

Reinvestigation of Phase Relations in the CaO- UO_2 System

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Received December 17, 1984; in revised form July 2, 1985

Phase relationships in the binary CaO- UO_2 system were reinvestigated. In a carefully controlled reducing atmosphere the formation of binary compounds was not detected and only extensive solid solubility of CaO in UO_2 was observed. In controlled atmosphere in wet hydrogen, a perovskite, $\text{Ca}_2(\text{Ca}_{0.67}\text{U}_{0.33}^{4+})\text{U}^{5+}\text{O}_{5.83}$ is formed as the single binary Ca compound containing uranium in a 4+ valence state. © 1986 Academic Press, Inc.

Introduction

Phase equilibria in binary systems of uranium dioxide with group II metal oxides have not been subjected to detailed studies. Studies under carefully controlled conditions with a large number of samples covering the entire composition range are scarce. As a result, controversial results have been reported in some systems.

A CaO- UO_2 phase diagram was first reported by Alberman *et al.* (1). The authors found the eutectic temperature to be 2080°C at 45 mole% of UO_2 . An extensive solid solution of CaO in UO_2 was noted, ranging from 20 mole% CaO at 1650°C to 47 mole% CaO at the eutectic temperature. Two compounds, Ca_2UO_4 (tetragonal) and CaUO_3 (cubic, 1.0748 nm) were claimed to form below 1750°C. The existence of CaUO_3 was confirmed by Scholder and Brixner (2) and Bobo (3). On the other hand, Lang *et al.* (4), found only one compound in addition

to the solid-solution fluorite lattice in the CaO- UO_2 system. The compound was identified as an orthorhombic perovskite-type phase and was assigned the formula $\text{Ca}(\text{U,Ca})\text{O}_x$. These results have been challenged by Belle (5) who suggested that Lang's samples were partially oxidized.

Voronov and Sofronova (7) reported a UO_2 -CaO phase diagram with extensive solid solution only and without binary compounds. The eutectic was determined to be 2080°C at 55 mole% of CaO. The existence of CaUO_3 also has been denied by Tagawa (6). In view of the controversial published data, a reinvestigation of the UO_2 -CaO diagram was undertaken.

Experimental

Starting materials were CaCO_3 (Merck, extra pure) and UO_2 (nuclear grade). The powders were mixed in appropriate amounts in petrolether in an agate mill. The dried powders were pressed into pellets and calcined in a hydrogen atmosphere at 700°C. The calcined pellets were subsequently fired at various temperatures in hy-

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hydrogen. Extra care was taken to control hydrogen purity.

Commercial hydrogen gas (Elektro-bosna) was purified by passing through a Deoxo purifier (Heraeus, type D) and dried by passing through molecular sieves at liquid nitrogen temperature. By measuring the oxygen partial pressure with a ZrO_2/CaO solid electrolyte cell, it was established that purified hydrogen before drying contained 0.1–0.3% water vapor, whereas the dried gas contained below 0.001% H_2O vapor.

Samples were fired in a furnace with a Mo or W heater. To ensure a dry hydrogen atmosphere, the evacuated furnace was filled with pure dry hydrogen and heated to 500°C, to reduce nonstoichiometric UO_{2+x} . Thereafter the furnace was evacuated again and refilled with dry hydrogen. After repeating the same procedure at 800 and 1000°C, the temperature was raised to the final soaking temperature, where the samples were kept for periods of 1–7 days.

Melting points were determined in a furnace with a W heater by means of an optical pyrometer (Pyrowerke). Readings were calibrated by measuring the melting points of pure Pt and Al_2O_3 .

The phase composition after firing was determined by powder X-ray analysis. The microstructures of samples were analyzed by an electron microprobe (Cambridge Microscan 9) using UO_2 , CaSiO_3 , and CaUO_4 as standards.

