



Investigation on the martensitic transformation and the associated intermediate phase in U–2 wt%Zr alloy

Chandrabhanu Basak^{a,*}, R. Keswani^a, G.J. Prasad^a, H.S. Kamath^a, N. Prabhu^b, S. Banerjee^{c,1}

^a Metallic Fuels Division, Bhabha Atomic Research Center, Trombay, Mumbai 400 085, India

^b Dept. of Met. Engg. and Mat. Sci., Indian Institute of Technology, Bombay, Powai, Mumbai 400 076, India

^c Bhabha Atomic Research Center, Trombay, Mumbai 400 085, India

ARTICLE INFO

Article history:

Received 18 June 2008

Accepted 29 May 2009

ABSTRACT

In most of the binary uranium alloy systems, different metastable phases can be retained at room temperature depending on the rate of cooling of the gamma phase. On the other hand, in U-rich U–Zr system, the gamma phase transforms into either martensitic α or Widmanstätten α depending on the cooling rate. It has not been ascertained so far if any intermediate phase is involved prior to the martensitic transformation in U-rich U–Zr system and, therefore, nature of the intermediate phase remains undetermined. Present investigation shows the existence of an intermediate phase prior to the final martensitic transformation. Although the equilibrium beta phase is known to undergo martensitic transformation, quenching from the γ phase appears to suppress the β phase formation. In fact the present experimental evidence suggests that the most likely intermediate phase is the monoclinic distortion of alpha phase (α''), and not the beta, when gamma phase of U–2 wt%Zr alloy is quenched rapidly.

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1. Introduction

Phase transformations during quenching of U-rich binary alloy systems follow a general sequence from $\gamma \rightarrow \gamma_s \rightarrow \gamma^0 \rightarrow \alpha'' \rightarrow \alpha' \rightarrow \beta \rightarrow \alpha$; where, γ , β and α are the equilibrium phases as seen in the U-rich U–Zr phase diagram (Fig. 1) and the rest are metastable phases. α' is a distorted α that forms martensitically and involves primarily a contraction of the b parameter, α'' is a monoclinic distortion of martensitic α' , γ_0 is a tetragonally distorted γ and γ_s is an even less severe deviation from the bcc γ phase [1]. The said sequence of phases is not always observed in every alloy system. Apparently, formation and room temperature retention of these intermediate phases largely depend on the alloy content, gammaizing temperature and cooling rate. Crystallography of the martensite and formation of the intermediate phases during martensitic transformation of uranium-rich alloy systems containing Ti, Nb, Mo and Re are reported in the literature [2–5]. However, the little information available in the open literature, regarding the phase transformation behaviour of U–Zr system under rapid cooling condition, indicate that the metastable α' martensite is obtained with rapid cooling rate whereas slower cooling rate yields supersaturated α in the alloys with <25 wt%Zr [6,7]. On the other hand alloys having more than 25 wt%Zr retains the metastable γ phase at room temperature under rapid cooling condition [7].

The present work attempts to investigate the transformation behaviour of the γ and β phases under rapid cooling conditions. The existence and identification of any intermediate phase, prior to the martensitic transformation of γ phase, is also explored.

2. Materials, processes and equipment

Vacuum induction melted uranium ingots and consumable arc melted zirconium bar were used for the alloy preparation. U–2 wt%Zr alloy was prepared by vacuum induction melting in an alumina wash-coated graphite crucible and subsequently casting into a transparent quartz mould of 12.5 mm diameter by vacuum injection technique. Chemical analysis was done using Inductively Coupled Plasma Atomic Emission Spectroscopy (ICP-AES) for determining the Zr content and the other impurities, whereas standard CNO analysis was carried out for quantifying carbon, nitrogen and oxygen impurities. Amount of total impurities, including C, N and O, was found to be of the order of 1600 ppm.

The slugs were cut into 50 mm length and copper jacketed for hot rolling at 850 °C in the γ phase region where there is complete solid solubility between uranium and zirconium. Total thickness reduction of ~50% was achieved by three passes with intermediate soaking at 850 °C for 10 min.

For the quenching dilatometric study a tube of 10 mm length and 4 mm OD with a wall thickness of 0.4 mm was machined out from the as-cast slug and subsequently homogenized at 900 °C for 200 h. The quenching dilatometer (model: DIL 805A/D, make:

* Corresponding author. Tel.: +91 22 2559 0672.

E-mail address: cbbasak@barc.gov.in (C.B. Basak).

¹ Director.

