$\alpha \rightarrow \omega$ Transition in shock compressed zirconium: A study on crystallographic aspects

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Abstract. In 1973, Usikov and Zilbershtein proposed that the α (hcp) $\rightarrow \omega$ (a three atom hexagonal) transformation in Zr and Ti proceeds via the β (bcc, a high temperature phase) intermediate. Based on this they derived two non-equivalent orientation relationships (OR) between α and ω phases. Their transmission electron microscopy (TEM) study carried out on these elements, that were $\alpha \rightarrow \omega$ -transformed under static high pressure, revealed only one of the two proposed ORs. Various TEM studies done thereafter on these elements and their alloys (ω transformed under static pressures) conform to either one of these ORs. In a recent TEM study by Song and Gray on Zr, ω -transformed under shock compression, a new OR has been observed which according to them is different than those given by UZ and they put forth the direct $\alpha \rightarrow \omega$ transformation mechanism. In the present study, we have generated additional TEM data on shock compressed Zr samples and have reconciled the above conflicting results. We find all our ORs (which contain the OR of SG also) to be described by the OR reported by UZ. The latter OR (i.e. of SG) is shown to be a subset of the former. These observations show that the same type of mechanism of transformation is operative both, under static and shock compression. Mechanism of the transition is discussed in terms of the required strains.

Keywords. Shock compression; phase transformations; crystallography; stereographic projection; correspondence matrices; transformation strains.

1. Introduction

The various aspects of phase transformations of the group IV B element Zr and its alloy with d-rich transition elements have received considerable attention experimentally as well as theoretically. This element found to occur in α i.e. the hexagonal close packed structure at room temperature transforms to β (bcc) structure at high temperatures (see Sikka *et al* 1982 and the references therein). The first high pressure studies on this element by Bridgman (1948, 1952) and Jayaraman *et al* (1963) using resistivity measurements reported a transition in it around 6 GPa. This new phase was later identified (Jamieson 1963, 1964) to be the ω phase (three-atom hexagonal) using X-ray diffraction measurements. High pressure studies using diamond anvil cell to still higher pressures (Xia *et al* 1990) in conjunction with energy dispersive X-ray diffraction measurements carried out subsequent to the theoretical prediction of the $\omega \rightarrow \beta$ transition in Zr under compression by Gyanchandani *et al* (1990) using linear muffin tin orbital method (Skriver 1984), verified the existence of a high pressure bcc phase in elemental Zr at 30 GPa. The present phase diagram of Zr is given in figure 1. Figure 2 displays the schematic phase diagram of Zr (A) alloyed with d-rich metal B as a function of concentration of metal B under pressure (Sikka *et al* 1982). The diagram shows that in

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Figure 1. Phase diagram of Zr from Xia *et al* (1990).

Figure 2. Metastable P-X diagram from experimental data for the A-B alloy.

alloys unlike in pure Zr (or Ti), a region of coexistence of β with α and ω is also present.

Since a last few decades transmission electron microscopy (TEM) has been actively used for an understanding of the crystallography of the parent/daughter phase (like α/β , α/ω , β/ω) relationships. Here, using selected area electron diffraction (SAD) measurements from which one can determine the orientation relationships (OR) between the two phases and from the microscopy of the material from small, selected area, one can understand the morphology of the two phases and decide on the circumstances of the formation of the daughter phase from the parent phase.

As the $\alpha \rightarrow \omega$ transition is irreversible, ω -phase can be retained partially or fully at ambient conditions after unloading, TEM investigations have been extensively used in the past on group IVB elements subjected to the pressure cycle. Now, though the existence of the pressure-induced phase transition from the ambient α to ω structure in elemental Zr (and Ti) is well established under both static and shock pressures, the crystallographic nature of the transition is still a controversial issue. Many TEM investigations have been carried out in the past on these elements.

