ANL/CMT/CP - 96870

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Phase Stability of Laves Intermetallics in a Stainless Steel–Zirconium Alloy

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Abstract

Phase transformations occurring in a stainless steel-15 wt% zirconium (SS-15Zr) alloy were studied by *insitu* neutron diffraction. Neutron diffraction patterns as a function of time were obtained on alloys that were held at various elevated temperatures (1084-1275°C). As-cast SS-15Zr alloys contain ferrite, austenite, $ZrFe_2$-type Laves polytypes C36 and C15, and small amounts of a $Fe_{23}Zr_6$-type intermetallic. Annealing at high temperatures resulted in an increase of the $Fe_{23}Zr_6$ intermetallic content. The C15 Laves polytype is the equilibrium phase for T ≤1230°C; C36 is the stable polytype at higher temperatures (~1275°C). Phase changes were slow for temperatures <1100°C. These findings have important implications for use of the SS-15Zr alloy as a nuclear waste form.

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Introduction

A stainless steel-15 wt% zirconium (SS-15Zr) alloy has been identified as a potential nuclear waste form for the disposal of metallic waste generated during the electrometallurgical treatment of stainless steel-clad spent nuclear fuel [1-3]. In the electrometallurgical process, uranium is electrorefined out of spent fuel in a molten salt electrolyte. The metallic remnants in the anode baskets of the electrorefiner are consolidated by melting and are cast into waste form ingots for eventual disposal in a geologic repository.

For acceptance in a repository, all nuclear waste forms must meet applicable performance requirements. An extensive testing program is underway at Argonne National Laboratory to evaluate the properties of SS-15Zr waste forms. Under the conditions expected at the Yucca Mountain geologic repository, the SS-15Zr waste forms display excellent corrosion resistance, favorable mechanical behavior, and superior thermophysical properties [2]. Since long-term (>1000 years) behavior of nuclear waste forms must be extrapolated from short-term laboratory tests [4], microstructural stability is an important criterion for radioactive waste forms.

The phases observed in stainless steel–zirconium alloy samples have been presented in previous articles [5, 6]. A typical microstructure of as-cast SS-15Zr alloy, shown in Fig. 1, contains the iron solid-solution phases, ferrite and austenite, $ZrFe_2$-type Laves polytypes C36 (dihexagonal, $MgNi_2$ structure) and C15 (cubic, $MgCu_2$ structure), and small amounts of a $Fe_{23}Zr_6$-type intermetallic. The composition of individual phases is listed in Table 1. The Laves intermetallics contain only 24 at% Zr, a substoichiometry of more than 25% from the expected 33.3 at% Zr. The Ni/Cr ratio is the main compositional difference between the C36 and C15 polytypes observed in SS-15Zr. For the C36 polytype Ni/Cr ~1.5, whereas Ni/Cr >2.5 for the C15 polytype. The $Fe_{23}Zr_6$ intermetallic has Ni/Cr ~1 and a $Fe_{23}Zr_6$ intermetallic very close to the stoichiometric value.

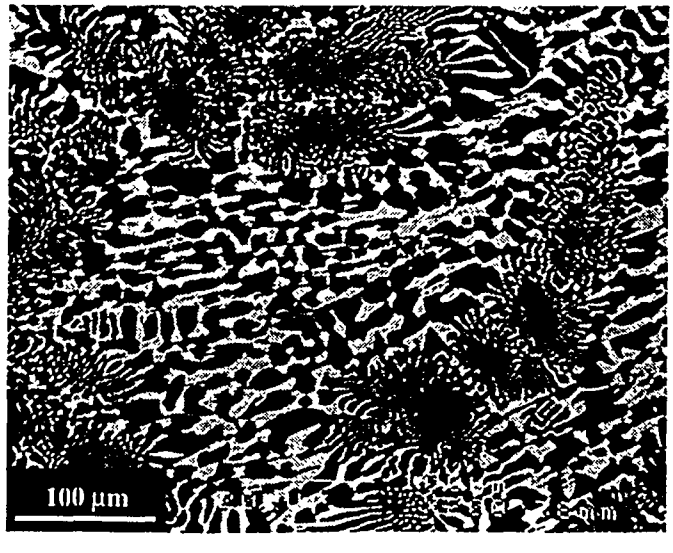

Fig. 1. Typical microstructure of as-cast SS-15Zr alloy. The dark areas contain ferrite and austenite; the bright areas are $ZrFe_2$-type Laves intermetallics.