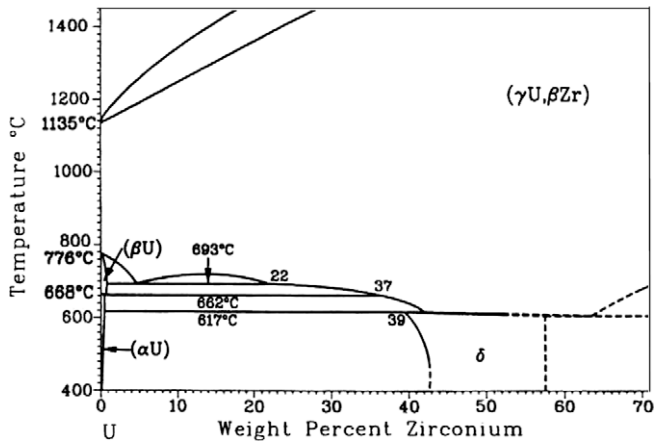


Fig. 1. U-rich portion of the U-Zr phase diagram.

Bahr Thermoanalyse GmbH, Germany) contains a water-cooled copper coil connected to a high frequency induction power supply (Fig. 2(a)). Helium was used as quenching gas because of its high thermal conductivity. Change in length was measured along the sample length (~10 mm) with the help of a linear variable differential transformer (LVDT) having least count of 0.05 μm . Temperature was sensed by an S-type thermocouple spot welded onto the sample surface as shown in Fig. 2(b). Accuracy of temperature measurement is 0.5 $^{\circ}\text{C}$.

Standard metallographic procedure was followed for the present study. Electroetching was carried out using 50% H_3PO_4 aqueous solution as electrolyte and SS304 as cathode with a constant potential of 2 V DC.

3. Experiments and results

3.1. Directly quenched samples

Samples of the rolled alloy were soaked for 120 h at 900 $^{\circ}\text{C}$ and then directly quenched into water. Fig. 3(a) and (b) show typical microstructures of the water quenched sample (from 900 $^{\circ}\text{C}$) exhibiting acicular martensitic morphology along with small amount of non-martensitic phase; prior γ grain boundary is also clearly visible. After metallography, a part of the quenched sample was analyzed in a differential scanning calorimeter (DSC) with a heating rate of 1 $^{\circ}\text{C}/\text{min}$ and the DSC result is presented in Fig. 4. Three transition temperatures are observed in the DSC curve; i.e. 589, 674 and 696 $^{\circ}\text{C}$.

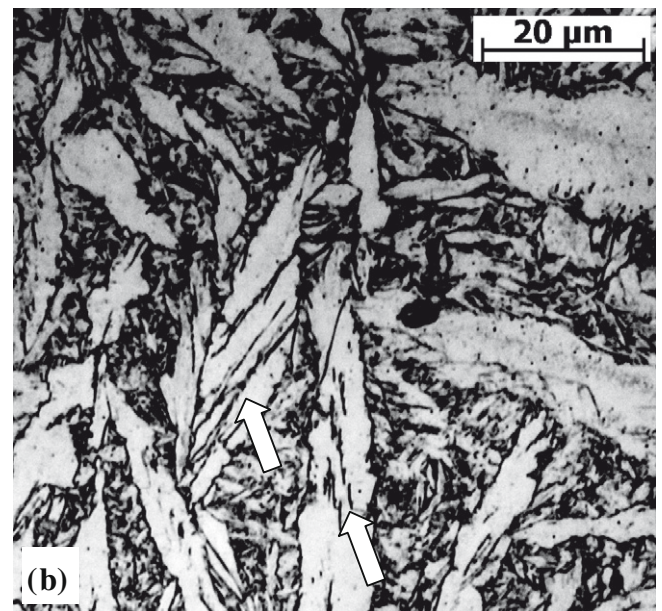
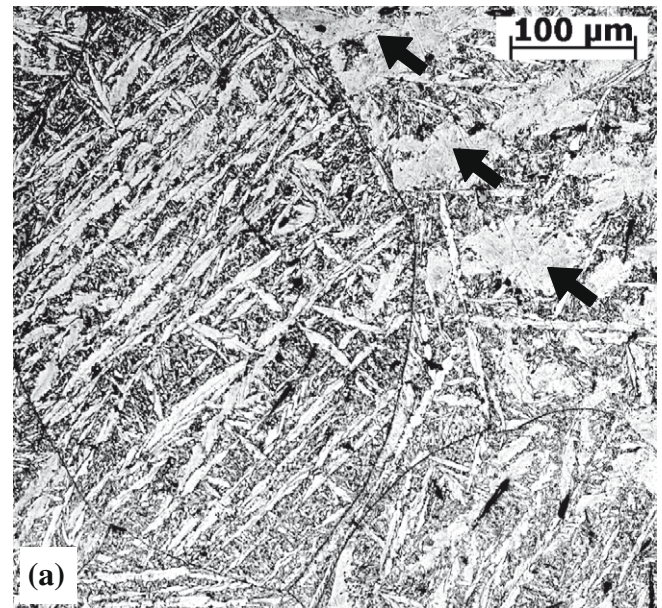


Fig. 3. Photomicrograph of directly water quenched (from 900 $^{\circ}\text{C}$) U-2 wt%Zr alloy showing prior γ grain boundaries and martensitic plates along with non-martensitic α (indicated by arrows) (a). High magnification photomicrograph showing jagged boundaries and heavy internal twinings of martensite plates, as indicated by the arrows (b).

