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THE ISOTHERMAL TRANSFORMATION OF METASTABLE BETA URANIUM
SINGLE CRYSTALS

A. N. Holden

November 19, 1952

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CONTENTS

	<u>Page</u>
Acknowledgement	9
Abstract	11
Introduction	13
Gross Features of the Transformation	13
Classification of the Transformation	13
Crystallography of the Transformation.	35
Conclusion.	36
References.	45

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7

KAPL-831

LIST OF ILLUSTRATIONS

			<u>Page</u>
1113950	(Figure 1)	Plates Formed by Isothermal Transformation of Beta Uranium Crystal at Room Temperature. Polarized Light. 100X	15
1113951	(Figure 2)	Growth of Plates at Room Temperature. Rate of Growth Approximately 0.5 mm per Hour. Polarized Light. 40X	17
1113952	(Figure 3)	Growth of Plate beneath Collodian Film Showing Developing Interference Pattern. Polarized Light. 40X	21
1113953	(Figure 4)	Examples of Shearing of Scratches by the Transformation. Polarized Light. 200X and 400X	23
1113954	(Figure 5)	Transformation Product Growing in a Deformed Region of a Beta Crystal. Polarized Light. 200X	25
KH-9A2360	(Figure 6)	Growth of Conventional and Uranium Martensite	27
1113955	(Figure 7)	Twins in Uranium Martensite Plates. Polarized Light. 400X	29
1113956	(Figure 8)	Slip in Beta Crystal near Junction of Two Martensite Plates. Polarized Light. 400X	31
1113957	(Figure 9)	Athermal Martensite Burst. Polarized Light. 100X	33
KH-9A1967	(Figure 10)	Pole Figure for Room Temperature Transformation of Beta to Alpha 002 Poles.	37
KH-9A1966	(Figure 11)	Pole Figure for Room Temperature Transformation of Beta to Alpha 040 Poles.	39

~~CONFIDENTIAL~~

~~CONFIDENTIAL~~LIST OF ILLUSTRATIONS (Continued)

	<u>Page</u>
KH-9A1968 (Figure 12) Pole Figure for Room Temperature Transformation of Beta to Alpha 110 Alpha Poles	41
KH-9A2361 (Figure 13) Typical Coincidence of Martensite Habit Plane with {321} Plane in Beta Matrix	43

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9

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11

ABSTRACT

The transformation of metastable beta uranium crystals was found to proceed by a martensitic reaction at room temperature. The features of the transformation of particular interest were that individual uranium martensite plates formed isothermally and grew at a slow rate isothermally.

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13

THE ISOTHERMAL TRANSFORMATION OF METASTABLE BETA URANIUM SINGLE CRYSTALS

A. W. Holden

INTRODUCTION

Single crystals of the beta phase of uranium were first grown and retained in metastable condition at room temperature in material containing 1 atomic % or more of chromium. These crystals were stable for months at room temperature and were used by Tucker¹ to determine the beta phase structure. Crystals of lower chromium contents, down to 0.3 atomic %, have been grown recently,² and these crystals transform to alpha much more rapidly. The results of a study of the transformation in these low chromium alloy crystals, both metallographically and by means of X-ray examination, are presented in this paper.

GROSS FEATURES OF THE TRANSFORMATION

The transformation in these dilute chromium-uranium solid solution alloys first interested us because the plates of alpha that were formed during room temperature isothermal transformation had an appearance not unlike martensite plates in iron alloys (Figure 1). In fact a great many of the transformation features were similar to martensite: the plates seemed to prefer only certain habit planes in the parent crystal; the surface of the beta crystal was distorted by the formation of an alpha plate; the distortion thus observed frequently appeared feathered like martensite; and deformation of the beta crystal greatly hastened its transformation, again similar to martensite.

However, other features of the transformation were unlike martensite of the usual type. The athermal transformation of beta-phase crystals to alpha could be completely suppressed by quenching them from the beta phase to room temperature*, a feature uncommon in the martensite transformation. Furthermore, the growth of the transformation plates occurred without audible clicks, and apparently the reaction went to completion isothermally at a slow rate.