Table I. Phase composition (at%) obtained by energy dispersive spectroscopy for as-cast SS-15Zr alloy sample

Phase	Fe	Cr	Ni	Zr	Expected Zr[a]	Ni/Cr
Ferrite, α	68	25	5	< 0.1	0	0.2
Austenite, γ	71	19	7	< 0.1	0	0.4
$ZrFe_2$-type C36	53	8	11	24	33.3	1.4
$ZrFe_2$-type C15	48	6	18	24	33.3	3
$Fe_{23}Zr_6$-type	57	10	10	20.5	20.7	1

[a]The Zr content at stoichiometry is shown for the intermetallic phases.

High-temperature annealing of as-cast SS-15Zr alloys leads to an increase in the $Fe_{23}Zr_6$ content and a corresponding decrease in the amount of austenite and Laves intermetallics [6]. Areas rich in zirconium (α-Zr) were observed within $Fe_{23}Zr_6$ (Fig. 2), indicating their intimate association with the phase transformation. A two-step mechanism was proposed to explain the transformation to $Fe_{23}Zr_6$ [6]: (1) the $ZrFe_2$ intermetallics transform into $Fe_{23}Zr_6$ and α-Zr, and (2) the α-Zr reacts with ferrite and/or austenite to form more $Fe_{23}Zr_6$.

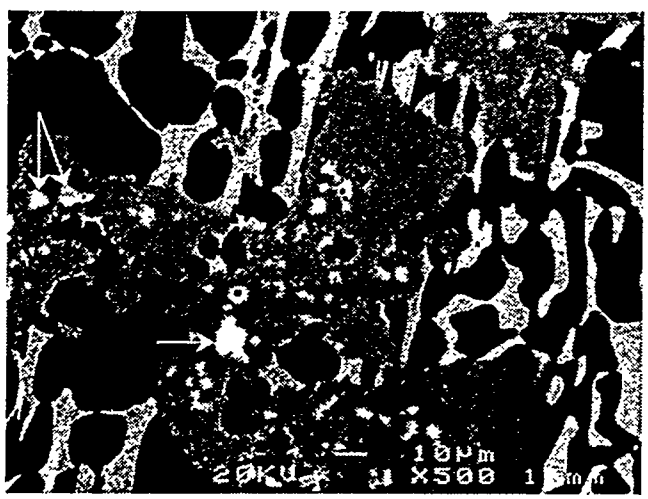

Fig. 2. Micrograph showing α-Zr areas (see arrows) within the $Fe_{23}Zr_6$ phase.

This article presents the results of *insitu* high-temperature neutron diffraction experiments on SS-15Zr alloys. Neutron diffraction patterns were obtained on alloy samples that were annealed at temperatures >1000°C to accelerate microstructural changes. Phase volume fractions obtained from Rietveld refinements of diffraction patterns were plotted as a function of time to determine transformation kinetics at temperature. The quantitative data obtained from diffraction measurements are complemented by qualitative results obtained by scanning electron microscopy (SEM).

Experimental

The SS-15Zr alloys were prepared by melting Type 316 stainless steel and zirconium metal in an induction casting furnace. The charge metals were contained within yttrium oxide crucibles and held at 1600°C for 1 h under a high-purity argon atmosphere. The furnace was switched off at the end of the holding period, and the ingots were solidified within the crucible. Bulk samples for neutron diffraction, 50.8 mm long and 9.5 mm dia, were obtained by sectioning the SS-15Zr ingots. The high penetration depth of neutrons enables the examination of bulk specimens by neutron diffraction.