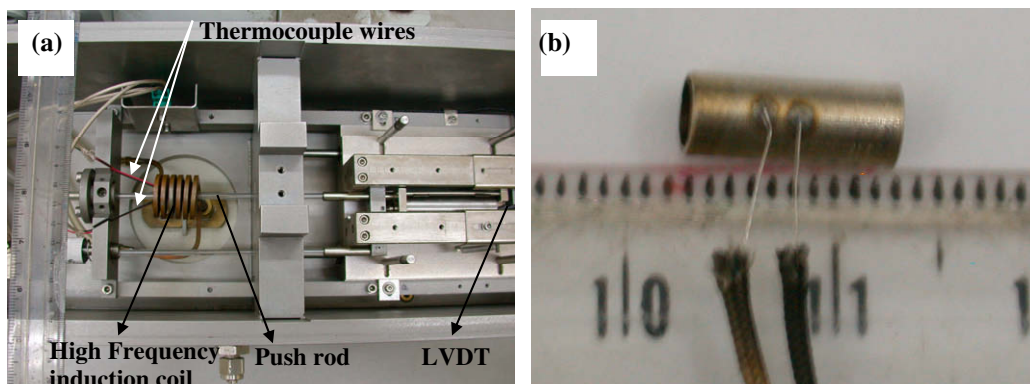


Fig. 2. (a) Components of quenching dilatometer; sample sits inside the induction coil at the end of push rod. (b) Thermocouple wires are spot welded onto the sample surface.

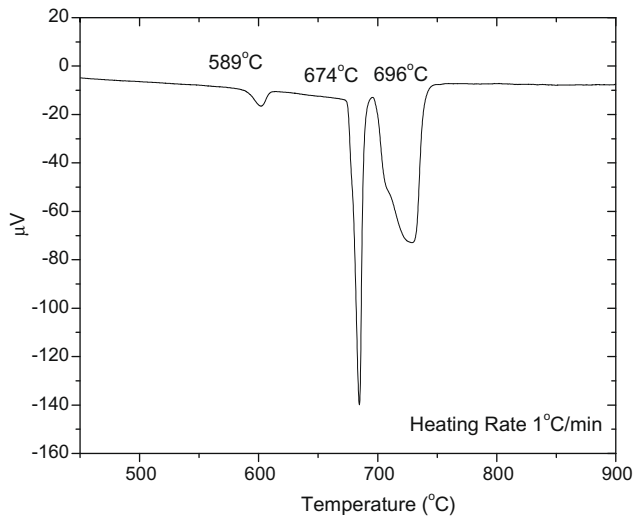


Fig. 4. DSC result of directly quenched (water quenched from 900 °C) U-2 wt%Zr sample with a heating rate of 1 °C/min. The peak observed at 589 °C is due to $\alpha'_a \rightarrow \alpha$ transformation; rest two peaks are the same as observed in the dilatometric experiment.

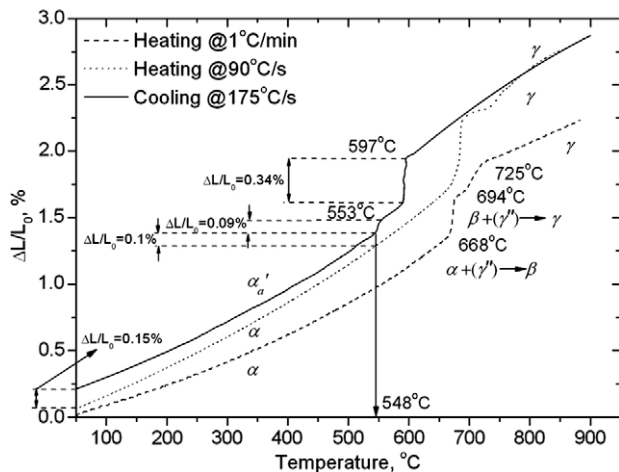


Fig. 5. Dilatometric results of U-2 wt%Zr with two different thermal loading. Experiment with slow heating was done separately. The experiment with rapid cooling and rapid heating are carried out separately. The vertical arrow indicates the temperature at which difference in the relative change in length was measured between the α and α'_a phases.

