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Journal of Nuclear Materials 247 (1997) 103–107

journal of nuclear materials

Section 4. Reactor fuel behavior and processing

Phase equilibria in the UO_2–austenitic steel system up to 3000°C

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Abstract

The pseudobinary UO_2–austenitic steel system was investigated by DTA up to 1500°C, by isothermal annealing up to 2000°C, by induction heating up to 2850°C and by arc melting up to about 3000°C. The system is characterized by a degenerate eutectic at 1433°C on the steel side and a monotectic at 2830°C and about 1 mol% steel. The maximum solubility of steel in solid UO_2 is 0.6 mol%, that in liquid UO_2 at 3000°C is about 4 mol%. UO_2 and steel form (Fe, Mn, $Cr)_2O_3$ precipitates between 1300 and 2600°C as UO_2 becomes hypostoichiometric. Liquid steel is stabilized to higher temperatures above its boiling point at 2790°C by dissolution of uranium and decomposes peritectically to liquid UO_{2-x} and gas at estimated 3200°C. The critical data of the single-phase UO_2-steel melt based on the application of the Redlich–Kister model are $T_c = 4900$°C, $p_c = 300$ bar and $x_{c,steel} = 0.41$. © 1997 Elsevier Science B.V.

1. Introduction

The knowledge of the chemical interactions between the uranium–plutonium oxide fuel and the austenitic steel cladding of fast breeder reactor pins at very high temperatures is required for the insight into the unlikely events of disruptive accidents. Melting, relocation and release of the fuel components, structural materials and volatile fission products in simulated transient power irradiations give information on the driving forces and the sequence of events as liquefaction of the metallic components, fuel melting and fragmentation. Special importance is attached to the chemical behavior between oxide fuel and steel at very high temperatures [1].

Chemical constitution work was hitherto performed in the UO_2–stainless steel AISI 316 L-fission product system with unknown fractions of the phases [2] and in the UO_2–stainless steel 1.4970 system with different fuel/steel ratios [3] in the temperature region above the melting point of UO_2, see Table 1. Metallographic examination of the arc melted material evidenced in both experiments immiscibility of the liquid phases [2,3]. On cooling from the liquid state, the steel had partly precipitated in the UO_2 in spheroids and the UO_2 had precipitated from the steel as dendrites. These observations indicated that the UO_2–steel system is of the monotectic type [2]. However, mutual solubilities were not investigated and reactions of steel components with oxygen released from UO_2 during heating were not considered. Therefore, four further experiments were conceived which are outlined in Table 1.

2. Experimental

2.1. Materials

The starting materials were granular uranium dioxide of nuclear grade with an oxygen-to-metal ratio 2.003. Stainless steel of the type AISI 316 L was taken from cladding tubes foreseen for fast breeder fuel pins; the composition is given in Table 2. UO_2–10 mass% steel (equivalent to about 35 mol% steel) was compacted to pellets and was foreseen for DTA and further heat treatment and melting experiments.

2.2. Melting point determinations and heat treatment

The DTA type 404/3 (Netzsch, Selb) was used for differential thermal analysis of AISI 316 L stainless steel in the liquidus and solidus regimes and of UO_2–AISI 316 L stainless steel in the eutectic temperature region. The

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PII S0022-3115(97)00033-0

Table 1
Initial composition (in mass%) and heat treatment of UO_2-austenitic steel specimens

Initial composition (mass%)	Heat treatment	Temperature (°C)	Ref.
UO_2–AISI 316 L	arc melting	> 2850	[2]
37% UO_2–63% 1.4970	arc melting	≈ 3000	[3]
90% UO_2–10% AISI 316 L	DTA	≤ 1500	this work
90% UO_2–10% AISI 316 L	≤ 2 h, quenching furnace	1500, 2000	this work
90% UO_2–10% AISI 316 L	arc melting	2600	this work
90% UO_2–10% AISI 316 L	induction heating	2830	this work

samples and equivalent amounts of Al_2O_3 as the reference were heated in Al_2O_3 crucibles with heating rates between 1 and 10 K/min. The temperature of the instrument was calibrated with the melting points of gold (T_m = 1064.4°C) and nickel (T_m = 1455.2°C). The accuracy of the temperatures was estimated to be ± 1.0°C.

Two compacted UO_2–AISI 316 L stainless steel specimens were annealed in a quench furnace (Bühler, Bodelshausen) under high vacuum up to 2 h at 1500°C and 2000°C, resp. The pellet geometry was preserved during heating. The temperatures were measured by a quotient pyrometer. At the end of the heating process, the molybdenum cage containing the specimens was dearrested to fall down into a liquid Ga–In bath.