Time-of-flight (TOF) neutron diffraction data were collected from alloy samples on the General Purpose Powder Diffractometer at the Intense Pulsed Neutron Source (IPNS) at ANL. The TOF experiments are carried out at a fixed scattering angle, and diffraction patterns are generated as a function of incident neutron wavelength. Diffraction data are obtained at six separate detector banks, each positioned at a fixed angle relative to the incident beam. Since each detector bank views the sample from a different orientation, an assessment of preferred orientation (texture) in the sample can be obtained from variations in intensity from bank to bank.

The *insitu* diffraction experiments were performed in a controlled-atmosphere, high-temperature furnace with flowing argon gas. Time-temperature profiles of the various experiments are shown in Fig. 3. Diffraction data were collected on three separate specimens annealed at (1) 1275°C for 38 h, (2) 1220°C for 44 h, (3) 1084°C for 14 h, then annealed at 1175°C for 14 h. For each experiment, diffraction data were collected continuously with a break every 30 min to mark time. In order to improve the statistical significance of results from the Rietveld profile refinements of the diffraction data, these 30-min datasets were later summed in groups of two (all 1084°C and 1175°C data, and the first half of the 1275°C data) or four (later stages of the 1275°C data). In each case, the grouped 30-min datasets were assigned as a single data point at the center of the time period. The estimated uncertainties on phase fractions range from ~1 to 5 vol%.

The SEM examination of alloy specimens was performed with a JEOL 6400 scanning electron microscope. Standardless quantitative analysis of individual phases was obtained with an EDS spectrometer and Vantage software from NORAN Instruments. The uncertainty in elemental compositions determined by this method is ±3% of the measured value.

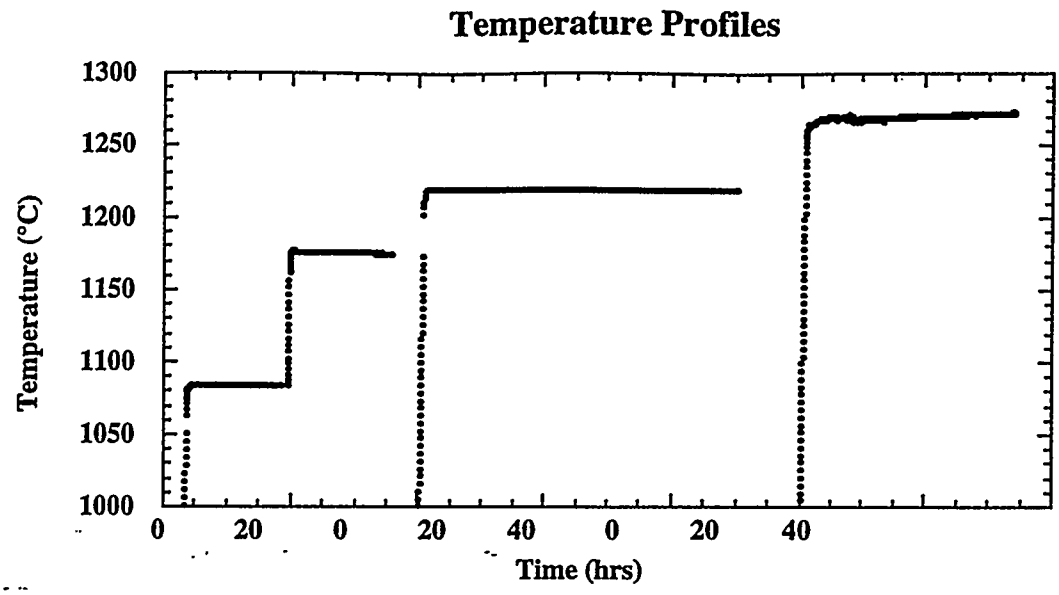

Fig. 3. Time-temperature profiles for SS-15Zr alloys examined by *insitu* neutron diffraction.