In order to examine the phase transformation behaviour under rapid cooling, a quenching dilatometry experiment was carried out, where the sample was quenched from γ phase (900 °C) with a cooling rate of 175 °C/s. The difficulty encountered during this experiment is due to the incandescence of the sample especially at $T > 700$ °C. Thus at $T > 700$ °C a second degree polynomial fit was adopted through the obtained data. The dilatometry result, presented in Fig. 5, indicates that two consecutive phase transformations take place at 597 and 553 °C, respectively while quenching from the gamma phase (900 °C). In order to check the repeatability of these signals the same experiment was carried out using an arc-melted sample (remelted for 5 \times in high purity Ar atmosphere), having a total impurity level of 520 ppm, homogenized for 200 h at 900 °C. Similar dilatometric result was obtained with the arc-melted sample with the same quenching rate (175 °C/s); however, the temperatures of phase transformation are found to be \sim 600 and 551 °C, respectively. Deviation in the temperature

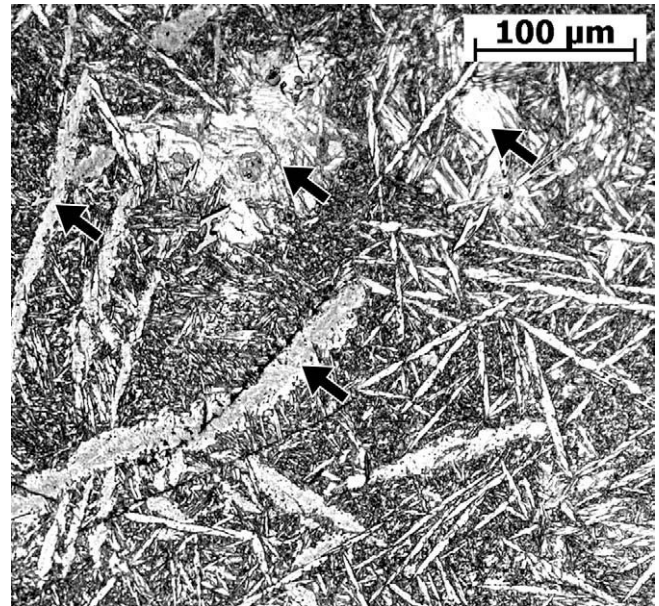


Fig. 6. Optical photomicrograph of U-2 wt%Zr alloy step quenched sample (from 900 °C quenched to 710 °C in liquid lead bath and held there for 5 min before water quenching) showing both martensite and non-martensitic α (arrows), same as directly water quenched sample, though the proportion of non-martensitic α is higher than that of directly water quenched sample.

values, in comparison to the values obtained with induction melted sample, could be due to the difference in the level of impurities. All other experiments reported here were carried out with the samples made by induction melting route.

From the metallography of the quenched sample it can be concluded that at least the final phase transformation (\sim 553 °C) is of martensitic type. From the Jominy end-quenched test results, Hills et al. have suggested that in U-5 at.%Zr (\sim U-2 wt%Zr) the α' martensite forms directly from the γ phase without a formation of any intermediate phase [6]; clearly the present findings do not favour this theory.

3.2. Step quenched samples

In order to predict the transformation behaviour of the β phase, two pre-homogenized samples were heated to 900 °C (γ field), subsequently one was quenched in liquid lead bath kept at 710 °C ($\gamma + \beta$ phase field) and held there for 5 min before water quenching and the second one was furnace cooled to 710 °C and held there for 10 h followed by water quenching. Phase fraction of γ and β as well as the Zr distribution between these phases are supposed to be far from the equilibrium with a shorter holding time at 710 °C; whereas, 10 h exposure at 710 °C is expected to yield an equilibrium phase fraction of γ and β with a near equilibrium Zr distribution.

Metallographic examination reveals almost similar microstructure in both the samples. In general the microstructure contains the same features as that of directly quenched sample; however, the abundance of the non-martensitic phase is higher as shown in Fig. 6. Image analysis of the optical micrographs with careful grey scale intensity adjustment shows that area fraction of the non-martensitic features is nearly about 18%. This value is well within the detectable limit of conventional XRD but there is not a single peak that can not be indexed with Cmc m space group; which leads to the conclusion that the non-martensite features are merely α phase.

EDS analysis was carried out on the step quenched samples to examine the Zr distribution. The sample having a history of

