

# DECOMPOSITION OF THE $\beta$ SOLID SOLUTION IN Nb, Mo, Al, AND V ALLOYED Zr

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X-Ray diffraction analysis of mono- and polycrystals and electron microscopy are employed for investigating the structural mechanism and kinetics of precipitation of  $\omega$  and  $\alpha$  phases and  $ZrMo_2$ ,  $Zr_3Al$ , and  $ZrV_2$  intermetallic compounds from a  $\beta$  solid solution. It is found that an ordered  $\omega_2$  phase is precipitated from an ordered body centered cubic of the  $\beta$  solid solution in the Zr-Mo-Al alloy.

Zirconium is of great interest in nuclear engineering due to its small thermal-neutron capture cross section. To obtain materials with high strength, plasticity and anticorrosion resistance, zirconium is alloyed with niobium, aluminum, molybdenum and other elements [1].

The present paper describes a study of phase transformations in zirconium alloyed with niobium, aluminum, molybdenum, and vanadium, in which phases with different formation mechanisms precipitate from the body centered cubic (BCC)  $\beta$  solid solution.

The alloys were prepared in an arc furnace in a purified-argon atmosphere. To obtain cross sectional uniformity of composition, each alloy was remelted six times. The starting materials were metals of the following purity: zirconium - 99.8%, aluminum - 99.99%, niobium - 99.85, molybdenum - 99.7, and vanadium - 98.9%. The composition of the alloys under study is listed in Table 1.

Table 1

Alloy	Constituents content in atomic %				
	Zr	Nb	Mo	Al	V
Zr-Mo-Al	75.5	—	10.5	14.0	—
Zr-Nb-Mo-V	77.0	10.5	5.5	—	7.0

The studies were performed by X-ray diffraction by poly- and monocrystals, by electron diffraction and by electron microscopy. Monocrystals for X-ray analysis and foils for electron microscopy were produced by electrical polishing.

Structural transformation in the BCC  $\beta$  solid solution were investigated in the course of isothermal tempering at 350-850°C. The single-phase  $\beta$  solid solution was obtained by heating the alloys for 1 hr

at 1100°C and oil quenching. Heating and quenching, as well as tempering were performed under a vacuum of  $2 \cdot 10^{-5}$  mm Hg.

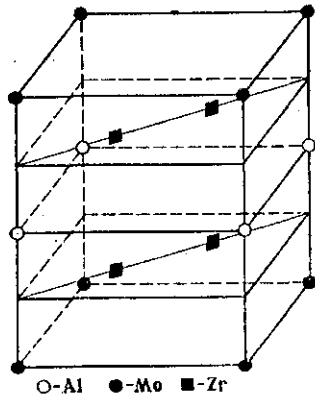


Fig. 1. Elementary cell of the  $\omega_2$  phase.

In the present study the precipitation of  $\omega$  and  $\alpha$  phases at low tempering temperatures was determined by X-ray diffraction analysis of monocrystals. After each tempering these were oriented by their  $\langle 110 \rangle$  or  $\langle 100 \rangle$  directions parallel to the X-ray beam. The experimental X-ray patterns were compared with schematic of X-ray patterns in which the locations of the  $\omega$  and  $\alpha$  reflections were calculated for both orientations of the  $\beta$  crystals [2]. The X-ray patterns were taken with mixed  $K_{\alpha}$  Mo radiation.

Investigation of Structural Transformations in the Zr-Mo-Al Alloy. After the alloy was quenched from  $1100^{\circ}\text{C}$ , the Debye crystallograms and X-ray diffraction patterns of a stationary monocrystal