Results and Discussion

Annealing at Temperatures <1220°C

The volume fraction changes occurring in an alloy annealed at 1084°C for 14 h, then heated to 1175°C and held for 14 h is shown in Fig. 4 and Table II. The changes were relatively slow at 1084°C. The austenite content decreased slightly from 9 to 6 vol%, whereas the ferrite content remained unchanged at 40 vol%. The amount of the C36 polytype decreased from 32 to 20 vol%, whereas the amount of the C15 polytype increased from 16 to 24 vol%. An increase was also observed for the $Fe_{23}Zr_6$ content, from 2 vol% (at room temperature) to 10 vol%.

Increasing the temperature to 1175°C did not appreciably increase the $Fe_{23}Zr_6$ content, which changed from 10 to 11 vol%. However, at this temperature the austenite content decreased rapidly to zero. Relatively rapid changes were also observed for the Laves intermetallics. The C36 Laves polytype decreased from 20 vol% at 1084°C to 9 vol% after 14 h at 1175°C, a total change of –23 vol% from the as-cast alloy content. The C15 Laves polytype increased from 24 vol% at 1084°C to 35 vol% after 14 h at 1175°C, a total change of +19 vol% from the as-cast alloy content. The sums of volume fractions for the iron solid-solution phases and the Laves intermetallics are also shown in Table II. Only marginal decreases are observed in these sums even though large changes are observed for the individual phases.

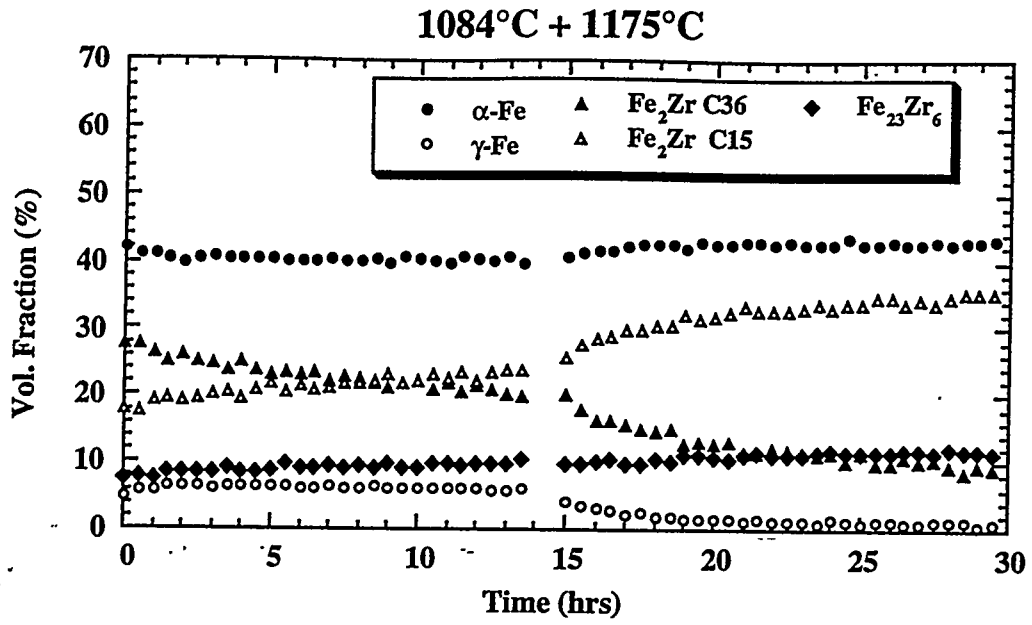

Fig. 4. Volume fractions of phases from a SS-15Zr alloy plotted as a function of time. The alloy was annealed at 1084°C for 14 h, then at 1175°C for another 14 h.

