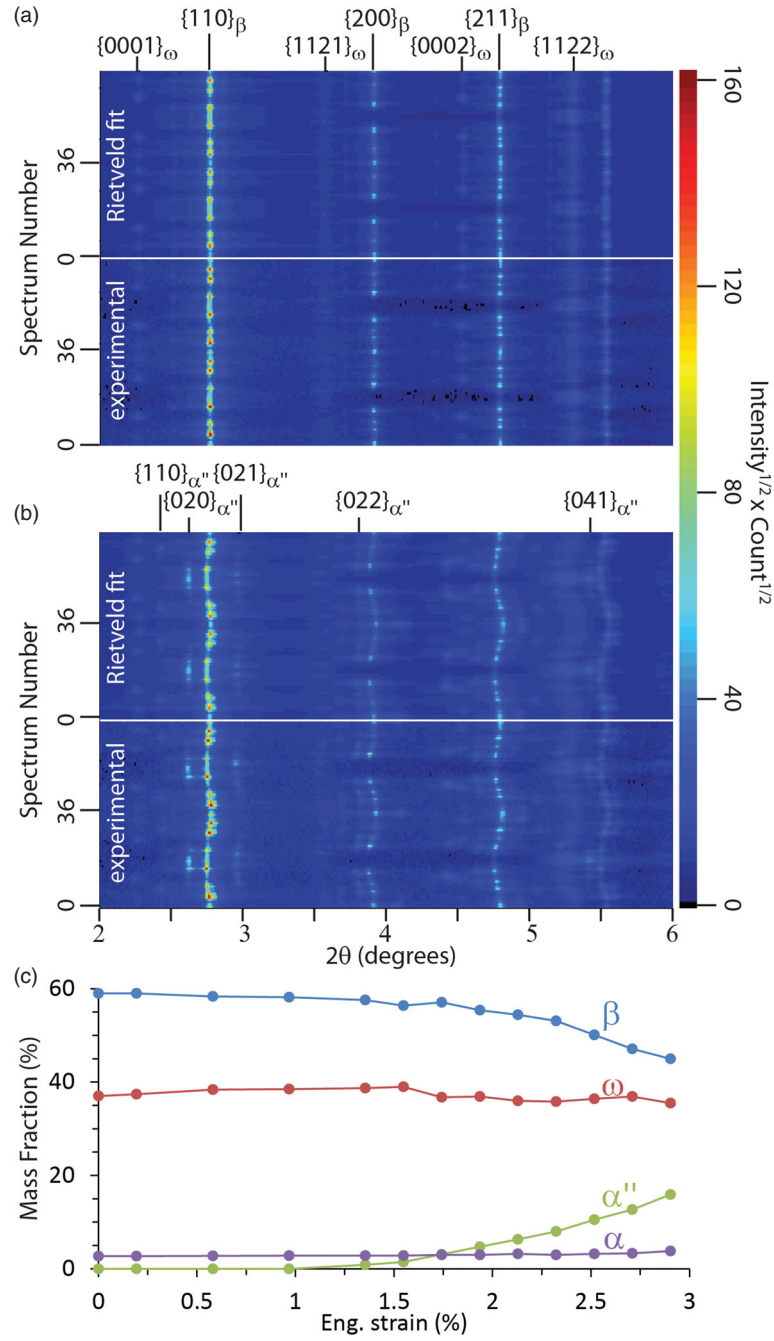


Figure 2. Synchrotron diffraction spectra during deformation; (a) before deformation, (b) at the strain of 3% and (c) evolution of phase fractions during deformation. The bottom of each figure in (a) and (b) shows the experimental results, the top of each figure in (a) and (b) is given by Rietveld refinement.

Table 1. Lattice parameters of different phases before and during deformation.

Condition	Phase	a (Å)	b (Å)	c (Å)
As annealed	α	2.9492 ± 0.0005		4.6752 ± 0.0003
	β	3.2778 ± 0.0001		
	ω	4.6481 ± 0.0011		2.8320 ± 0.0003
@stress = 493 MPa	α	2.9529 ± 0.0006		4.6862 ± 0.0015
	β	3.2814 ± 0.0000		
	ω	4.6547 ± 0.0014		2.8344 ± 0.0003
	α''	3.1526 ± 0.0017	4.8699 ± 0.0015	4.6554 ± 0.0024

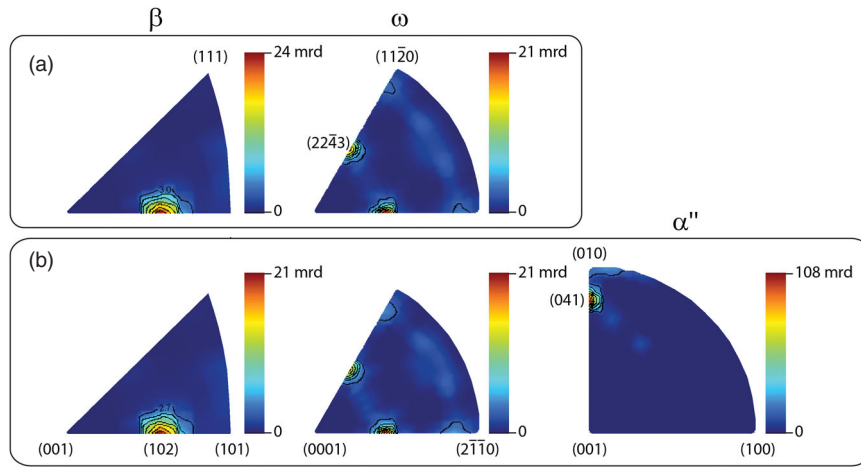


Figure 3. Inverse pole figures of the sample's axial direction of different phases: (a) before deformation and (b) at the strain of 3%.