exhibit reflections of only disordered BCC  $\beta$  solid solution. After 15 hr tempering at  $350^{\circ}\text{C}$  the Debye crystallogram contains weak superstructure lines, which point to ordering of atoms in CsCl - the  $\beta$  matrix. The micro-electron diffraction patterns of  $(110)_{\beta}$  and  $(131)_{\beta}$  show, in addition to reflections of the  $\beta$  solid solution, also reflections of the hexagonal  $\omega$  phase. The appearance of superstructure reflections points to ordering of atoms in the phase. The superstructure reflections were retained even when the foil was inclined by  $2-6^{\circ}$ , which means that these reflections do not arise due to double diffraction. The superstructure reflections of the  $\omega$  phase are also present on the X-ray diffraction patterns of nonmoving monocrystals. It was found by analysis the micro-electron and X-ray diffraction patterns that the elementary cells of the ordered  $\omega$  phase ( $\omega_2$ ) contains six atoms, instead of the three in the disordered  $\omega$  phase, and its constants are:  $a = 4.98 \text{ \AA}$  and  $c = 5.96 \text{ \AA}$ . Figure 1 depicts an elementary cell of the  $\omega_2$  phase. Figure 2 shows a micro-electron diffraction pattern of  $(110)_{\beta}$  with reflections of the  $\beta$  solid solution and of the  $\omega_2$  phase.

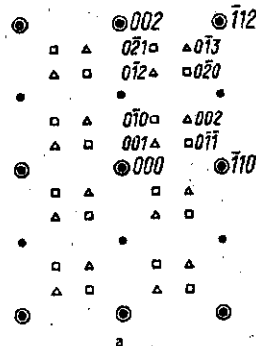


Fig. 2. Schematic of micro-electron diffraction pattern of the  $(110)_{\beta}$  plane (a); experimental micro-electron diffraction pattern of the Zr-Mo-Al alloy after 15 hr of tempering at  $350^{\circ}\text{C}$  (b).

The  $\omega$  phase forms by slip of atoms in the  $\beta$  lattice in  $\langle 111 \rangle$  directions [3]. This phase forms over the temperature range over which the elastic constant  $C'$ , equal to  $(C_{11} - C_{12})/2$  decreases. The presence of the ordered  $\omega_2$  phase in metals is detected in this study for the first time.

The intensity of reflections of the  $\omega_2$  phase on the X-ray diffraction pattern of the monocrystal increases when the tempering time at  $350^\circ\text{C}$  is raised to 30 and 45 hr. Tempering for 5 and 15 hr at  $450^\circ\text{C}$  results in precipitation of the  $\omega_2$  and  $\alpha$  phases (Table 2). The absence of reflections of intermetallic compounds after 15 hr tempering at  $450^\circ\text{C}$  points to the low rate of their formation, for which reason the subsequent study of structural transformations in the Zr-Mo-Al alloy was performed at tempering temperatures of  $750^\circ\text{C}$ .

As is seen from Table 2, after 4 hr tempering at  $750^\circ\text{C}$ , the  $\alpha$  phase and  $\text{ZrMo}_2$  precipitate from the  $\beta$  matrix, after 25 hr and 50 hr  $\text{Zr}_3\text{Al}$  is also precipitated in addition to the two former. The microdiffraction pattern of the electrons shows that the  $\alpha$  phase in foils is twinned along the  $(10\bar{1}2)$  plane and the  $[10\bar{1}1]$  direction. The twinning of the  $\alpha$  phase in zirconium alloys occurs, as shown by the first of the present authors with her coworkers [4], upon electrolytic thinning out of foils (Fig. 3).

The higher kinetics of  $\alpha$  phase precipitation in this alloy as compared with the  $\text{ZrMo}_2$  and  $\text{Zr}_3\text{Al}$  intermetallic compounds is a result of the fact that the nuclei of the  $\alpha$  phase, as of the  $\omega$  phase are formed by the slip mechanism [5]. The formation of nuclei of the  $\text{ZrMo}_2$  and  $\text{Zr}_3\text{Al}$  compounds and their growth involves the diffusion mechanism.

Studies at tempering temperature of  $850^\circ\text{C}$  shows that at this temperature phase transformations occur at a very high rate, after 5 hr the  $\alpha$ ,  $\text{ZrMo}_2$  and  $\text{Zr}_3\text{Al}$  phases precipitate from the  $\beta$  matrix. Increasing the tempering time at  $850^\circ\text{C}$  to 15 hr results in the vanishing of lines of the  $\beta$  solid solution on the Debye crystallogram.