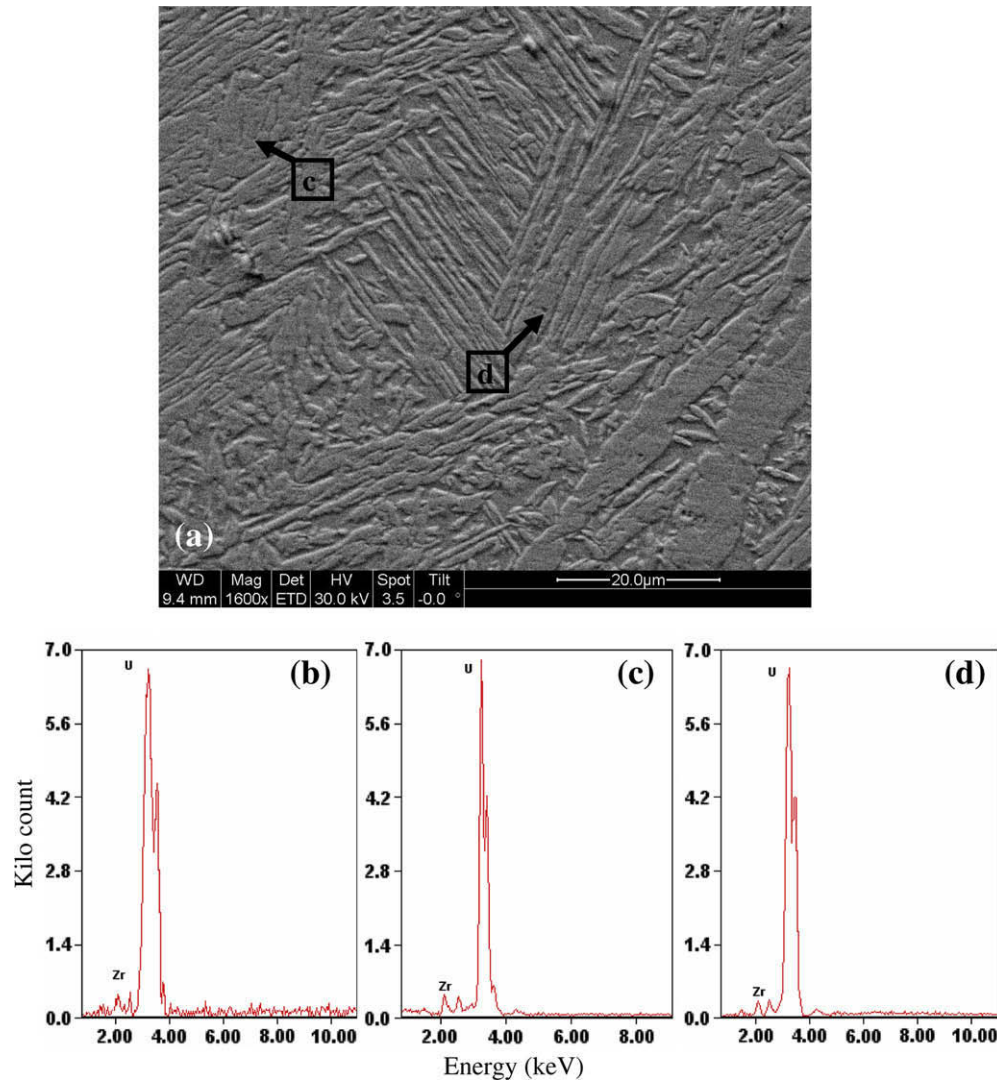


Fig. 7. (a) Secondary electron image of U-2 wt%Zr alloy step quenched sample (from 900 °C quenched to 710 °C in liquid lead bath and held there for 5 min before water quenching). EDS spectra of – (b) overall area (1.99 wt%Zr); (c) non-martensitic α as indicated in the image (2.01 wt%Zr), (d) martensitic α as indicated in the image (1.96 wt%Zr). Such variations in Zr content are within the error limit of the EDS.

5 min holding at 710 °C does not show any significant variation in Zr concentration between the non-martensitic α and α'_a as expected (Fig. 7(a–d)). On the other hand most of the non-martensitic α , in the sample soaked at 710 °C for 10 h, contains more than 2 wt%Zr (i.e. supersaturated α). EDS result, of the same sample, indicates a variation in Zr concentration in different martensite plates, from 1.24 wt% to upto 3.04 wt% (Fig. 8(a–d)).

4. Discussions

The experimental observations and the data generated provide a reasonable basis for the following sequence of arguments. Quenching dilatometry results suggest the formation of a single intermediate phase (~ 597 °C) in U-2 wt%Zr alloy when it is quenched directly from the γ phase region (~ 900 °C) prior to the final martensitic transformation ($M_s \sim 553$ °C).

Metallographic examinations of the heat treated samples (directly quenched sample and samples soaked at 710 °C for 5 min and 10 h) show the presence of both martensitic α'_a (subscript *a* indicates acicular morphology) and non-martensitic α phase. SEM examination with EDS analysis of the sample soaked at 710 °C for 10 h show that majority of the non-martensitic α phase is

supersaturated with Zr (more than 2 wt%). This suggests that most of the non-martensitic supersaturated α phase was formed from the γ phase during quenching alongwith the martensite. This conclusion, based on the Zr distribution, is well supported by the phase diagram since at 710 °C, γ contains ~ 4 wt%Zr and β contains ~ 1 wt%Zr. Also, in the directly quenched sample (water quenched from 900 °C) similar non-martensitic α is observed though in a very small proportion. Based on the facts stated above it can be reasonably inferred that decreasing cooling rate (i.e. lowering gamma-matizing temperature) yields more non-martensitic α phase from the γ phase. The β phase also gives rise to non-martensitic α as suggested by the EDS results, however, the fraction is smaller in comparison to the amount of non-martensitic α phase generated from the γ phase.

