



Formation of the monoclinic α'' phase in quenched U–3.6 at.% Ti–4.7 at.% W alloy

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Abstract

The effect of quenching on the structure of ternary U–3.6 at.% Ti–4.7 at.% W alloy was studied by X-ray diffraction and transmission electron microscopy. It was found that in addition to the orthorhombic α' martensite a monoclinic α'' phase forms in the quenched material. The lattice parameters and the space group of the monoclinic α'' phase were determined by the Rietveld refinement method and then were verified by electron diffraction. The unit cell of the monoclinic structure was treated as a side-centered parallelepiped with the unique axis b . The space group was determined as $C2/m$ and the lattice parameters were: $a = 0.5838$ nm, $b = 0.2858$ nm, $c = 0.4973$ nm and $\beta = 91.08^\circ$. Orientation relationship between α' and α'' lattices was determined from the analysis of the electron diffraction patterns. It was shown that the formation of α' and α'' structures from the cubic γ structure can be explained by the model similar to that suggested for U–Mo and U–Nb systems, and the α'/α'' orientation relationship observed in the experiment excellently fits this model. © 1997 Elsevier Science B.V.

1. Introduction

It is well known that uranium-based alloys quenched to room temperature from the field of γ phase stability yield a wide variety of metastable structures [1]. For relatively small additions of alloying elements the high temperature body-centered cubic γ phase of uranium transforms martensitically to nonequilibrium α' phase, which has base-centered orthorhombic unit cell and can be considered as slightly distorted equilibrium alpha-uranium. With increasing content of solute atoms a monoclinic (α'') modification of the orthorhombic α phase occurs upon quenching from the γ phase region. A further increase in alloy concentration results in the quenched γ° structure, a tetragonal distortion of the parent γ phase. All these transformations, $\gamma \rightarrow \alpha'$, $\gamma \rightarrow \alpha''$, $\gamma \rightarrow \gamma^\circ$, are thought to be accom-

plished by shear and by displacive mechanisms requiring cooperative, short-range movements of the atoms [2].

Systematic studies of metastable α' and α'' phases obtained by quenching from the γ field were performed on numerous binary uranium systems, such as U–Mo [3–6], U–Nb [7,8], U–Ti [9,10], U–Ru [11], U–Re [12]. As to ternary alloys, to the authors' knowledge, only two systems, U–Mo–Ti [13] and U–Nb–Zr [14], were investigated systematically, and appearance of orthorhombic (α') and tetragonal (γ°) phases has been confirmed for quenched structures. However, occurrence of the metastable monoclinic α'' phase in quenched ternary alloys has not been observed. In his work on ternary U–2.5 wt%Zr–7.5 wt%Nb alloy Vandermeer [14] assumed that because of the high content of solute in this alloy the atomic lattice apparently becomes 'stiffer' making shear more difficult, thus suppressing α'' formation during quenching.

The present paper reports that in ternary U–3.6 at.% Ti–4.7 at.% W alloy the monoclinic α'' phase forms upon quenching. This phase was identified by electron diffrac-

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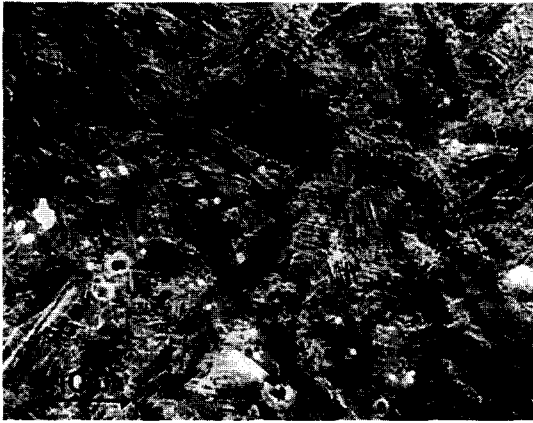


Fig. 1. Martensitic structure produced in ternary U–3.6 at.% Ti–4.7 at.% W alloy by quenching from the γ -field into water. White inclusions were identified as W-particles.



Fig. 2. TEM micrograph showing martensitic plates formed in quenched U–3.6 at.% Ti–4.7 at.% W alloy. The plates were identified as α'' monoclinic phase.

tion in a transmission electron microscope (TEM) and by X-ray diffraction analysis. The unit cell parameters and the value of the monoclinic angle were determined.