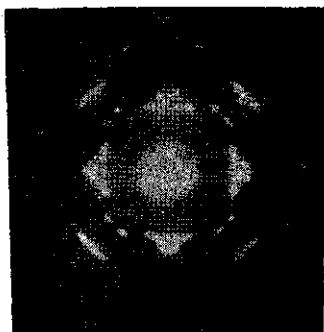


Fig. 3. Microelectron-diffraction pattern  $(001)_\beta$  with reflections of the  $\alpha_2$  phase.

Investigation of the Re-Resolution of  $\text{Zr}_2\text{Al}$  at  $550^\circ\text{C}$ . Upon cooling of the Zr-Mo-Al solution and the attendant solidification, the  $\text{Zr}_2\text{Al}$  compound precipitates from the  $\beta$  matrix; the formation of this compound is detrimental to the properties of Zr-Al alloys. The presence of  $\text{Zr}_2\text{Al}$  in the alloy is undesirable for optimal utilization of Zr-Al alloys in nuclear power reactions. It is hence of great interest to investigate the re-resolution of the  $\text{Zr}_2\text{Al}$  in the  $\beta$  matrix, which was performed after heating the alloy at  $550^\circ\text{C}$ .

After solidification of the alloy, the X-ray diffraction pattern of the monocrystal contains reflections of the BCC  $\beta$  solid solution and of  $\text{Zr}_2\text{Al}$ . After 4, 9, 35 and 75 hr of heating at  $550^\circ\text{C}$  the X-ray diffraction pattern of the monocrystal contains reflection of  $\beta$ ,  $\alpha$  and  $\text{Zr}_2\text{Al}$ .

Table 2  
Phase Composition of an Alloy of Zirconium with 10.5% Mo and 14% Al  
According to X-ray Diffraction Analysis of Monocrystals (XM),  
Polycrystals (XP) and Electron Microdiffraction (EM)

		Tempering time of alloy quenched from 1100°C									
Tempering temperature, °C		0	4 hr	5 hr	10 hr	15 hr	25 hr	30 hr	45 hr	50 hr	
350	$\beta$					$\beta + \omega 2$		$\beta + \omega 2$	$\beta + \omega 2$		XM
	$\beta$					$\beta + \omega 2$		$\beta + \omega 2$	$\beta + \omega 2$		EM
450				$\beta + \omega 2 + \alpha$		$\beta + \omega 2 + \alpha$					XM
				$\beta + \omega 2$		$\beta + \omega 2 + \alpha$					EM
750	$\beta$		$\beta + \alpha + ZrMo_2$				$\beta + \alpha + ZrMo_2 + Zr_3Al$			$\alpha + ZrMo_2 + Zr_3Al$	XP
					$\beta + \alpha 2$		$\beta + \alpha 2$			$\alpha 2 + ZrMo_2 + Zr_3Al$	EM
850				$\beta + \alpha + ZrMo_2 + Zr_3Al$		$\alpha + ZrMo_2 + Zr_3Al$					XP
				$\beta + \alpha + \alpha 2$		$\alpha 2 + ZrMo_2$					EM
		Heating time of alloy after solidification									
Heating temperature, °C		0	4 hr	9 hr	35 hr	75 hr	105 hr	150 hr	175 hr	210 hr	
550	$\beta + Zr_3Al$		$\beta + \alpha + Zr_2Al$	$\beta + \alpha + Zr_2Al$	$\beta + \alpha + Zr_2Al$	$\beta + \alpha + Zr_2Al$	$\beta + \alpha + Zr_2Al + Zr_3Al$	$\beta + \alpha + Zr_2Al + Zr_3Al$	$\beta + \alpha + Zr_2Al + Zr_3Al$	$\beta + \alpha + Zr_2Al + Zr_3Al$	XM
	$\beta + Zr_3Al$		$\beta + Zr_3$		$\beta + Zr_2Al + FCC$		$\beta + Zr_2Al + FCC$	$\beta + Zr_2Al + FCC$			EM

(see Table 2). When the heating time is increased to 105, 150 and 210 hr, Debye rings of  $Zr_3Al$  additionally appear on the X-ray diffraction pattern of the monocrystals (Fig. 4). Reflections of  $Zr_2Al$  do not vanish even after 210 hr of heating. Hence, in order to dissolve the  $Zr_2Al$  the Zr-Al alloys should be quenched from 1000-1100°C and then tempered at 750°C in order for  $Zr_3Al$  to precipitate from the  $\beta$  solid solution.