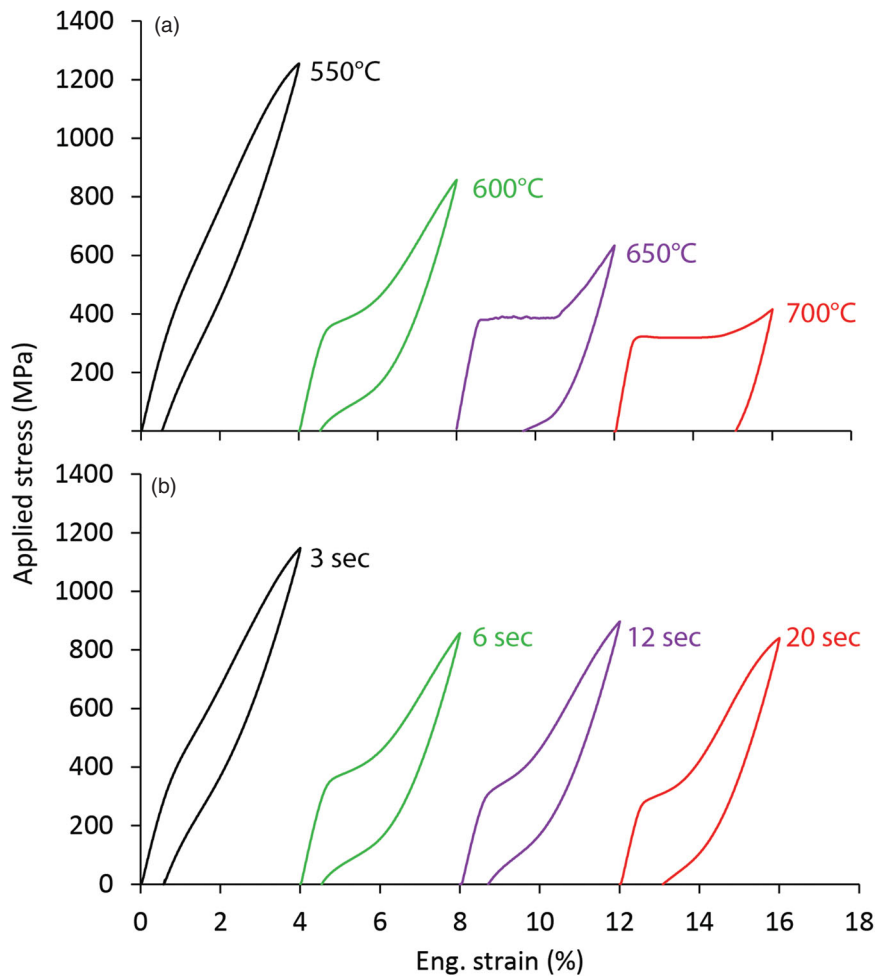


Figure 4. Stress-strain curves of samples heat treated (a) at different temperatures for 6 seconds and (b) at 600°C for different time.

strength, which is likely related to the large amount of residual work hardening from the cold-drawing process. Higher temperatures and longer time decreased the

total recoverable strain as the lower material strength caused by prolonged annealing could promote plastic deformation in the β -matrix and thus suppressed

the reversal phase transformation during unloading. These observations match the contradictory influences of residual cold work on the SIM phase transformation; while the residual cold work products (e.g. dislocations, textures) assist the formation of SIM,[1] too much dislocations will suppress the martensitic phase transformation.[17] Thus, an intermediate annealing rather than solution treatment after cold work is always used to improve the pseudo-elastic or super-elastic behavior of β -Ti alloys.[4,18] In the current case, the maximum of $\sim 3.5\%$ strain recovery was obtained when the cold drawn wire was heat treated at 600°C for 6 seconds. The Young's modulus is ~ 62 GPa, the yield and tensile strengths are 356 MPa and 977 MPa, respectively.

Although above results show good application potential for this alloy, more studies are yet to be done. For example, it was recently noticed that this material exhibits an aging effect (i.e. increase in strength, but decrease in strain recovery) at room temperature; and aging appeared to be promoted by the residual cold work. This room temperature aging could be responsible for the conflicts shown between Figure 1(a) and Figure 4. In Figure 1(a), the sample heat treated at 750°C and tested after 3 weeks had a yield strength of ~ 550 MPa, which is ~ 200 MPa higher than that tested right after the 700°C heat treatment (Figure 4). Room temperature aging in other β -Ti alloys has been reported before, where the formation of the ω -phase during aging reduces the martensite transformation temperature and raises the strength for SIM.[19] A similar reaction is expected in this alloy. A complete understanding of the mechanisms of room temperature aging in this alloy and its influence on alloy properties will require more research.

Conclusions In summary, *in situ* synchrotron X-ray diffraction tensile testing was carried out to study the deformation behavior of a Ti-17Nb-1Cr alloy at room temperature. A large amount of β -phase was found in this alloy due to the strong β -phase stabilizing effect of the Cr. Although this alloy did not show significant transformation peaks by DSC, SIM phase transformation was found during deformation, and its reverse transformation increased the total recoverable strain. A maximum of $\sim 3.5\%$ strain recovery was obtained after proper heat treatment. Unlike other alloys that have a *bcc* crystal structure, a strong $(210)_\beta$ texture was found in the β -phase, providing an evidence to support the previous suggestion that all meta-stable β -Ti alloys have a tendency of a similar texture instead of the well-known $(110)_\beta$ texture after cold-drawing. The ω -phase has a $(2243)_\omega$ texture, which was maintained during deformation. The strong $(041)_{\alpha''}$ fiber texture in the α'' -phase was formed from the $(210)_\beta$ texture based on their crystal orientation relationship.

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Disclosure statement No potential conflict of interest was reported by the authors.

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