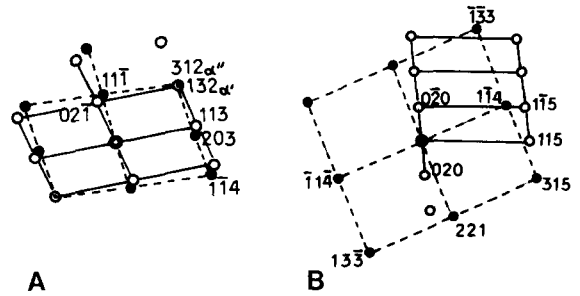


Fig. 4. Key diagrams (A) and (B) for the diffraction patterns shown in Fig. 3A, B, respectively. Open circles represent reflections of the α' phase, filled circles relate to the α'' phase.

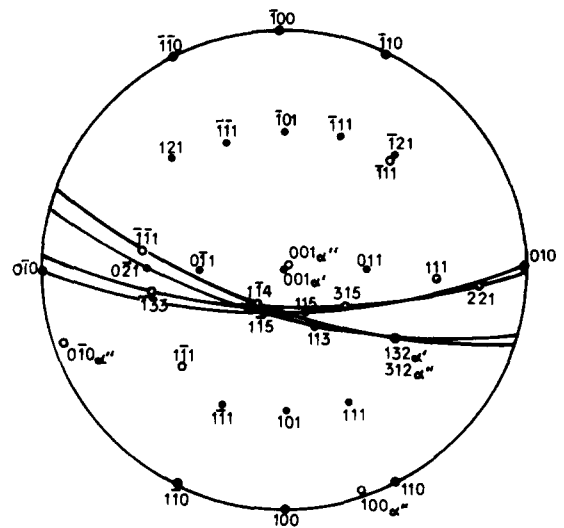


Fig. 5. Superimposed stereographic projection representing orientation relationship between α'' and α' structures as obtained from the analysis of electron diffraction patterns in Fig. 3. Filled circles are related to the α' phase, open circles refer to the α'' phase. The zones of α'' reflections fall within few degrees of the corresponding zones of α' -reflections.



Fig. 3. Selected area diffraction patterns for two orientations of the α'' plates shown in Fig. 2.

2. Experimental

The U–3.6 at.% Ti–4.7 at.% W alloy was prepared in an arc-melting furnace with a water cooled copper hearth in the atmosphere of purified argon. The ingot was remelted several times and then annealed at 1020°C for 24 h in order to achieve good homogeneity. Afterwards the lump of alloy was heated under vacuum in the γ phase region (at 930°C) for 45 min and then quenched into water at ambient temperature. The composition of the alloy was checked by chemical analysis and the total impurities were less than 200 ppm. Uncertainty in tungsten concentration was within 0.01 at.%.

The specimens for X-ray examination were prepared by standard polishing technique followed by electropolishing to provide a stress-free surface. X-ray diffractograms were taken with a Phillips PW-1050 diffractometer operating in scan-step mode with Cu-K α radiation. The K β was re-

moved by a graphite monochromator. The Rietveld program (version DBWS-9411PC) was used for structure refinement and determination of the lattice parameters.

Specimens for TEM analysis were cut in the form of slices, 0.3 mm thick. 3 mm disks were then punched and ground to reduce their thickness and finally thinned in a twin-jet electropolishing unit ('Tenupol') in a solution of 60% methyl alcohol, 34% butyl alcohol and 6% perchloric acid cooled to –20°C.

3. Experimental results

Water quenching from the γ phase field produces the typical microstructure represented by Fig. 1. Large acicular martensite laths, presumably associated with the α' phase, dominate the structure. In addition white inclusions identi-