Table II. Volume fractions of phases calculated from Rietveld refinements conducted on neutron diffraction patterns obtained from a SS-15Zr alloy

Phase	As-Cast	14 h at 1084°C	Change[a]	14 h at 1175°C	Change[a]
Ferrite, α	40	40	0	43	+ 3
Austenite, γ	9	6	- 3	0	- 9
$ZrFe_2$-type C36	32	20	-12	9	- 23
ZrFe2-type C15	16	24	+8	35	+ 19
$Fe_{23}Zr_6$-type	2	10	+8	11	+ 4
α + γ	49	46	-3	44	- 5
C36 + C15	48	44	-4	44	- 4

[a] Change is with respect to the as-cast alloy

Insitu diffraction patterns obtained at 1220°C showed that the austenite and C36 contents decreased rapidly to zero. After 44 h at this temperature, the alloy contained only three phases: ferrite, C15 and $Fe_{23}Zr_6$. Diffraction patterns obtained after the alloy was cooled to room temperature showed that the phase contents were similar to those at 1220°C. A micrograph of the cooled alloy is shown in Fig. 5. The bright areas seen within the $Fe_{23}Zr_6$ phase are Zr-rich (~98 at% Zr). Peaks corresponding to α-Zr were not observed in the diffraction patterns, presumably because of the low volume content of this phase.

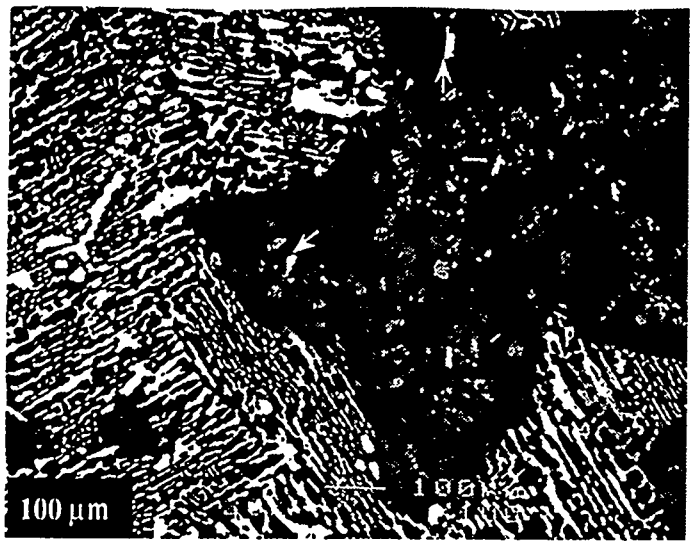

Fig. 5. Micrograph of a SS-15Zr alloy that was heated at 1220°C for 44h, then cooled to room temperature. The C15 Laves polytype is seen along with ferrite (dark) and Fe23Zr6. Bright Zr-rich areas (see arrows)are visible within Fe23Zr6.

The above experiments demonstrate that annealing SS-15Zr alloys at high temperatures (≤1220°C) results in a three phase microstructure containing ferrite, C15 and $Fe_{23}Zr_6$. These are also the equilibrium phases for the SS-15Zr alloy at room-temperature. Austenite and the C36 polytype present in the as-cast alloy are metastable and will transform to the equilibrium microstructure under favorable conditions.

Annealing at T = 1275°C

The melting point of the SS-15Zr eutectic alloy is ~1335°C. The 1275°C annealing temperature was chosen to accelerate the phase change kinetics of the alloy. However, extended holding periods at this temperature resulted in alloy softening, which was seen as a diffuse liquid-like background in the diffraction patterns (see Fig. 6). This diffuse background presented some problems during Rietveld refinement and appears to have affected the absolute value for the ferrite and C36 phases.

The volume changes occurring in the alloy are shown in Fig. 7 and Table III. The C15 polytype and austenite phase fractions rapidly decreased to zero by the time the furnace temperature reached 1275°C. The C36 intermetallic peaks were prominent in the 1275°C patterns, indicating that this phase is the stable polytype at temperatures near melting. Similar polytype preferences in binary Laves intermetallics are observed in the Cr-Hf, Cr-Ti and Cr-Zr alloy systems. For example, the C15 polytype of the Cr_2Zr intermetallic is stable for temperatures up to 1592°C and the C36 polytype is stable at higher temperatures [7].