EDS analysis of the sample soaked at 710 °C for 10 h is quite interesting; a significant variation in Zr concentration is observed for different martensitic plates. Martensite plates with less than 2 wt%Zr suggest that the β phase was the parent phase. Whereas, the martensite plate with higher than 2 wt%Zr has to form from the γ phase. Thus it can be concluded that both γ and β undergo martensitic transformation. Martensitic transformation of β phase is well known and the mechanism is same for all the U-rich alloys

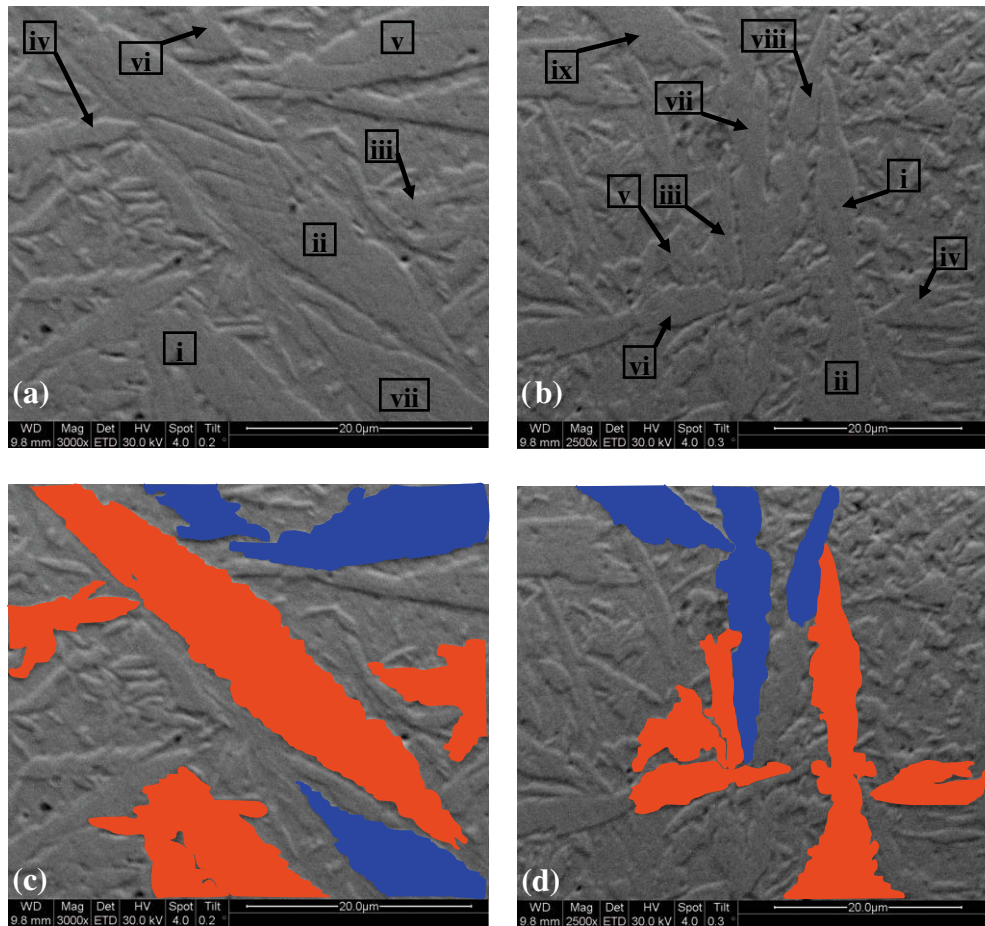


Fig. 8. Secondary electron images of U–2 wt%Zr alloy step quenched sample (from 900 °C furnace cooled to 710 °C and held there for 10 h before water quenching) with EDS analysis showing variation in Zr concentration of different martensite plates and non-martensitic α , these EDS results were obtained operating the beam in mini-window mode rather than point focus mode to get a better statistical average of chemical composition. Zr conc. are: (i) 2.76%, (ii) 2.44%, (iii) 2.22%, (iv) 2.15%, (v) 1.6%, (vi) 1.47% and (vii) 1.24% as indicated in (a). (i) 3.04%, (ii) 2.64%, (iii) 2.55%, (iv) 2.28%, (v) 2.18%, (vi) 2.14%, (vii) 1.80%, (viii) 1.69% and (ix) 1.28% as indicated in (b). Results suggest that martensitic plates have wide variation in Zr conc. whereas most of the non-martensitic α phase contains more than 2%Zr. (a) and (b) are from different locations from the same sample. (c) and (d) are the color rendition of (a) and (b), respectively; where red color indicates Zr conc. more than 2 wt%; where as blue indicates the reverse.

with direct $\beta \rightarrow \alpha'$ transformation without the involvement of any intermediate phase [8].