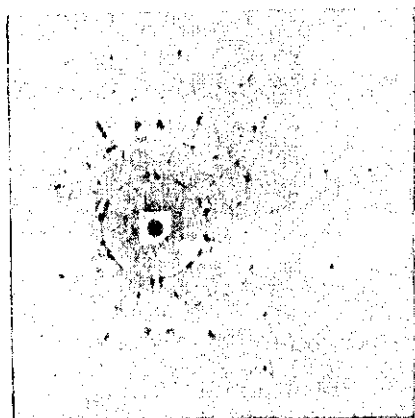


Fig. 4. X-Ray diffraction pattern of a monocrystal of Zr-Mo-Al after 210 hr heating at 550°C. The orientation is along an X-ray parallel to  $(011)_\beta$ .

**Investigation of the Structural States in the Zr-Nb-Mo-V Alloys.** After solidification, and also after quenching the alloy from 1100°C the X-ray and the micro-electron diffraction patterns of the monocrystal contain only reflections of the  $\beta$  solid solution and diffusion arcs, which point to the appearance of linear defects in the  $\beta$  matrix. However, these linear defects are not correlated along the  $\langle 111 \rangle$  directions, and hence the metastable  $\alpha$  phase does not form in this alloy by the slip mechanism. The structure of the alloy does not change after 1, 4, 5 and 8 hours of tempering at 350°C. After 15 and 25 hr of tempering  $\alpha$  phase crystals are precipitated from the  $\beta$  matrix (Table 3).

Tempering of the alloy for 65 hr at 450°C resulted in the precipitation of only the  $\alpha$  phase from the  $\beta$  matrix, hence specimens of the Zr-Nb-Mo-V alloy tempered under the above conditions, were subsequently retempered at 550°C. The X-ray diffraction pattern of the monocrystal after 60 hr of tempering shows smeared out maxima of the second precipitating phase. When the tempering time was increased to 120, 160 and 210 hr the maxima remained smeared out, which made it possible to calculate the cross sectional dimensions of the precipitating crystals. These were found to change during tempering of 60 to 210 from 22 to 36 Å (Table 4). It was determined from the inter-plane distances that the diffusion maxima pertain to the  $ZrMo_2$ .

This means that the  $ZrMo_2$  compound precipitates very slowly also at 550°C, and hence the subsequent study of the breakup of the matrix was performed at 750°C. After the alloy was tempered for 20 min, the X-ray diffraction pattern of the monocrystal contains, in addition to intensive reflections of the  $\beta$  matrix and  $\alpha$  phase weak smeared out reflections of  $ZrMo_2$ . After the tempering time was raised to 45 min and to 1 hr 30 min, the reflections of  $ZrMo_2$  on the X-ray diffraction pattern of the monocrystal remain smeared out. The dimensions of the  $ZrMo_2$  crystal for tempering times from 20 min to 1 hr 30 min increase from 30 to 90 Å (Table 4).

After 7 and 15 hr of tempering at 750°C the reflections of  $ZrMo_2$  on the X-ray diffraction pattern of the monocrystal become clearer. Electron diffraction data confirm the results of the X-ray examination. This means that after 15 hr of tempering at 750°C the Zr-Nb-Mo-V alloy is in the  $\beta + \alpha + ZrMo_2$  three-phase

Table 3  
Phase Composition of an Alloy of Zirconium with 10.5% Nb, 5.5% Mo and 7% V  
According to X-ray Diffraction Analysis of Monocrystals (XM),  
Polycrystals (XP) and Electron Microdiffraction (EM)