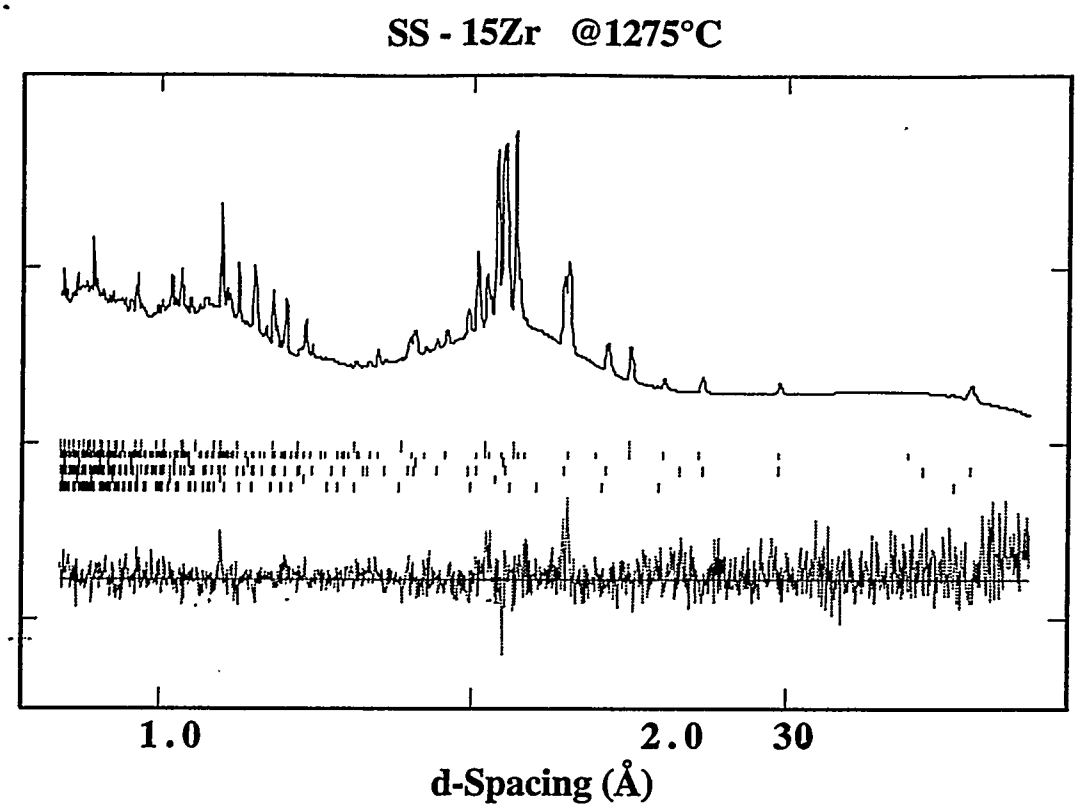

Fig. 6. Diffuse scattering in SS-15Zr alloy annealed at 1275°C for 38 h.