Results and Discussion

X-Ray analysis of UO_2 -CaO compositions with molar ratios 1:1 and 1:2 after firing at 1000°C in wet hydrogen indicated a quantitative chemical reaction in the sample with a UO_2 :CaO ratio of 1:2, whereas in the sample with a UO_2 :CaO ratio of 1:1 components reacted only partially. Reaction products were identified as a perovskite phase $\text{Ca}_2(\text{Ca}_{0.67}\text{U}_{0.33})\text{UO}_6$ (8) and a UO_2 -CaO solid solution. The stoichi-

ometry of the calcium uranate phase was determined by firing in oxygen at 800°C, where Ca_2UO_5 is stable.

From the weight gain the composition of the perovskite phase was determined to be $\text{Ca}_2(\text{Ca}_{0.67}\text{U}_{0.33})\text{U}^{5+}\text{O}_{5.83}$ (9). The same nonstoichiometric composition was obtained by reducing Ca_2UO_5 in wet hydrogen at 850–1000°C (9).

Contrary to the experiments described above, firing of UO_2 -CaO in compositions of 1:1 and 1:2 in pure, dry hydrogen resulted in the formation of UO_2 solid solution (and CaO) only. It is therefore evident that the only oxocompound of U^{4+} and Ca is $\text{Ca}_2(\text{Ca}_{0.67}\text{U}_{0.33})\text{U}^{5+}\text{O}_{5.83}$ and that compounds with all U in a (+4) valence state do not exist. It is true, however, that the diffraction patterns of “ CaUO_3 ” and “ Ca_2UO_4 ” “compounds” (1) closely resemble the diffraction pattern of the perovskite phase (9).

Figure 1 represents the UO_2 -CaO phase diagram based on the results of this investigation. The eutectic composition at 63 mole% CaO melts at $1850 \pm 20^\circ\text{C}$. This value is considerably lower than the value reported in (1) (2080°C). The difference may be due to indirect temperature measurements in (1), i.e., by the power input to the furnace. Electron microprobe analysis

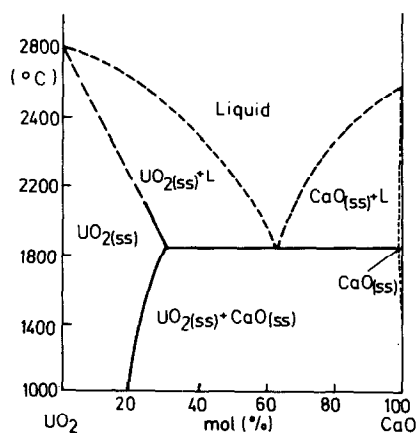


FIG. 1. UO_2 -CaO phase diagram.

revealed maximum solubility of CaO in UO_2 30 mole% and UO_2 in CaO 0.35 mole%.

The stoichiometry of the UO_2 -CaO solid solution, prepared in dry hydrogen, was checked also by reoxidizing 33 mole% CaO-67 mole% UO_2 compositions in oxygen at 800°C. Under these conditions, the stable oxidised product is CaU_2O_6 (10). From the weight gain, the composition of the solid solution was found to be $\text{U}_{0.67}\text{Ca}_{0.33}\text{O}_{1.68}$, close to the expected value $\text{U}_{0.67}\text{Ca}_{0.33}\text{O}_{1.67}$. Deviation from the expected value may be due to (a) slight oxidation of the quenched sample and (b) the existence of a composition region in the fluorite CaU_2O_6 phase within the limits $\text{CaU}_2\text{O}_{5.94}$ - $\text{CaU}_2\text{O}_{6.05}$ (10).

Conclusions

1. The UO_2 -CaO phase diagram, determined in pure, dry hydrogen, shows only solid solubility, up to 30 mole% CaO in UO_2 and up to 0.35 mole% of UO_2 in CaO. Binary compounds are not formed in dry hydrogen.

2. In wet hydrogen (0.1% water vapor), the perovskite $\text{Ca}_2(\text{Ca}_{0.67}\text{U}_{0.33}^{4+})\text{U}^{5+}\text{O}_{5.83}$

phase with $\frac{1}{4}$ of uranium in a 4+ valence state is formed.

Acknowledgment

The authors gratefully acknowledge the financial support of the Research Council of Slovenia.

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