The first such study on pressure treated elemental Ti (Sargent and Conrad 1971) found the (0001) basal plane of ω phase to be parallel to the (11 $\bar{2}$ 0) plane of the

α phase. From the TEM study on statically compressed Zr and Ti, Usikov and Zilbershtein (1973) conjectured that the $\alpha \rightarrow \omega$ transformation proceeds via intermediate β structure (which is thermodynamically unstable at pressures and temperatures under considerations). They arrived at this conclusion on the basis that the ORs obtained by them on these samples could be described by the correspondence matrices obtained from the product of the matrices of correspondence ($\alpha_\omega = \alpha_\beta \cdot \beta_\omega$) for the well understood α to β (α_β) and β to ω (β_ω) transformations. Two crystallographically non-equivalent sets (for direct and reciprocal lattice) of matrices of correspondence between α and ω phases were derived, which are compatible with the following two variants

$$\begin{array}{ll} (0001)_\alpha \parallel (01\bar{1}1)_\omega & (0001)_\alpha \parallel (11\bar{2}0)_\omega \\ \text{(I)} & \text{(II)} \\ [11\bar{2}0]_\alpha \parallel [10\bar{1}1]_\omega & [11\bar{2}0]_\alpha \parallel [0001]_\omega. \end{array}$$

They found all the ORs between the α and ω phases in their SAD patterns to be described by the correspondence matrices associated with the variant I OR. Later TEM studies (Vohra *et al* 1980, 1981) on high pressure treated Ti–V alloys, a prototype omega forming alloy system, displayed the presence of β phase also along with the ω phase in the α -phase grains. This was claimed to be a direct evidence of the occurrence of β as an intermediate state during $\alpha \rightarrow \omega$ transformation. Both the variants (I and II) suggested by Usikov and Zilbershtein (1973) were also observed. Shortly afterwards, Rabinkin *et al* (1981) carried out electron diffraction measurements on pressure treated Zr samples. They observed that all their SAD patterns could be described by three crystallographic equivalents of variant II OR given by UZ. The results were explained in terms of a different diffusionless mechanism of transformation. Yet another study (Gupta *et al* 1985), employing neutron diffraction measurement on the bulk Zr samples transformed to ω phase, observed plane parallelism between the initial α and the transformed ω phase compatible with both the ORs of UZ. However, complete ORs could not be determined.

OR studies have also been carried out on shock treated Zr. The first one by Kutsar *et al* (1990) reported the α/ω OR in the shock treated Zr to be the same as the variant II OR of UZ. In recent investigations, Song and Gray (1994, 1995) observed a new OR between the α and ω phase in shock loaded Zr

$$\begin{array}{l} (0001)_\alpha \parallel (10\bar{1}1)_\omega \\ [1\bar{1}00]_\alpha \parallel [11\bar{2}\bar{3}]_\omega. \end{array}$$

This, according to them, does not agree with those previously reported in hydrostatic pressure experiments. Based on this they proposed a different transformation mechanism

Table 1. ORs obtained by different authors in pressure treated (static and dynamic) Zr, Ti and their alloys.

Material	OR	Reference
Ti & Zr (Static)	Variant I of UZ	Usikov and Zilbershtein (1973)
Ti–V (Static)	Variants I and II of UZ	Vohra <i>et al</i> (1981)
Zr (Static)	Variant II of UZ	Rabinkin <i>et al</i> (1981)
Zr (Shock)	Variant II of UZ	Kutsar <i>et al</i> (1990)
Zr (Shock)	New OR	Song and Gray (1994)
Zr (Shock)	Variant II of UZ	Dobromyslov and Taltus (1995)

in which the α phase transforms directly to ω phase without involving any intermediate β structure. This study, also raises a question whether the α - ω transition mechanism in Zr is same or different under static pressure loading and shock wave compression. More recent TEM study (Dobromyslov and Taltus 1995) on Zr shock compressed using spherical shock waves, again however, report the presence of only variant II OR of UZ in their samples. A summary of the observed ORs is given in table 1.

In the present study we have generated additional TEM data on shock compressed Zr and have reconciled the above conflicting results for the ORs between the α and ω phases. The possible mechanism of transformation is also examined.