High frequency induction heating was chosen for the melting experiments of UO_2–AISI 316 L stainless steel in the monotectic temperature region. The generator with 50 kW induction power at 350 kHz frequency (EMA, Hirschhorn) allowed HF-heating with small heat capacities, that is easy to control up to high temperatures. Other advantages of this method are the arrangement and events that can be observed outside and inside the graphite crucible including temperature measurements at its surface. The temperatures were measured by a recording photocell quotient pyrometer and a visual null-point pyrometer. The temperatures were corrected for differences between the center and the surface of the crucible by a no-load test and for protection glass and lens absorptions. Details of these experiments are reported in Ref. [4].

The arc melting technique was used to heat UO_2–1.4970 stainless steel specimens in different compositions above 2850°C for some minutes [3]. The UO_2–63 mass% 1.4970 steel specimen (composition in Table 2) was selected for detailed X-ray microanalysis. A further UO_2–10% AISI 316 L steel specimen was heated in an arc melting furnace (Bühler; Bodelshausen) under reduced argon pressure at about 2600°C by repeated turnover of the button. This temperature was estimated by an arc melting experiment of molybdenum with the melting temperature 2623°C under identical conditions of electrical current.

Table 2
Composition of AISI 316 L and 1.4970 stainless steels used in the experiments

Steel	AISI 316 L		1.4970	
	mass%	mol%	mass%	mol%
Fe	65.1	65.2	66.0	66.1
Cr	17.3	18.7	14.7	15.8
Ni	12.2	11.7	15.1	14.4
Mn	1.9	1.9	1.9	1.9
Mo	2.5	1.5	1.3	0.8
Si	0.5	1.0	0.4	1.0
others	0.5	–	0.6	–

2.3. X-ray microanalysis

X-ray microanalysis was performed with the Camebax Microbeam instrument (Cameca, Courbevoie) by point analysis of all components, inclusive oxygen in the different phases. The measured X-ray intensities were converted to mass concentrations by a modern correction program.

3. Results

3.1. Steel melting temperature region

The solidus temperature of the AISI 316 L steel was observed by DTA at (1433 ± 1)°C; the liquidus temperature (high melting carbides and other precipitates are disregarded) was measured at (1447 ± 2)°C. No decrease of the solidus temperature of the steel was stated in equilibrium with UO_2. Hence, T_e = 1433°C is also the eutectic temperature of the degenerate UO_2–AISI 316 L steel system.

A UO_2–10 mass% AISI 316 L steel mixture was heated at 1500°C for 2 h under high vacuum and was quenched in a liquid Ga–In bath. Three phases were observed by metallography: steel, UO_2 and a second ceramic phase. Uranium and oxygen were not detected in the solidified steel melt, the concentration of these elements are below the detection limit of 0.02 mol%. Hence, the system is a degenerate eutectic with the eutectic composition $x_e > 99.98$ mol% steel. The maximum solubility of the steel components, mainly Cr with 0.22%, in UO_2 is 0.38 mol% steel at 1500°C, see Table 3. A second ceramic phase was observed in small amounts with the composition $(Cr_{0.58}Fe_{0.38}Mn_{0.02}U_{0.02})_2O_3$ which is formed from the

Table 3
Composition of the ceramic and metallic phases after different heat treatments specified in Table 2

Temperature (°C)	Phase	Concentration (mol%)							
		U	O	Fe	Cr	Ni	Mn	Mo	Si
1500	UO_2	33.1 ± 0.2	66.5 ± 0.2	0.1	0.22	0.03	0.02	0.01	0
	AISI 316 L	0	0	74	7	16	0	2.7	0
	$(Fe, Cr)_2O_3$	1	≈ 60	16	24	0	0.7	0	0
2000	UO_2	33.1 ± 0.2	66.4 ± 0.2	0.20	0.32	0	0	0.01	0
	AISI 316 L	0.03	0	58	1	27	0	(≤ 14) [b]	0
≈ 2600	UO2	33.4	66.0	0.17	0.34	0	0.09	0	0
	AISI 316 L	< 0.1	0.2	73	9	14	< 0.5	4	0
	$(Fe, Cr)_2O_3$	1	61	12	25	0.04	0.5	0.06	0
≈ 3000	UO_2	32.3 ± 0.7	65.0 ± 0.9	1.2 ± 0.3	1.6 ± 0.9	0.8 ± 0.3	0.2	0.1	0.1
	1.4970	2	0	66	16	14	0.7	1.6	0.4
	1.4970 [a]	2–14	0	48–55	19–42	6–13	≈ 2.2	≈ 0.1	≈ 0.5

[a] Small metallic precipitates within the UO_2 phase.
[b] Reaction of steel with the Mo cage.