It is seen from the DSC result (Fig. 4) that total three phase transformations take place while heating the directly quenched sample of U–2 wt%Zr alloy. Among these transition temperatures, transformations at 674 °C and 696 °C are equivalent to the temperatures obtained from the dilatometric result (heated at 1 °C/min); i.e. 668 and 694 °C. The apparent differences in these temperatures (with respect to the dilatometric results) are due to the oxide scale formation on the sample surface causing sluggishness in temperature sensing. Details of these transformations will be discussed later. The only important feature in the DSC result is about the transformation occurs at 589 °C. Since the starting sample contains martensitic α' , hence the peak corresponding to 589 °C can be attributed to the $\alpha'_a \rightarrow \alpha$ transformation.

The identification of the intermediate phase prior to the martensitic transformation from the γ phase still remains undetermined. In order to identify the intermediate phase it is considered that the phase involved here could be one of those intermediate phases found in the entire range of U-rich binary alloy systems; namely γ_s , γ^0 , α'' , β and ω , as reported in the literature [1–9]. Among these phases ω could be ruled out for U-rich Zr alloys, since $\omega \rightarrow \alpha'$ transformation is restricted due to certain crystallographic constraints especially for low Zr concentration, as reported in the literature [6].

In order to cross check the correctness of the relative volume change calculated from the dilatometric result; relative volume change near 50 °C between α and α'_a is calculated to be 0.45% (from Fig. 5), from the difference between 175 and 90 °C/s curves at 50 °C temperature, and from the XRD analysis (Table 1) the same is found to be 0.42%; which are in reasonably good agreement.

From the quenching dilatometry results it can be seen that the relative change in length from γ to the intermediate phase is about 0.34% (relative volume change $\sim 1.02\%$); whereas, from the intermediate phase to α'_a transformation it is only 0.09% (relative volume change $\sim 0.27\%$). Conventional dilatometry experiment of U–2 wt%Zr alloy (Fig. 5) during slow heating shows that at 668 °C (corresponding to the eutectoid decomposition at 662 °C as indicated in the phase diagram) α and γ' combine to form β ; where volume fraction of equilibrium α would be 97% (100% α is expected

Table 1

Variation in lattice parameters of U–2 wt%Zr alloy alongwith lattice volume for annealed and water quenched samples as calculated from the XRD analysis [8]. Note the relative change in lattice volume is around 0.42%.

Heat treatment	Phase	a (Å)	b (Å)	c (Å)	Volume (Å ³)
Annealed	α	2.8523	5.8732	4.9616	83.1034
water Quenched	α'	2.8656	5.8536	4.9745	83.4598

Table 2

Comparisons between experimental and literature values of relative change in length and volume for different phase transformations. It is interesting to note that the relative change in length for $X \rightarrow \alpha'$ is almost equal to the same for $\gamma \rightarrow \gamma^0$ and $\alpha \rightarrow \alpha'$ where the latter reactions involve small amount of lattice shear. This indicates $X \rightarrow \alpha'$ transformation is associated with small amount of lattice shear.

Transformation	Temp (°C)	$\Delta L/L$ (%)	$\Delta V/V$ (%)	Comment
$\gamma \rightarrow X$	597	0.34	1.02	Quenching dilatometric analysis
$\gamma \rightarrow \gamma^0$	~600	0.1	0.3	Ref. [11]
$\gamma \rightarrow \gamma_s$	~600	<0.1	<0.3	Ref. [1]
$\gamma \rightarrow \omega$	Not permissible in low Zr alloy			Ref. [10]
From the above data it can be concluded that X cannot be γ^0 , γ_s or ω phase				
$\alpha \rightarrow \alpha'$	50	0.15	0.45	Dilatometric analysis
$\alpha \rightarrow \alpha'$	50	0.14	0.42	XRD analysis, matches well with above data
$\alpha \rightarrow \beta$	548	0.51	1.53	Dilatometric analysis
$\alpha \rightarrow \alpha'$	548	0.1	0.3	Dilatometric analysis
$\beta \rightarrow \alpha'$	548	0.41	1.23	Calculated from above two data
$X \rightarrow \alpha'$	553	0.09	0.27	Quenching dilatometric analysis
From the above data it can be concluded that X cannot be β phase				

in case of Zr supersaturation). In fact recent study shows that the room temperature phase is α completely supersaturated with Zr [10]. Thus for all practical purposes it can be concluded that the associated volume change is solely due to the $\alpha \rightarrow \beta$ formation. Under rapid heating condition the form of dilatometric signals of the phase transformations remain the same in comparison to the result of the slow heating dilatometry. Thus, for the present analysis only rapid heating/cooling curves will be considered. From the rapid heating dilatometric result it can be seen that relative change in length for $\alpha \rightarrow \beta$ (likely to be supersaturated) is about 0.51% (relative volume change $\sim 1.53\%$). Since, instead of α phase α'_a is of interest; the volume change associated with the hypothetical $\alpha'_a \rightarrow \alpha$ transformation can be calculated from the rapid heating and rapid cooling curve (Fig. 5). At 548 °C (near to 553 °C), indicated by a vertical arrow in Fig. 5, the difference in the relative change in length from α to α'_a is about 0.1% (i.e. relative volume change of $\sim 0.3\%$). The relative change in volume for the hypothetical $\beta \rightarrow \alpha'_a$ transformation at 548 °C, therefore, would be about 1.23% (i.e. 1.53% minus 0.3%) as against the observed volume change of 0.27% associated with the final martensitic transformation at 553 °C. From the preceding discussions it seems unlikely that the intermediate phase is β .