2. Experimental

Experiments were carried out using the gas-gun (Gupta *et al* 1992) at our laboratory. A large sample was prepared in the form of a 1 mm thick circular disc of 12 mm diameter from a high purity iodide grade Zr crystal bar containing about 200 ppm oxygen. The sample was fitted into a matching hole in an SS304 circular disc of the same thickness. This disc, along with a steel (SS 304) cover plate, was emplaced in a threaded steel capsule that was fixed in the centre of a target ring. Velocity of the impactor plate attached to the nose of the projectile, just before the impact was measured to be 0.6 mm/ μ s. Using the measured projectile velocity in conjunction with the available Hugoniot data of steel and Zr as input, the pressure in the sample was computed using hydrodynamic codes. The simulations estimate a peak pressure of 11.8 GPa in Zr, attained in a few reverberations (between the front steel cover plate and the steel capsule) in a time period of 640 nsec. The simulated pressure profile is displayed in figure 3. Figure 4 gives the X-ray diffraction pattern of the sample after shock compression. The pattern shows substantial amount of ω phase coexisting with the parent α phase. From the recovered sample, many thin slices 400 μ m thick and 3 mm in

Figure 3. The simulated pressure profile in Zr.

Figure 4. X-ray diffraction pattern of Zr after shock compression.

diameter were made, polished and subjected to jet thinning in a 6% perchloric, 60% N-butanol and 34% methyl alcohol solution. The thin samples were examined using a JEOL 2000 FX electron microscope.

3. Results and discussion

The samples were first examined to verify the uniformity of microstructure. Tilting experiments were carried out in a given field of view to obtain symmetric diffraction patterns where OR can be established between the α and ω phases with an accuracy of about 1° to 2° . Kikuchi line pattern which gives definitely more accurate ORs could not be observed in areas exhibiting clear reflections of both α and ω phases in these shock loaded samples. Selected area used is $1\mu\text{m}$. From a number of areas scanned, a large number of diffraction patterns (~ 25) and corresponding micrographs were examined. Table 2 tabulates for a few representative patterns, the indices of planes and directions corresponding to the two phases that remain parallel in these patterns. It can be noted from this table that the OR of pattern # 3 is the same as the OR for variant I given by UZ while the OR of the pattern # 7 is identical to the one reported by SG. A few typical patterns along with their micrographs are shown in figures 5–7.

To further examine the crystallographic relationship between α and ω structures, the $(0001)_\alpha$ and $(01\bar{1}1)_\omega$ stereographic projections were superimposed maintaining a coincidence between the $[2\bar{1}\bar{1}0]_\alpha$ and $[\bar{1}011]_\omega$ directions. This corresponds to OR for variant I of UZ. This superposition of stereograms shows (figure 8) that the direction

Table 2. Description of various ORs obtained in our SAD patterns by different correspondence matrices.

#	OR	α_{ω}^*	α_{ω}	$\alpha_{\omega 2}^* \text{UZ}$	$\alpha_{\omega 2} \text{UZ}$	$\omega_{\alpha}^* \text{SG}$	$\alpha_{\omega} \text{SG}$	δ_c
#1	$(1\bar{1}02)_{\alpha} \parallel (\bar{2}201)_{\omega}$ $(\bar{5}143)_{\alpha} \parallel [11\bar{2}0]_{\omega}$	Y*	Y	Y	N*	N	Y	0.0
#2	$(0\bar{1}11)_{\alpha} \parallel (\bar{1}2\bar{1}0)_{\omega}$ $[\bar{5}413]_{\alpha} \parallel [\bar{1}01\bar{1}]_{\omega}$	Y	Y	Y	N	N	N	2.16
#3	$(0001)_{\alpha} \parallel (01\bar{1}1)_{\omega}$ $[2\bar{1}\bar{1}0]_{\alpha} \parallel [\bar{1}011]_{\omega}$	Y	Y	N	N	Y	N	0.0
#4	$(01\bar{1}1)_{\alpha} \parallel (\bar{1}101)_{\omega}$ $[7\bar{5}23]_{\alpha} \parallel [\bar{2}113]_{\omega}$	Y	Y	Y	N	N	N	0.0
#5	$(1\bar{2}11)_{\alpha} \parallel (\bar{1}100)_{\omega}$ $(\bar{1}102)_{\alpha} \parallel (20\bar{2}1)_{\omega}$ $[\bar{8}173]_{\alpha} \parallel [\bar{1}\bar{1}26]_{\omega}$	Y Y	 Y	 Y	 N	 N	 N	2.13 2.54
#6	$(0002)_{\alpha} \parallel (01\bar{1}1)_{\omega}$ $[\bar{1}100]_{\alpha} \parallel [2\bar{1}\bar{1}0]_{\omega}$	Y	Y	N	N	Y	N	0.0
#7	$(0002)_{\alpha} \parallel (01\bar{1}1)_{\omega}$ $[\bar{1}010]_{\alpha} \parallel [11\bar{2}3]_{\omega}$	Y	Y	N	N	Y	Y	0.0