Tempering temperature, °C	Tempering time of alloy quenched from 1100°C													
	0	20 min	45 min	1 hr	90 min	3 hr	4 hr	5 hr	6 hr	7 hr	8 hr	15 hr	25 hr	65 hr
350	$\beta + \text{d.a.}$			$\beta + \text{d.a.}$				$\beta + \text{d.a.}$				$\beta + \alpha$	$\beta + \alpha$	XM
	$\beta + \text{d.a.}$						$\beta + \text{d.a.}$				$\beta + \text{d.a.}$			EM
450						$\beta + \alpha$			$\beta + \alpha$					XM
						$\beta + \alpha$			$\beta + \alpha$					EM
750		$\beta + \alpha + \text{s.m.}$	$\beta + \alpha + \text{s.m.}$		$\beta + \alpha + \text{s.m.}$	$\beta + \alpha + \text{ZrMo}_2$				$\beta + \alpha + \text{ZrMo}_2$		$\beta + \alpha + \text{ZrMo}_2$		XM
				$\beta + \alpha$						$\beta + \alpha + \text{ZrMo}_2$				EM
													$\beta + \alpha + \text{ZrMo}_2 + \text{ZrV}_2$	XP

Phase Composition of Alloy After Tempering at 550°C  
of Specimens First Tempered for 65 hr at 450°C

550		30 hr	60 hr	120 hr	160 hr	210 hr	
	$\beta + \alpha$	$\beta + \alpha + \text{s.m.}$	$\beta + \alpha + \text{s.m.}$	$\beta + \alpha + \text{s.m.}$	$\beta + \alpha + \text{s.m.}$	$\beta + \alpha + \text{s.m.}$	XP
		$\beta + \alpha$			$\beta + \alpha 2$		EM

d.a. = diffraction arcs, s.m. = smeared out maxima.

Table 4

Tempering temperature, °C	Tempering time; min, hr	Gross sectional dimensions of ZrMo <sub>2</sub> crystals, (Å)
550	60 hr	22
	120 hr	27
	160 hr	27
	210 hr	36
750	20 min	28
	45 min	37
	3 hr	92

state. A further increase in the tempering time at 750°C to 25 hr results in the appearance, on the Debye crystallogram, the lines of ZrV<sub>2</sub>, in addition to the three aforementioned phases (see Table 3).

**Conclusions.** Our investigation shows that nuclei of the metastable ω<sub>2</sub> and equilibrium α phase form by the slip mechanism, and hence the kinetics of precipitation of these phases is very high even at low tempering temperature.

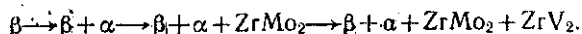
Crystals of ZrMo<sub>2</sub>, Al<sub>3</sub>Zr and ZrV<sub>2</sub> are formed by the diffraction mechanism.

Hence the ZrMo<sub>2</sub> compound in the Zr-Nb-Mo-V alloy has, even after tempering for 210 hr at 550°C, dimensions of only tens of angstroms.

According to results of X-ray testing of Zr-Mo-Al and Zr-Nb-Mo-V, the rate of precipitation of ZrMo<sub>2</sub> is higher than of Al<sub>3</sub>Zr and ZrV<sub>2</sub> compounds. Since the mechanism of formation and the structure of all the three compounds are the same (BCC), the difference in the rate of their precipitation is determined, most probably, by the difference in the diffusion coefficients of molybdenum, aluminum and vanadium in β zirconium. This assumption is confirmed by the data listed in [6]. The coefficient of diffusion of molybdenum in α zirconium is  $6.22 \cdot 10^{-8}$  cm<sup>2</sup>/sec, whereas for vanadium  $D = 1.22 \cdot 10^{-8}$  cm<sup>2</sup>/sec. Although these data pertain to a diffusion in α zirconium, there is sufficient basis for assumption that the coefficient of diffusion of Mo also in β zirconium is also higher than for vanadium.

This investigation of the Zr-Mo-Al has for the first time established the precipitation of the order ω<sub>2</sub> phase with ratio of axes  $c/a = 1.24$  from the ordered β solid solution.

The structural mechanism of transformations in the Zr-Nb-Mo-V alloy is:



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