Formation mechanism of γ_s , γ^0 , α'' and α' from the γ phase is well documented in literature for different U based alloy systems that follows a general trend [2–4]. It suffices here to mention that progressive shear on the $\{1\ 1\ 2\} \langle 1\ 1\ 1 \rangle$ slip system of γ phase promotes $\gamma \rightarrow \gamma_s \rightarrow \gamma^0 \rightarrow \alpha'' \rightarrow \alpha'$ transformation sequence with the increase in shear stress (depending on the alloy system and concentration some phase may be absent). The relative change in volume of γ_s or γ^0 with respect to the γ phase is very nominal since quite small amount of shear is associated with it. Experimental result, for U–3.8 wt%Mo, shows that associated relative volume change for $\gamma \rightarrow \gamma^0$ is only about 0.3% [11]; whereas in the present case $\gamma \rightarrow$ intermediate phase associated with a relative volume change of about 1%. Hence, it seems most unlikely that γ_s or γ^0 would be the intermediate phase (γ_s is associated with even less distortion of γ , as stated earlier). The preceding discussion is summarized in Table 2.

Since, α'' can be transformed to α' with a relatively small amount of shear and lattice dialation, the relative change in volume is expected to be low. In the present case intermediate phase $\rightarrow \alpha'$ transformation is associated with a relative change in length of only 0.09% and relative volume change of 0.27%. These values are almost similar to the corresponding values of $\gamma \rightarrow \gamma^0$ or $\alpha'_a \rightarrow \alpha$ (see Table 2) where only small amount of shear is involved. From the preceding discussions it seems likely that α'' is the only probable intermediate phase. It is to be noted that ther-

modynamic calculation suggests that γ can be transformed into α through the intermediate β phase [10]. However, present study clearly shows that phase transformation during rapid cooling does not follow the equilibrium thermodynamics. Moreover, it is to be noted that in U–2 wt%Zr alloy α'' is an unstable phase which cannot be retained at room temperature irrespective of the given heat treatment.

In the directly quenched sample the prior γ grain boundary is well resolved (Fig. 3(a)) which suggests that major phase transformations are likely to be shear-dominant. Moreover the martensite plates formed from the γ phase exhibit highly jagged boundaries and heavy twinning across the plates; as seen in the Fig. 3(b), a typical signature of a second transformation. It is therefore proposed that double martensitic transformation is most likely to occur while quenching the U–2 wt%Zr alloy from the γ phase field with a transformation sequence of $\gamma(\text{bcc}) \rightarrow \alpha''(\text{monoclinic}) \rightarrow \alpha'$ (orthorhombic); which is also supported by the fact that $\gamma \rightarrow \alpha''$ transformation is martensitic in nature [3]. However, a parallel reaction is also likely to take place, probably by nucleation and growth mechanism, which causes formation of the non-martensitic α phase. On the other hand the martensitic α'_a transforms into equilibrium α phase at 589 °C upon heating without going through any intermediate phase.

5. Conclusions

From the preceding discussions the following conclusions can be drawn regarding the martensitic transformation and the associated intermediate phase in U–2 wt%Zr alloy –

- (i) Both β and γ phase undergo martensitic transformation upon quenching and neither of these phases is retained at room temperature.
- (ii) Along with the formation of α'_a martensite, non-martensitic α also is formed.
- (iii) Low gammatizing temperature or slower cooling rate yields more non-martensitic α phase.
- (iv) Quenching from γ phase results in formation of intermediate α'' monoclinic phase prior to the final martensitic transformation. Thus the proposed sequence of transformation is $\gamma \rightarrow \alpha'' \rightarrow \alpha'_a$ where transformation temperatures are 597 and 553 °C respectively.
- (v) While quenching from the γ phase both the transformations, i.e. $\gamma \rightarrow \alpha''$ and $\alpha'' \rightarrow \alpha'_a$, are likely to be shear dominated martensitic in nature.
- (vi) Martensitic α can be transformed to equilibrium α phase by heating and this $\alpha'_a \rightarrow \alpha$ transformation occurs at 589 °C.

Acknowledgements:

Authors greatly acknowledge the technical assistance of Binay K. Mondal, MFD, BARC.

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