*Y or N in columns 3–8 indicates whether or not the OR is satisfied by the respective plane and zone correspondence matrices of the present authors, of UZ and of SG.

$[\bar{1}010]_{\alpha}$ is coincident with the direction $[11\bar{2}3]_{\omega}$, which corresponds to the OR of our pattern number # 7 and reported by SG. This means that the OR for variant I of UZ is equivalent to that reported by SG. Moreover, the plot of great circles representing directions for all of the ORs listed in table 2 also shows that the directions in the α -phase match with corresponding directions in the ω -phase. From this it can be concluded that all these ORs are equivalent to the OR of variant I of UZ. Further, two more direction equivalences given by SG, $[1\bar{5}40]_{\alpha} \parallel [\bar{2}113]_{\omega}$ and $[4\bar{2}23]_{\alpha} \parallel [\bar{1}2\bar{1}6]_{\omega}$ are also satisfied as indicated by the overlap of the corresponding great circles. These observations indicate that the OR operative in the α to ω transition under static and dynamic loading is the same. This suggests that the mechanism of transformation under the two loading conditions is also the same.

The ORs so determined were used to compute the ω to α correspondence matrices, α_{ω} and α_{ω}^* for the direct and reciprocal lattice transformation respectively. These matrices are found to be almost identical to the correspondence matrices of variant I ($\alpha_{\omega 1}$ and $\alpha_{\omega 1}^*$) of UZ but are different from the ones given by SG. The matrices are,

$$\begin{aligned}
 \alpha_{\omega}^* &= \begin{pmatrix} -0.70 & -0.35 & 0.35 \\ 0.38 & -0.29 & 0.29 \\ -0.70 & -0.35 & 0.35 \\ -0.75 & -0.76 & 0.60 \end{pmatrix} \\
 \alpha_{\omega} &= \begin{pmatrix} 1.05 & -1.56 & 0.55 \\ 0.00 & 0.51 & 0.51 \end{pmatrix}
 \end{aligned}$$

Moreover, these correspondence matrices are compatible with the ORs reported by SG also. It may be noted that the matrices of SG were found to satisfy only one OR

(table 2). Table 2 also gives the computed angle δ_c , between the α plane (as indexed in the SAD pattern) and the α plane that is obtained by the operation of correspondence matrix (the indices of which usually come in fraction) on the ω plane of the corresponding OR.

Figure 5. (a) A bright field micrograph and (b) the corresponding SAD pattern indexed as in (c). The zone axis is $[2\bar{1}10]_z \parallel [\bar{1}011]_{\omega}$.

Figure 6. (a) and (b) are the dark field micrographs of SAD pattern, (c) indexed as in (d). The zone axis is $[1010]_{\alpha} \parallel [11\bar{2}3]_{\omega}$.

In order to further understand the α to ω transformation, at the outset it is useful to visualize the transformation to be taking place in two steps, $\alpha \rightarrow \beta$ and $\beta \rightarrow \omega$ for which the strains are already well known (Burgers 1934). For instance, the atomic configurations of the (110) plane of β lattice (figure 9b) are produced from the (0001) plane of

Figure 7. (a) and (b) are the bright and dark field pair of micrographs of SAD pattern, (c) indexed as in (d). The zone axis is $[7523]_{\alpha} \parallel [2113]_{\omega}$.