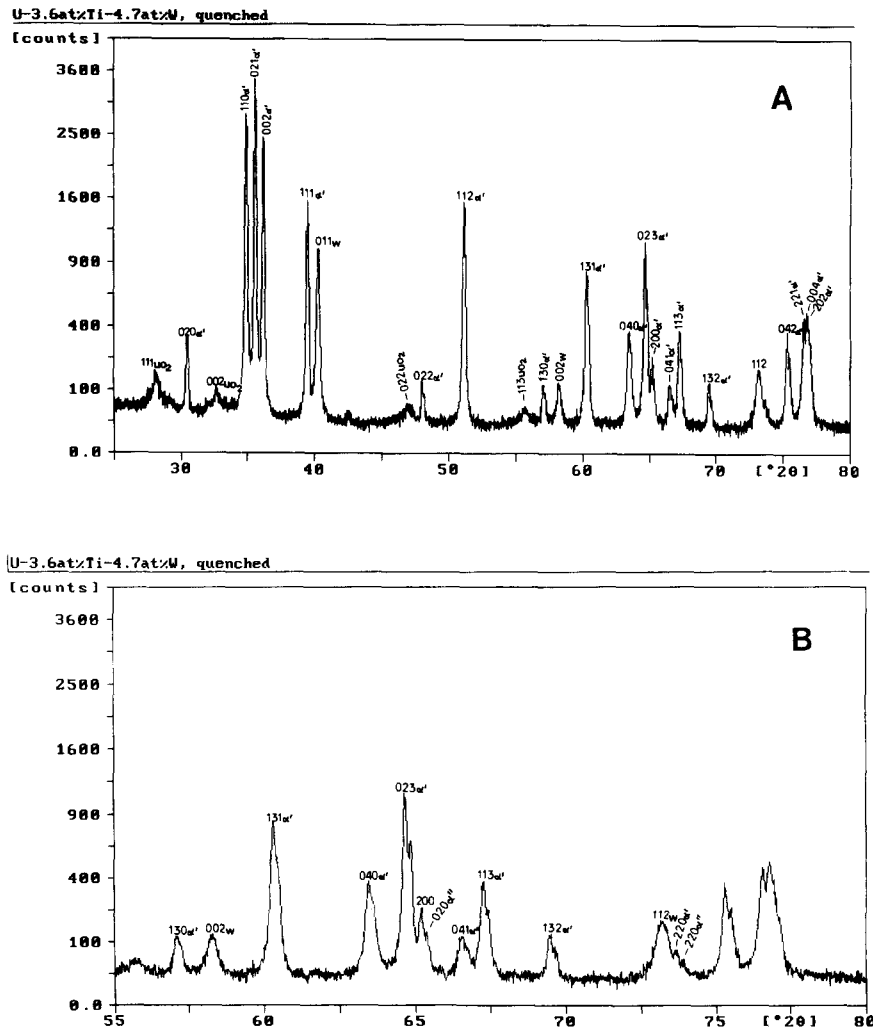


Fig. 6. (A) X-ray diffraction pattern of the U–3.6 at.% Ti–4.7 at.% W alloy quenched from the γ field in water. (B) A portion of the diffractogram on the enlarged scale showing splitting of some α' peaks.

fied by EDS analysis as W-particles and stacks of fine plates (marked by arrows) can be easily seen in the micrograph. At higher magnifications in the TEM these fine plates appear as groups of needles shown in bright field image in Fig. 2. The corresponding selected area diffraction patterns for two foil orientations are given in Fig. 3(A, B). Both patterns contain two systems of diffraction spots (see key diagrams in Fig. 4) and faint diffraction rings of a surface oxide layer (UO_2) which were used as an internal standard for accurate calibration of the camera constant. While one system of reflections (open circles) was easily related to the orthorhombic α' phase with lattice constants $a = 0.2859$ nm, $b = 0.5856$ nm and $c = 0.4962$ nm, the second system (solid circles) could not be interpreted in terms of the α' structure. However, its successful indexing was done on the basis of a monoclinic unit cell with the following lattice parameters: $a = 0.5838$ nm, $b = 0.2858$ nm, $c = 0.4973$ nm and $\beta = 91.08^\circ$. The lattice parameters for both structures were deduced from the analysis of the X-ray diffractogram described below.

Fig. 5 shows superimposed stereographic projection representing the orientation relationship between α'' and α' phases as obtained from the analysis of electron diffraction patterns. The zones of α'' reflections appearing in the electron diffraction patterns in Fig. 3 fall within a few degrees of the corresponding zones of α' reflections. On the basis of the superimposed stereographic projection it is possible to summarize the following α'/α'' relationship: $(001)_{\alpha'} \parallel (001)_{\alpha''}$ and $(100)_{\alpha'}$ is 20° away from $(100)_{\alpha''}$.