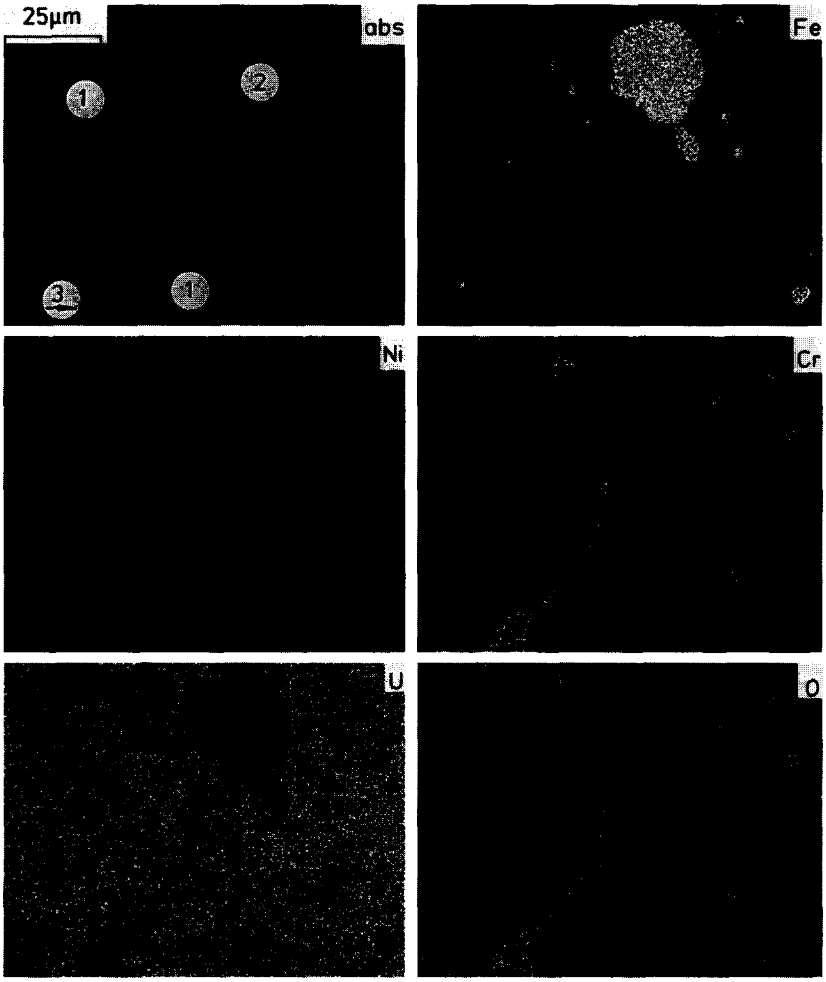

Fig. 1. Electron optical three-phase microstructure and element distributions of (1) UO_{2-x}, (2) Cr depleted steel and (3) (Fe, Mn, Cr) oxide precipitates of a UO_2–austenitic steel specimen annealed at 2000°C for 1.5 h.

steel components and oxygen released from the fuel which becomes hypostoichiometric above 1300°C; the composition is compiled in Table 3.

3.2. Solid UO_2–liquid steel region

A UO_2–10 mass% AISI 316 L steel mixture was heated at 2000°C for 1.5 h under high vacuum and was quenched in a liquid Ga–In bath. Three phases were observed: steel, UO_2 and a second ceramic phase. Element distribution images of the phases are illustrated in Fig. 1. The solidified steel melt contains 0.03 mol% U; it is enriched in Ni and strongly depleted in Cr. The maximum solubility of the steel components in UO_2, again mainly Cr with 0.32%, is 0.54 mol% steel at 2000°C, see Table 3. $(Cr, Mn, Fe)_2O_3$ or $(Cr, Mn, Fe)_3O_4$ was formed during heat treatment, however, this ceramic phase was not analyzed quantitatively in the metallographic section.

A UO_2–10 mass% AISI 316 L steel mixture incompletely arc melted at 2600°C yielded three phases: (1) the solidified steel melt containing < 0.1 mol% U and 0.2 mol% oxygen which are dissolved in the steel matrix, Cr is depleted; (2) the fuel phase containing about 0.6 mol% steel components; (3) a second ceramic phase with the composition $(Cr_{0.65}Fe_{0.31}Mn_{0.01}U_{0.03})_2O_3$ which again is formed from the steel components and oxygen released from the fuel; the composition is compiled in Table 3.