α lattice (figure 9a) by application of two strains, a homogeneous strain ϵ_1 and a shuffle strain ϵ_2 . The homogeneous strain causes 3.6% contraction along the $[1\ 1\ 2\ 0]$ direction, 6.2% expansion along $[1\ \bar{1}\ 0\ 0]$ direction, 1.2% reduction between $(000\ 1)$ planes and provides shear to decrease the hexagonal 120° angle to 109.47° degree (atom

Figure 8. $\{0001\}_\alpha$ and $\{01\bar{1}1\}_\omega$ stereographic projections showing the great circles corresponding to the ORs listed in table 2. The α and ω stereograms are superimposed along the great circles $[2\bar{1}10]$ and $[\bar{1}011]$ respectively.

positions a–f of α change to the corresponding ones of β). The shuffle strain provides shift of atoms in the central plane (i.e. the atoms g–k) along $[10\bar{1}0]$ by one sixth of the length of the longer diagonal of the basal plane formed after the application of strain ε_1 . The $\beta \rightarrow \omega$ transition then can be considered to be arising from the shuffle ε_3 effected by softening of the longitudinal $2/3(111)_\beta$ phonon mode. In terms of atomic movements, the ω lattice is obtained as a result of only a collapsing of a pair of consecutive (111) planes in the bcc lattice to the intermediate position leaving the next plane unchanged (figure 9d). The atomic movements required are $\pm a_\beta\sqrt{3}/12$ where a_β is the bcc cell constant. The resulting atomic positions are those shown in $(01\bar{1}1)$ plane of the ω lattice (figure 9c).

Now as can be seen from the SAD patterns given above the ω -reflections are sharp and intense (figures 5–7). Moreover, the micrographs corresponding to these patterns show the formation of the ω -phase from the α -phase in the form of long plates. This lamellar structure was observed throughout the specimens. This means that the ω is forming directly from α . For, if the $\alpha \rightarrow \omega$ transformation proceeds via β phase, four variants are expected which appear as tiny particles of ω in the parent matrix

Figure 9. Projections of (a) α structure on (0001) plane, (b) β on (110) plane, (c) ω on (011) plane (in these figures, shaded circles denote the atoms in the respective reference planes whereas open circles are the atoms in between two such planes whose height (in Å units) from the reference plane is given in the corresponding brackets) and (d) planes in a bcc lattice and their collapse to generate hexagonal omega.

(see Vohra *et al* 1981). But none of the micrographs show such a feature. The SAD patterns also do not support the existence of these variants. Here also, only a single ω variant is observed contrary to the expected four variants.

When Usikov and Zilbershtein (1973) proposed that an intermediate β structure is formed, it implies that the two strains ε_1 and ε_2 act first. The strain ε_3 acts later, thus following the $\alpha \rightarrow \beta \rightarrow \omega$ transformation path. However, it appears from the above results that the three strains may not necessarily act in this sequence. All the strains may be coupled and act simultaneously without forming the ideal intermediate bcc structure and thus giving direct ω formation from the parent α phase.

It is interesting to note that all the SAD patterns that were obtained by UZ and all of our patterns are described by the variant I OR of UZ. None of the SAD patterns satisfied the variant II class OR. Actually it can be readily noted from table 1 that in all the studies to date either variant I or variant II only is observed in pure Zr. Now, as we find above, though the formation of ω from α takes place directly, conceptually the path

of formation could be seen as $\alpha \rightarrow \beta \rightarrow \omega$ (as explained above) as the atomic movements required to form ω from α do not appear to be much different than those required for a $\alpha \rightarrow \beta \rightarrow \omega$. Therefore, perhaps depending on the sample history (see also Gupta and Chidambaram (1994) for an example of the intermediate structures obtained under different conditions), one non-equivalent of this particular path i.e. either variant I or variant II propagates and the direct ω phase formation takes place. Moreover, even otherwise, the two variants are shown to be twin related to each other (Al'shevskiy *et al* 1984). It may be noted however, that the study of Vohra *et al* (1980) gives the evidence of the presence of the intermediate β phase as they have observed not only the patterns belonging to each class of ORs, I and II but also all the four variants of ω . However, their study was on Ti–V alloy in which β -phase (stable or metastable) was observed along with the ω -phase in the parent matrix.