The experimental work on this transformation has been concerned with two aspects of the problem, namely to classify the transformation as either a martensitic transformation or a nucleation and growth transformation of the standard type, and to study the crystallography of the transformation.

CLASSIFICATION OF THE TRANSFORMATION

In order to classify the transformation as martensitic or nonmartensitic, a martensitic transformation must be rather carefully defined.

*Occasional athermal transformation occurred as noted later in this paper.

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Martensitic transformations are characterized as follows:

1. The product shall be platelike (lens or needle shaped in two-dimensional section) and be formed by the cooperative shift of large volumes of material within the plate through fractional atom distances.
2. A composition change is not required by the transformation.

Other formerly accepted criteria for a martensite transformation must be considered fallible in the light of recent experimental exceptions to these rules. For example, it was thought that martensite formed only upon cooling, hence the term athermal has been applied to its formation, but the complete suppression of athermal martensite by rapid quenching has been observed by Kurdjumov et al.^{3,4} and recently by Cech and Hollomon.⁵ Furthermore martensite transformations have been reported by Kurdjumov to proceed extensively isothermally, and this fact has also been corroborated in the recent work cited.⁵ Another criterion of the martensite transformation that has persisted until recently is that individual martensite plates grow extremely rapidly. Slow growth of martensite individuals, however, has been reported by Kurdjumov⁴ for a copper-tin alloy transforming at -190°C .

In applying the two remaining criteria, namely the cooperative shear requirement and the requirement that no composition change occurs, to the transformation at hand, there are certain accepted tests that may be made.

The test for a composition change is to measure the rate of growth of the transformation product. If it grows more rapidly than any element will diffuse in the bulk matrix, no composition change must have occurred. If the transformation product does not grow faster than elements diffuse, the test is inconclusive. Transformations that have all the characteristics of martensite, with the sole exception that the rate of growth of the transformation plates has been reconciled with bulk diffusion rates, are usually known by the generic term bainite, although there is no assurance that diffusion actually played the retarding role in their growth.

The test that can be made for the cooperative shear of the transformation product is to observe what happens to parallel scratches on the specimen surface during the transformation. No martensite transformation can fail to shear the scratches wherever a transformation plate occurs, and furthermore the sheared scratches will bear the same angle with the matrix throughout the plate.

The rate of isothermal growth of the plates formed on transforming beta-uranium crystals at room temperature was studied by the simple technique of photographing the product at intervals. For this work a polished crystal was studied using polarized light to reveal the transformation. Figure 2 is a sequence of photographs over a period of an hour showing the growth to be continuous and at a rate of approximately 0.5 mm increase in length per hour. While this growth is slow for the general class of martensite, it is decidedly more rapid than chromium can diffuse, and therefore a composition change seems unlikely and a martensite transformation is indicated.

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FIGURE 1

Plates Formed by Isothermal Transformation of
Beta Uranium Crystal at Room Temperature.
Polarized Light. 100X

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2:50 P.M.

3:05 P.M.

3:20 P.M.

3:53 P.M.

FIGURE 2

Growth of Plates at Room Temperature. Rate of
Growth Approximately 0.5 mm per Hour. Polarized
Light. 40X

1113951

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Some indication of the surface distortion caused by the growth of plates in a beta crystal was obtained by first coating a polished crystal with collodian and then observing, as the plated formed, the number of interference lines that formed in the collodian film over the growing plates. These lines correspond to contour lines and suggest considerable surface upheaval, estimated to be 10^{-2} or 10^{-3} mm. A sequence of pictures showing the plate growth in a film-coated crystal is presented in Figure 3.

The question of shearing of scratches was investigated by observing what happened to a finely scratched beta crystal surface during the transformation. These scratches were applied to the specimen before the crystal was grown because it was found that any scratching subsequent to growth caused immediate transformation of the crystal surface and obscured any shearing effect. A definite unidirectional and apparently homogeneous shearing of the scratches was observed upon transformation, and two photographs of this phenomenon are shown in Figure 4.

There seems little doubt that the room temperature transformation of beta-uranium crystals is by a martensite mechanism. Shearing of the product is accomplished, as can be seen in the shifting of scratches, and there is little chance that composition changes can occur in the time required for plate growth.