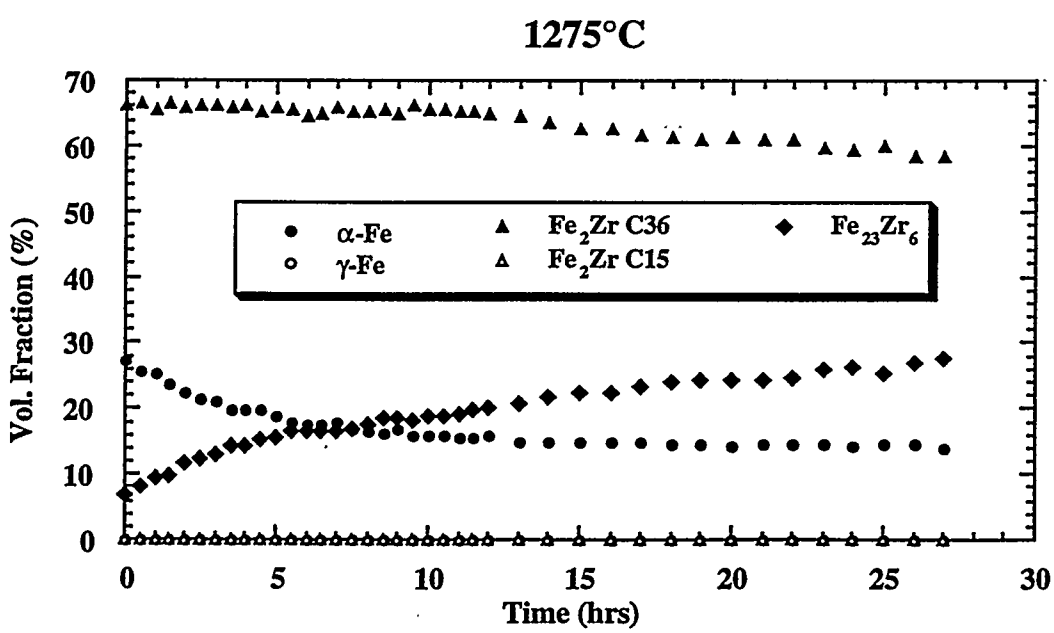

Fig. 7. Volume fractions of phases from a SS-15Zr alloy plotted as a function of time. The alloy was annealed at 1275°C for 38 hours; only data till 27 hours is shown. The time axes corresponds to the hold time at 1275°C.

Table III. Volume fractions of phases calculated from Rietveld refinements conducted on neutron diffraction patterns obtained from a SS-15Zr alloy

Phase	As-Cast	30 hrs at 1275°C	Change[a]	After Cooling	Change[a]
Ferrite, α	40	14	- 26	34	- 6
Austenite, γ	9	0	- 9	0	- 9
$ZrFe_2$-type C36	32	58	+ 24	43	+ 11
$ZrFe_2$-type C15	16	0	- 16	12	- 4
$Fe_{23}Zr_6$-type	2	28	+ 26	11	+ 9

[a]Change is with respect to the as-cast alloy

The $Fe_{23}Zr_6$ content increased to 28 vol% after 27 h, with the fastest increase occurring in the first 5 h at test temperature. A correspondingly rapid decrease was observed in the ferrite phase, whereas a gradual decrease was observed in the C36 content. The $Fe_{23}Zr_6$ is believed to form from the ferrite and C36 at 1275°C.

Diffraction patterns obtained on the alloy that was annealed at 1275°C, then cooled to room temperature, showed the reappearance of the C15 phase (but not the austenite). The C36 phase content decreased from 58 vol% at 1275°C to 43 vol% in this alloy after cooling. A decrease was also observed in the $Fe_{23}Zr_6$ content, from 28 vol% at 1275°C to 11 vol% in the after-cooled alloy. This finding indicated that the phase had reverted into ferrite and the Laves intermetallics. The microstructure of the after-cooled alloy, shown in Fig. 8, is clearly different from the eutectic microstructure of the as-cast alloy (Fig. 1), probably due to grain growth at 1275°C. Ferrite, $Fe_{23}Zr_6$, and C36 are clearly seen in Fig. 8; the C15 Laves polytype is often seen as a bright border on the C36 phase.

The 1275°C annealing experiment shows that the equilibrium phases in SS-15Zr at elevated temperatures such as 1275°C are different from the equilibrium phases expected at room temperature and at repository-relevant temperatures such as 200°C. Hence, the phase transformation kinetics measured at 1275°C cannot be extrapolated to make predictions at the lower temperatures.