To summarize, the correspondence matrices obtained from the ORs observed in our SAD patterns are the same as the correspondence matrices for OR I given by UZ. Further, since we find all our SAD patterns, including the one which is exactly the same as that reported by SG, to be explained by these matrices, and also that the superposition of the stereographic projections of the α and the ω phases show the equivalence of the ORs corresponding to the two different models proposed i.e. of UZ and of SG, it is clear that the mechanism of phase transition under shock loading and static compression is the same and the OR reported by Song and Gray (1994, 1995) is equivalent and is a subset of the variant I OR of UZ. Moreover, we feel that as the ORs obtained from SAD measurements provide the crystallographic relations between the initial and final structures only (i.e. the end states) of a transformation, these cannot be utilized to establish unambiguously the mechanism of transition in terms of the atomic movements during the transition. The symmetry of the diffraction spots in the SAD patterns and nature of the micrographs of the sample, however, suggest that ω is forming directly from α in a plate like structure, very close to the path of $\alpha \rightarrow \beta \rightarrow \omega$.

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References

- Al'shevskiy Yu L, Kulnitskiy B A, Konyayev Yu S and Usikov M P 1984 *Phys. Met. Metall.* **58** 795
- Bridgman P W 1948 *Proc. Am. Acad. Arts Sci.* **76** 55, 71
- Bridgman P W 1952 *Proc. Am. Acad. Arts Sci.* **81** 165
- Burgers W G 1934 *Physica (Utrecht)* **1** 561
- Dobromyslov A V and Taltus N I 1995 *Fizika Metallov i Metallovedenie* **79** 3
- Gupta Satish C, Agarwal R G, Gyanchandani J S, Suresh N, Roy S, Sikka S K, Kakodkar A K and Chidambaram R 1992 *Shock compression in condensed matter-1991* (eds) S C Schmidt, K D Dick, J W Fowles and D G Tasker (Amsterdam: Elsevier) p. 834
- Gupta S C and Chidambaram R 1994 *High Pressure Res.* **12** 51
- Gupta S C, Sikka S K and Chidambaram R 1985 *Scr. Metall.* **19** 1167
- Gyanchandani Jyoti S, Gupta Satish C, Sikka S K and Chidambaram R 1990 *J. Phys: Condens. Matter* **2** 301
- Jamieson J C 1963 *Science* **72** 140

- Jamieson J C 1964 *Metallurgy at high pressures and temperatures* (eds) K A Gschneidner Jr, M T Hepworth and N A D Paslee (New York: Gordon and Breach) p. 201
- Jayaraman A, Klement Jr W and Kennedy G C 1963 *Phys. Rev.* **131** 644
- Kutsar A R, Lyasotski I V, Podurets A M and Sanches-Bolinches A F 1990 *High Pressure Res.* **4** 475
- Rabinkin A, Talianker M and Botstein O K 1981 *Acta Metall.* **29** 691
- Sargent G A and Conrad H 1971 *Mater. Sci. Engg.* **7** 220
- Sikka S K, Vohra Y K and Chidambaram R 1982 *Prog. Mater. Sci.* **27** 245
- Skriver H L 1984 *LMT0 Method* (Berlin: Springer)
- Song S and Gray III G T 1994 *High pressure science and technology-1993* (eds) S C Schmidt, J W Fowles, G S Samara and M Ross (New York: AIP Press) p. 251
- Song S and Gray III G T 1995 *Philos. Mag.* **A71** 275
- Usikov M P and Zilbershtein V A 1973 *Phys. Status Solidi* **a19** 53
- Vohra Y K, Sikka S K, Menon E S K and Krishnan R 1980 *Acta Metall.* **8** 683
- Vohra Y K, Menon E S K, Sikka S K and Krishnan R 1981 *Acta Metall.* **29** 457
- Xia H, Duclos S J, Ruoff A L and Vohra Y K 1990 *Phys. Rev. Lett.* **64** 204