The X-ray diffractogram obtained from a sample of

U–Ti–W alloy quenched from the γ phase in water is depicted in Fig. 6A. In agreement with the results of metallographic and TEM examinations it may be seen that the X-ray pattern contains peaks of α' uranium and peaks of tungsten. Weak peaks of UO_2 also appear in the pattern, consistent with the observation of oxide rings in the electron diffraction patterns. However, detailed scrutiny of the diffraction peaks reveals that the reflections (110), (111) and (112) are slightly broadened and some peaks, such as (113), (200), (220) are distinctly splitted (see the portion of diffractogram on the enlarged scale in Fig. 6B) as compared with the peaks obtained from the slowly cooled alloy, thus indicating the possible formation of the monoclinic α'' phase.

Supposing that the α'' phase exists in the quenched alloy the Rietveld refinement method was applied to determine the parameters of the unit cell and the atomic positions in the α'' structure. The pattern fitting was performed in the 20° to 80° 2θ -range, using a pseudo-Voigt function for peak profile, March–Dollase model for preferred orientation (the [110] preferred orientation direction for the α'' phase was chosen) and refinable background function available in the 9411-version of the DBWS computer program [15]. The best fitting of calculated and observed diffraction peaks was achieved for the following structural parameters of the monoclinic phase: $a = 0.5838$ nm, $b = 0.2858$ nm, $c = 0.4973$ nm and $\beta = 91.08^\circ$. The lattice constants of the orthorhombic α' phase were: $a = 0.2859$ nm, $b = 0.5856$ nm and $c = 0.4962$ nm. The space group for the monoclinic phase was established as C2/m, with

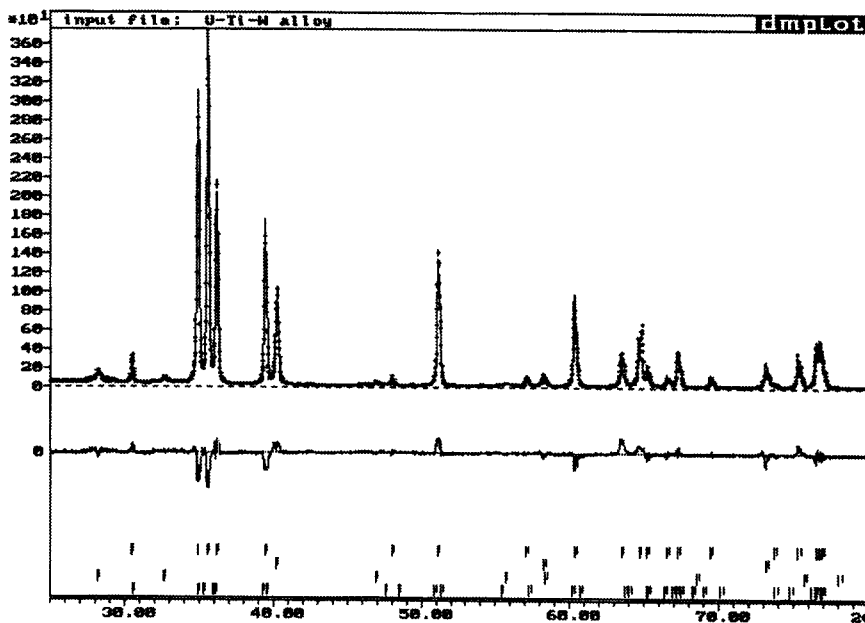


Fig. 7. Rietveld plot for U–3.6 at.% Ti–4.7 at.% W alloy quenched from the γ field. The calculated pattern is shown by solid-line curve. The crosses are the observed intensities. The difference between the observed and calculated intensities at each step of calculation is presented below by the difference curve. The short vertical bars at the bottom of the figure indicate the positions of the Bragg reflections.