The effect of deformation on the transformation seems to be one of introducing critical size nuclei, because while the rate of growth of the individual plates in strained regions remains slow, the plates begin to form immediately. In a nondeformed region, a few hours at room temperature is required to produce any visible plates. A photograph of the plates growing from a region of high deformation next to the cut produced by shearing is shown in Figure 5. The slip bands do not seem to constitute barriers to the migration of the plates.

The question that remains to be answered is why the martensite transformation in uranium proceeds by slow growth of individual plates, while steel martensites grow with velocities approaching that of sound. There must be a retarding mechanism operating in the case of uranium.

One possibility is that the simultaneous local deformation of the matrix which occurs in rapidly growing conventional martensite does not take place readily in uranium. The beta phase of uranium deforms by slip at room temperature only on $\{110\}$ type planes and in the $\langle 001 \rangle$ direction.² It would be highly fortuitous if the two possible systems were oriented so as to relieve the shear stress in beta, and, in fact, the habit plane* for uranium martensite is 30° from the slip plane.

The alpha plates, on the other hand, could twin readily⁶ so that a large proportion of the transformation stress is relieved by deformation of the uranium martensite plate itself. The growth of the plates would be slowed down by the requirement that twins continually nucleate and relieve

*Habit plane determination is discussed in a succeeding section of this paper.

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the transformation stress. The motion of the plate would be intermittently rapid and slow; immediately after twinning it would move rapidly for a distance, and then as the stress increased, slow down until another twin formed.

The stresses associated with conventional martensite are relieved by the motion of dislocations in the matrix, since a large number of deformation systems are available for volume adjustment of the matrix, and the growth of conventional martensite is only limited by the velocity of propagation of dislocation which may approach sound velocities.

The relief of strains associated with the growth of conventional and uranium martensites is visualized as shown in Figure 6.

High magnification microscopy has revealed that individual plates of alpha do appear to be twinned. A photograph of these twin markings in several plates is presented in Figure 7. Furthermore, there were signs of secondary shearing of scratches within the twins, although the twins were thin compared to the scratches and limit of resolution of the microscope was approached in trying to observe the secondary shear.

There is no evidence that conventional steel martensite deforms by a twinning sort of secondary shear, although the (112) martensite plane is postulated for the second homogeneous shear in the double shear mechanism of Greninger and Troiano⁷ and that plane is a twinning plane in body-centered-cubic or body-centered-tetragonal lattices.

In uranium, slip is often observed on one or both slip systems of the beta matrix in the stressed region near the junction of two or more large alpha plates. The combination of stresses resolves to cause slip in these regions. Such a region is pictured in Figure 8.

Several, but by no means all, of the beta crystals had a few large martensite plates already formed by the time the first observation was made. In general, less than 5 minutes from quenching to observation was necessary, so these plates could hardly have grown during their sojourn at room temperature unless they grew much faster than any measured rate of growth. It is the preferred explanation that these grew athermally at some higher temperature, perhaps even above 350°C, in a region where alpha uranium slips readily and where the beta phase may also deform by slip at a reasonable stress and on a greater number of slip systems. Many of these plates appear to be bursts where one plate has triggered another. A photograph of such an athermal burst is shown in Figure 9.

There is another feature common to many martensite reactions, namely that in the absence of any competing reactions they are reversible upon heating.

A partially transformed beta crystal was rapidly heated by plunging it into a lead pot to 625°C, a temperature high in the alpha equilibrium range. It was held for 10 minutes and then quenched. It was found to be a single beta crystal again with no sign of transformation.

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FIGURE 3

Growth of Plates beneath Collodian Film Showing
Developing Interference Pattern. Polarized Light.
40X

1113952

FIGURE 4

**Example of Shearing of Scratches by the
Transformation. Polarized Light. 200X
and 400X**

1113953

FIGURE 5

**Transformation Product Growing in a
Deformed Region of a Beta Crystal.
Polarized Light. 200X**

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**CONVENTIONAL MARTENSITE
GROWTH WITH SLIP IN MATRIX
PERMITTING SHEAR ADJUSTMENT.**