The activation energy for the $Fe_{23}Zr_6$ formation will be calculated from the *insitu* experimental data and will be used to predict transformation kinetics at repository-relevant temperatures (≤200°C). Future diffraction studies will identify the transition temperature between the C15 and C36 phases. The activation energy for $Fe_{23}Zr_6$ formation will be obtained from experiments conducted below this transition temperature. Our experiments have shown that the production of $Fe_{23}Zr_6$ is relatively slow at temperatures less than 1100°C. Hence, the as-cast microstructure will be stable at the temperatures expected in the Yucca Mountain repository.

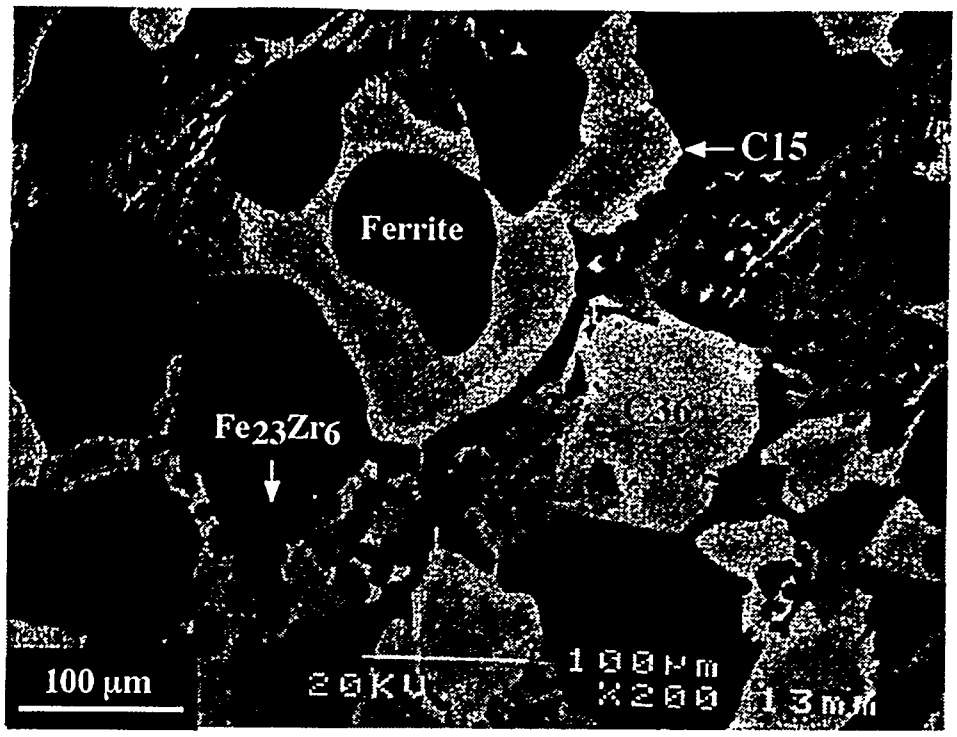

Fig. 8. Ferrite (dark), $Fe_{23}Zr_6$ and C36 are seen in this micrograph of a SS-15Zr alloy that was heated to 1275°C for 40 h and then cooled to room temperature. The C15 polytype appears as a bright border on the C36 intermetallic.

Conclusions

1. The as-cast microstructure of the SS-15Zr alloy is metastable. The equilibrium phases at room temperature are ferrite, $Fe_{23}Zr_6$ and C15 Laves intermetallic.
2. The equilibrium phases at 1275°C are ferrite, $Fe_{23}Zr_6$, and C36 Laves intermetallic. Larger amounts of $Fe_{23}Zr_6$ are observed in the alloy at this temperature.
3. Production of $Fe_{23}Zr_6$ is slow at temperatures less than 1000°C. The phases present in as-cast SS-15Zr waste forms will be stable at the temperatures expected at the Yucca Mountain repository.

Acknowledgments

This work has benefited from the use of the Intense Pulsed Neutron Source at ANL. This facility is funded by the U.S. Department of Energy (DOE), BES-Materials Science, under Contract No. W-31-109-ENG-38. This work was also supported by the DOE, Nuclear Research and Development Program, under Contract No. W-31-109-ENG-38.

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