Table 1

Comparison of observed and calculated intensities for diffraction peaks related to α'' monoclinic phase in gamma quenched U–3.6 at.% Ti–4.7 at.% W alloy

No.	hkl	D_{hkl}	$I_{obs.}$	$I_{calc.}$
1	200	2.919	36	36
2	110	2.567	7816	8849
3	20-1	2.538	57	59
4	201	2.497	59	57
5	002	2.485	67	63
6	11-1	2.288	166	189
7	111	2.273	149	188
8	20-2	1.910	21	9
9	202	1.875	18	8
10	11-2	1.793	95	91
11	112	1.778	96	91
12	31-1	1.538	123	137
13	311	1.524	159	132
14	20-3	1.452	13	9
15	203	1.429	8	9
16	020	1.429	101	108
17	40-1	1.408	8	11
18	11-3	1.397	9	8
19	401	1.393	11	10
20	113	1.387	8	8
21	220	1.283	324	391
22	22-1	1.245	249	300
23	221	1.240	283	299
24	02-2	1.239	25	27
25	022	1.239	27	28

four atoms per cell at 4(i) Wyckoff positions. The atomic coordinates in the monoclinic unit cell were as follows: (0.081, 0, 0.25), (-0.081, 0, 0.75), (0.581, 0.5, 0.25), (0.419, 0.5, 0.75). The Bragg R -factor characterizing the agreement between the observed and calculated data for the α'' phase was 15.7%. Fig. 7 shows the observed and Rietveld generated diffraction patterns as well as a plot of residuals. The experimental and calculated intensities and the values of d -spacing for the monoclinic structure are presented in Table 1. The differences between the calculated and observed intensities are due to the presence of residual texture.

4. Discussion

Transmission electron microscopy and X-ray diffraction analysis reveal that both the orthorhombic α' and the monoclinic α'' phases form simultaneously in the quenched U–3.6 at.% Ti–4.7 at.% W alloy. Comparing this observation with the results of the previous work [16] showing that in the binary U–Ti alloy with approximately the same Ti content (4 at.%) only the α' martensite is generated upon quenching, it seems reasonable to assume that it is the presence of some amount of tungsten solute in the quenched α matrix that causes its monoclinic distortion and formation of the metastable monoclinic phase of an α'' type.

The lattice constants for the orthorhombic α' phase were determined as $a = 0.2859$ nm, $b = 0.5856$ nm and $c = 0.4962$ nm. The monoclinic phase was obtained as slightly distorted α' phase with $a = 0.5838$ nm, $b = 0.2858$ nm, $c = 0.4973$ nm and $\beta = 91.08^\circ$. It is to be noted that inverted metrical relationships between the a and b parameters for the monoclinic and orthorhombic structures are due to the fact that the representation of the monoclinic unit cell in our work differs from that used in studies on U–Mo and U–Re systems [4,6,12]. While in the previous studies the α'' monoclinic structure was treated as a base-centered parallelepiped with unique axis c ($\gamma \neq 90^\circ$), in the present work the unit cell was side-centered and the unique axis was set parallel to b ($\beta \neq 90^\circ$). Such selection of the unit cell was predetermined by the crystallographic consideration that a monoclinic Bravais lattice exists only as a primitive or side centered lattice. It was also important to represent the unit cell in exact correspondence with the crystallographic classification in order to provide correct use of the Rietveld refinement program. It follows from the choice of b as the unique axis that in the monoclinic α'' structure the (001) $_{\alpha''}$ side face of the unit cell spanned by basis vectors a and b has to be rectangular and should correspond to the (001) $_{\alpha'}$ base centered plane in the orthorhombic α' uranium. The structure of the monoclinic α'' phase, as determined in the present study, is shown schematically in Fig. 8A.

It is interesting to compare the lattice parameters a , b , and c for the orthorhombic α' with the corresponding values obtained for the monoclinic α'' phase. Keeping in mind that the b parameter of α' corresponds to the a parameter of α'' , it can be easily seen that the value $b = 0.5856$ nm for α' is markedly reduced to the value of 0.5838 nm for α'' , while two other sizes of the α' unit cell change to a smaller extent. This result is fairly consistent

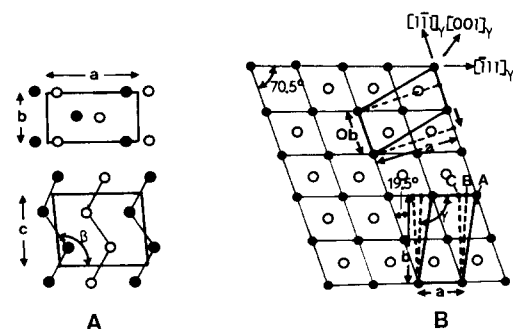


Fig. 8. (a) The structure of the monoclinic α'' phase, as determined in the present study. The face spanned by the vectors a and b is the centered side face of the unit cell. The unique axis is parallel to b . The lattice constants are: $a = 0.5838$ nm, $b = 0.2858$ nm, $c = 0.4973$ nm and $\beta = 91.08^\circ$. (b) A schematic illustration of generating the α' or α'' structures from the γ (BCC) lattice (see Tangri and Williams [4]). The plane of the drawing is (110) $_{\gamma}$. Filled circles represent atoms in the plane of the drawing and open circles represent those in the layer below.