**RATE OF GROWTH LIMITED TO
VELOCITY OF DISLOCATION
MOTION OR $\sim$ SOUND VELOCITY.**

**URANIUM MARTENSITE GROWTH
WITHOUT SLIP IN BETA MATRIX
BUT WITH TWINNING IN ALPHA
PLATE PERMITTING SHEAR
ADJUSTMENT.**

**RATE OF GROWTH LIMITED BY
REPEATED STRESS BUILD UP
AND REPEATED NUCLEATION
OF TWINS.**

**FIGURE 6 - GROWTH OF CONVENTIONAL AND
URANIUM MARTENSITE**

FIGURE 7

**Twins in Uranium Martensite Plates.
Polarized Light. 400X**

1113955

FIGURE 8

**Slip in Beta Crystal near Junction of
Two Martensite Plates. Polarized
Light. 400X**

1113956

FIGURE 9

Athermal Martensite Burst. Polarized Light.
100X

1113957

CRYSTALLOGRAPHY OF THE TRANSFORMATION

X-ray work was carried out in several ways initially, but ultimately a new pole figure technique⁸ was developed to simplify the work.

The first attempts were to orient large isolated plates by a back reflection Laue method using a very fine beam. These attempts failed because the plates were evidently strained sufficiently to give distorted patterns that could not be oriented, and furthermore the exposure times with the fine beam were so long that excessive oxidation of the crystal occurred.

Attempts were then made to obtain a pole figure of the transformed alpha after the transformation was complete, using cylindrical rather than square crystals, and using standard film techniques. These attempts were not successful because the simple planes (110) and (002) occur in a triple reflection together with the (021), making it very difficult to separate the three on film and almost impossible to correctly assign indices to isolate diffraction spots of the triplet group.

The equipment currently being used is a completely modified Schultz-type goniometer in conjunction with a Geiger counter spectrometer. The goniometer was designed to automatically move the specimen so that reflection occurs sequentially from all the planes whose normals would trace a spiral path on a stereographic projection. A record of the reflected intensities along this spiral path was made for several planes of interest and pole figures were plotted from this record. Good resolution of the (110) (021) (002) triplet was obtained with this instrument. The results of the X-ray work are presented as a series of typical pole figures. The (002) alpha pole figure for the transformation is shown in Figure 10, plotted directly over the projection of the beta crystal matrix. The (040) alpha planes were found in positions shown in Figure 11, and the (110) alpha pole figure for the transformation is shown in Figure 12. Thus far it has not been possible to fit these pole figure data with a single orientation relationship, and the work has not progressed to the point where any relationships deduced from the pole figure data are considered positive. It is hoped that the results of more thorough orientation study may be the subject of a future paper.

The habit plane for the martensite transformation of beta uranium to alpha has been identified by metallographic studies of the traces of plates in adjacent faces of rectangular cross-section crystals. The principle habit plane appears to be the {321}-type beta plane. Figure 13 is a typical plot of the observed poles of the plates on a stereographic projection of the parent beta crystal.

The {321} plane, according to Tucker's work, is an unimportant plane having an extremely low relative intensity value for reflected X rays. This choice of a crystallographically unimportant habit plane seems characteristic of martensite. Geisler⁹ has considered that the irrational

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habit planes for martensite transformations are a consequence of either slip or twinning of the martensite plate itself and that the actual lattice matching occurs across smaller segments of boundary that are not parallel to the general plane of the large plate. Since habit planes are usually reported for the macroscopic plate, these planes are not necessarily important.

CONCLUSION

The room temperature beta to alpha transformation of quenched uranium-chromium-alloy crystals is martensitic. The transformation may be suppressed completely by quenching and occurs isothermally at a slow measurable rate by the relatively slow growth of martensite individuals.

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FIGURE 10
POLE FIGURE FOR ROOM TEMPERATURE
TRANSFORMATION OF BETA TO ALPHA
002 POLES

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FIGURE 11
POLE FIGURE FOR ROOM TEMPERATURE
TRANSFORMATION OF BETA TO ALPHA
040 POLES

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FIGURE 12
POLE FIGURE FOR ROOM TEMPERATURE
TRANSFORMATION OF BETA TO ALPHA
110 ALPHA POLES

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FIGURE 13

TYPICAL COINCIDENCE OF MARTENSITE
HABIT PLANE WITH {321} PLANE IN
BETA MATRIX

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