3.3. UO_2 melting temperature region

A UO_2–10 mass% AISI 316 L steel mixture was induction-heated up to the melting point of the prevailing phase as described in [4]. The melt was observed visually and acoustically and the melting point was registered by two pyrometers. The measured temperature is 2650°C to which +70°C were added for quartz glass and lens absorption. A further correction was made by $+(110 \pm 40)$°C for the temperature difference between the center and the surface of the crucible in a blank experiment. Boiling of the steel rich phase was not detected. The metallographic observation of a cut from the solidified melt evidenced two liquids. Hence, the system is monotectic in this temperature range with a monotectic temperature $T_{mon} = (2830 \pm 40)$°C, a maximum solubility $x_{max} = 0.6$ mol% steel in UO_2 extrapolated from lower temperatures and an estimated monotectic concentration $x_{mon} = (1 \pm 0.4)$ mol% steel. X-ray microanalysis was not performed on this specimen.

3.4. Liquid UO_2–liquid steel region

Arc melting experiments were made on several UO_2–1.4970 steel specimens in the range above the melting point of UO_2 ($T_m = 2847$°C [5]) at an estimated temperature of 3000°C. Melting was sustained for several minutes. The microstructure of the solidified two-phase melt was studied thoroughly. Semi-quantitative X-ray microanalysis was reported [3]. One specimen with the composition UO_2–63 mass% 1.4970 steel was selected for detailed X-ray microanalysis. Three phases were observed: (1) metallic ingots which are nearly identical in their composition with the initial composition of the steel; (2) the fuel phase which contains about 4 mol% steel components, primarily Cr with 1.6%; (3) tiny metallic precipitates in the UO_2 matrix with diameters up to 5 μm which contain uranium up to 14 mol% and steel components in varying compositions, but no oxygen. $(Fe_xCr_{1-x})_2O_3$ precipitates were not observed. The compositions of the phases are compiled in Table 3.

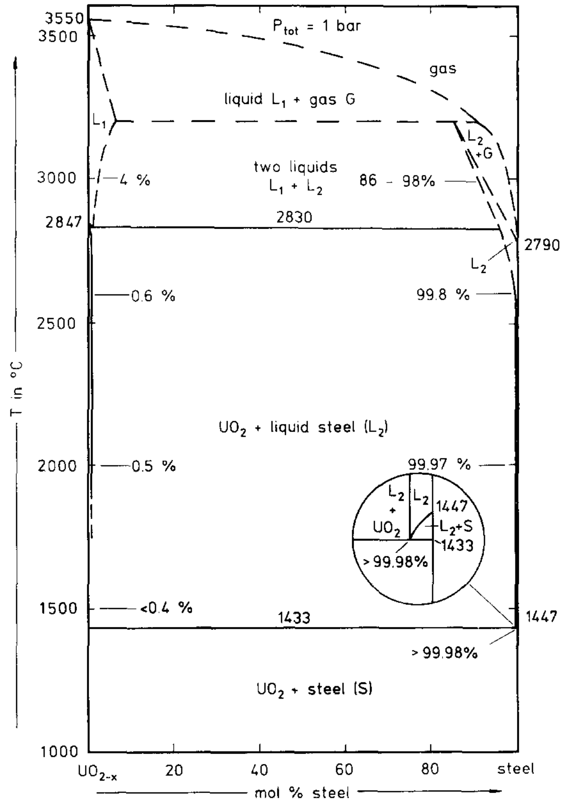

Fig. 2. Phase diagram of the pseudobinary UO_{2-x}–austenitic steel system.

The phase diagram of the UO_{2-x}–austenitic steel system based on these experimental results is illustrated in Fig. 2.

4. Discussion

UO_2 and austenitic steel form a degenerate eutectic on the steel side at 1433°C. Further, they form a monotectic at about 1 mol% steel and 2830°C, this temperature is slightly lower than the melting point of UO_2 at 2847°C [5]. The formation of a second ceramic phase (Fe, Cr, Mn, U)$_2$O$_3$ by reaction of UO$_{2+x}$ ($x \geq 0$) with steel can be understood with the relative partial molar Gibbs energy of oxygen in UO$_{2\pm x}$ [6] and in the Cr/Cr$_2$O$_3$ and Mn/MnO couples [7] which is illustrated in Fig. 3. UO$_2$ is reduced to O/U = 1.999 by oxidation of steel components at temperatures up to about 2600°C. The reaction is not possible above this temperature. The thermodynamics are in agreement with the experiment at about 3000°C where no steel oxides were observed, and at 1500°C, 2600°C and qualitatively at 2000°C where (Fe, Cr, Mn, U)$_2$O$_3$ precipitates were found. Fig. 4 characterizes schematically the three-phase field UO$_{2-x}$–Cr depleted steel–Cr$_2$O$_3$ in the pseudoquaternary system U–Fe$_{0.87}$Ni$_{0.17}$–Cr–O at 2000°C. The three-phase field develops from the UO$_2$–steel non-equilibrium.