Table 2
Lattice parameters of the monoclinic α'' phases in uranium alloys

System	at.% of solute	Parameters (nm)				Ref.
		<i>a</i>	<i>b</i>	<i>c</i>	γ	
U–Mo	10	0.2866	0.5752	0.4940	92.28°	[4]
U–Ti	11	0.2866	0.5733	0.4970	90.68°	[9]
U–Nb	11.2	0.2850	0.5789	0.4990	90.88°	[8]
U–Re	9	0.2870	0.5760	0.4960	92.00°	[12]
U–Ti–W	3.6Ti, 4.7W	0.5838	0.2858	0.4973	$\beta = 91.08^\circ$	present work

with the previous reports on the predominant contraction of the *b* parameter when α'' phase is generated in systems U–Mo[4], U–Nb[8] and U–Re[12]. Besides, the value of 91.08° for the monoclinic angle γ , as calculated in the present study, also falls within the range from 90.2° to 93.5° determined for other systems.

Table 2 lists the comparative data on lattice parameters of the monoclinic α'' reported for various uranium binary systems. The results of the present work are presented in the last line.

It remains now to understand whether the presentation of the monoclinic unit cell, as shown in Fig. 8A, is compatible with the well recognized model for $\gamma \rightarrow \alpha''$ and $\gamma \rightarrow \alpha'$ transformation developed by Tangri and Williams [4]. According to this model the α' and α'' structures can be obtained from the quenched γ_{BCC} matrix by shear in only one direction of $\langle 111 \rangle$ -type, lying in $(110)_\gamma$ cubic plane. Formation of the monoclinic structure is ascribed to stiffening of the parent γ lattice, thus leading to the limited shear **AB**, which results in an angle $\gamma \neq 90^\circ$ in $(001)_{\alpha'}$ face, as illustrated in Fig. 8B (bottom corner). Greater amount of shear **AC** results in an orthorhombic structure.

It may be easily seen that the approach of Tangri and Williams [4] also allows one to generate the monoclinic α'' structure with the rectangular $(001)_{\alpha''}$ face which is in fact the side face of the α'' unit cell. At the top right hand corner in Fig. 8B the rectangular $(001)_{\alpha''}$ face of the α'' cell is shown which can be obtained by proper amount of shear in $[\bar{1}\bar{1}\bar{1}]$ direction, by analogy to the atomic movement needed for producing the orthorhombic structure. An additional shear, however, is required to produce an angle $\beta \neq 90^\circ$ in the face **ac** perpendicular to the paper. Such shear can be associated with $[\bar{1}\bar{1}\bar{1}]$ displacements in adjacent (110) planes of the cubic γ lattice. In light of the proposed model and referring to the Fig. 8B it can be easily seen that the $(001)_{\alpha''}$ plane is parallel to the $(001)_{\alpha'}$ plane and $(100)_{\alpha''}$ should be 19.5° away from $(100)_{\alpha'}$. Such relation between α' and α'' lattices excellently fits the α'/α'' orientation relationship observed in our experiments (see Fig. 6).

5. Conclusions

(1) The α'' monoclinic phase is formed in as quenched ternary U–3.6 at.% Ti–4.7 at.% W alloy.

(2) The α'' structure, as determined by Rietveld refinement method, can be described on the basis of a side-centered unit cell with the unique axis *b*. The monoclinic angle $\beta = 91.08^\circ$ and the α'' lattice constants are: *a* = 0.5838 nm, *b* = 0.2858 nm, *c* = 0.4973 nm. The space group of the structure is C2/m.

(3) The model of Tangri and Williams [4] developed for $\gamma \rightarrow \alpha''$ transformation can also be used for generating the monoclinic α'' structure with the rectangular $(001)_{\alpha''}$ side-centered face.

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