The mutual solubility of UO$_2$ and steel increases with temperature. The liquid phases exist also above the boiling point of pure austenitic steel 1.4970 at 2790°C and 1 bar [8]. The steel melt is stabilized to higher temperatures by dissolution of elemental uranium; up to 14 mol% U in steel were observed at 3000°C. It is assumed that the melt decomposes peritectically into a liquid uranium rich (U, steel)O$_{2-x}$ phase and a steel rich gas phase at about (3200 ± 150)°C under 1 bar pressure.

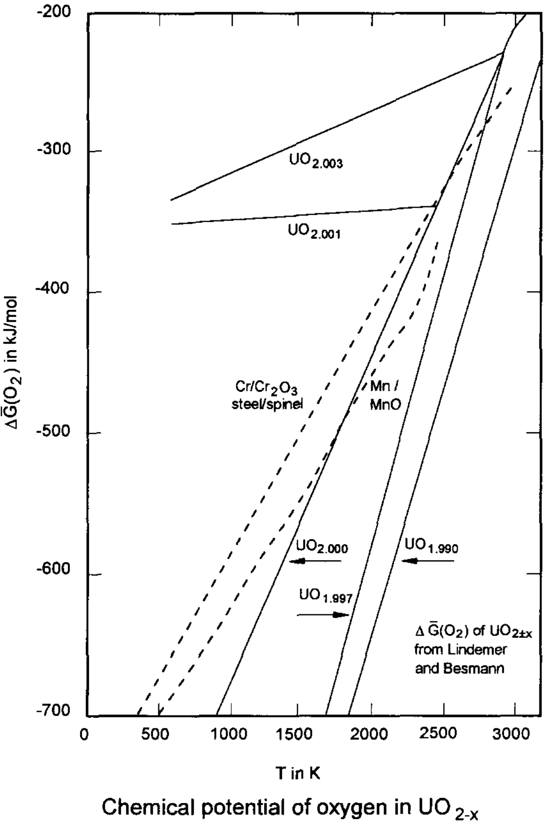

Fig. 3. Relative partial molar Gibbs energy of oxygen within the homogeneity range of UO$_{2\pm x}$ and of oxygen in the Cr/Cr$_2$O$_3$ and Mn/MnO couples [7,8].

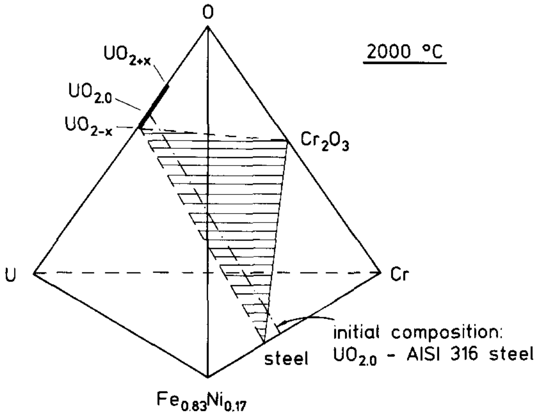

Fig. 4. Coexistence of UO$_{2-x}$, (Cr$_{1-x}$Fe$_x$)$_2$O$_3$ and Cr depleted steel in the pseudoquaternary U–Fe$_{0.83}$Ni$_{0.17}$–Cr–O system at 2000°C (schematic). The dash-dotted non-equilibrium line pierces the shaded three-phase field.

A mutual solubility of 4 mol% steel in UO$_2$ and 10 mol% UO$_2$ in steel at 3000°C was used to describe the liquid UO$_2$–liquid steel two-phase field by application of the Redlich–Kister model [9]. The parameters $A = 83$ kJ/mol and $B = -11$ kJ/mol of the model were adjusted to the experimental results of the phase boundaries at 3000°C and 1 bar, see Fig. 2. A total pressure of 2.5 bar resulted from the calculations on the basis of the experimental mutual solubilities. The model was further used to estimate the critical data for a continuous solution of the UO$_2$–steel melt. The critical temperature $T_c = 4900$°C, the critical mole fraction $x_c = 0.41$ of steel and the critical pressure $p_c = 300$ bar were obtained.

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