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Metal alloy particles in spent nuclear fuel

This memo is intended to provide additional information concerning the occurrence of metal alloy particles in spent nuclear fuel. In particular, the aim is to provide the following:

1. A detailed description of the occurrence of the Mo-Tc-Ru-Rh-Pd alloy in spent nuclear fuel, including the radial distribution and particle size distribution.
2. A detailed account of long-term stability of the alloy.
3. A detailed description of the effect the formation of the alloy has on the oxidation state of the spent nuclear fuel

1 The occurrence of the 5-metal alloy

Certain fission products formed through ^{235}U or ^{239}Pu fission in reactors have low affinity for oxygen, which is expressed quantitatively through the relatively high oxygen potential of the metal/oxide system. The oxygen potential of a metal/oxide system is the partial molar free energy of oxygen in equilibrium with the metal/oxide system at the given temperature. Thus the oxygen potential of the spent fuel is the partial molar free energy of oxygen in equilibrium with the fuel. In a so-called Ellingham diagram (e.g. Fig. 2 in Kleykamp 1985), the oxygen potentials of various metal/oxide systems are plotted as a function of the temperature. Certain metal/oxide systems, as Ag, Pd, Rh, Ru, Te, Tc, Sb, Cd, In and Sn have oxygen potentials which are higher than that of UO_2 containing various amounts of Pu. These fission products are then expected to exist in metallic form in the fuel matrix. The atoms of these fission products are produced in fission events and through thermal diffusion meet other atoms which also are in metallic form (due to their low affinity for oxygen, expressed by high oxygen potential) and form metallic particles. The diffusion is more intense in zones with high temperature, thus in the central part of the fuel pellet the metallic particles are larger, while at the rim of the pellet, where the temperature is lower, they are extremely small. Fuels which have been operated with high linear heat ratings reach higher temperatures and metallic particles are larger in such fuels. For normally run LWR fuels, centre temperatures rarely exceed $1200\text{ }^\circ\text{C}$, hence the metallic particles are usually less than a micron in diameter, even in the hottest central part of the pellet. Direct detection of sub-micron metallic particles is not possible with SEM (Scanning Electron Microscope) and the same holds also for their analysis by EPMA (Electron Probe Micro Analysis). Thus Kleykamp (1990) states that "The composition and the radial dependence of the metallic Mo-Tc-Ru-Rh-Pd phases could not be measured in the usual quantitative manner, because they were precipitated in the $1\text{ }\mu\text{m}$ diameter range due to the moderate linear heat ratings and low temperatures, respectively, though the burnup was rather high". However, by producing platinum-carbon replicas of the fuel surface, Hastings et al. (1976) were able to extract and analyze metallic particles about $0.2\text{ }\mu\text{m}$ in diameter by using SEM. Kleykamp et al. (1985) performed x-ray microanalysis of micro-drilled FBR(Fast Breeder Reactor) fuel and of fuel residues after dissolution in 7- 10 M HNO_3 , determining their chemical composition by EPMA and lattice parameters by XRD (X-ray Diffraction).

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Only using TEM (Transmission Electron Microscope), it is possible to detect such small particles and a few studies which report metallic particle detection are discussed below.

Thomas and Günther (1989) reported TEM analysis of 2 PWR and one BWR fuel samples with burnups in the 31-34 MWd/kg U range and low fission gas release. Near the outer edge of the fuels up to mid-radius, extremely fine scale intra- and inter-granular precipitation was observed. Particles and bubbles within UO₂ grains ranged in size from only 1 to 8 nm and were distributed uniformly in particle-bubble pairs. The smallest observable particles and bubbles were at the resolution limit for imaging. All particles large enough for analysis were composed of an ϵ -Ru phase alloy. The intra-granular particles were too small for analysis, but were believed to be (based on analysis of larger particles) also ϵ -phase. At the pellet centres 50-100 nm intra-granular ϵ -phase particles are reported, while at the grain boundaries ϵ -phase particles up to 1000 nm (1 μ m) are reported.

Thomas et al. (1992) report TEM analysis of LWR fuels of burnup 44 and 48 MWd/kg U. Particles of metallic precipitates of spherical shape and 10-100 nm in size were detected in the ring stretching from the rim to pellet mid-radius, both in the grains and grain boundaries. The particles are ϵ -phase alloy hexagonal (hcp) phase. Near the pellet centre the metallic particles were 20-100 nm in size for one of the fuels which experienced relatively low (900 °C) maximal temperatures, while for the fuel which had maximal temperatures of 1700 °C in the centre, the metallic particles were 3000-10000 nm. Auger analysis revealed enrichment of the surface of intra-granular precipitates in Ag and Pd. These elements constitute very small α -phase particles of fcc symmetry, typical for FBR (Fast Breeder Reactor) fuels. Thomas et al. (1989) also report high density of small particles and bubbles 5 to 10 nm in diameter in grain interiors, while ϵ -particles at grain boundaries were about 30 nm in diameter. EDS (Energy Dispersive X-ray Spectroscopy) analysis showed typical composition of ϵ - particles.

Matzke et al. (1989) report local microstructure of a UO₂ fuel of 24.4 MWd/kg U burnup and subject to a transient test with high power rating (44 kW/m) during 24 hours. Near the fuel periphery a high density of metallic precipitates (up 10^{16} cm⁻³) and less than 8 nm in diameter are observed.

Ray et al. (1992) report TEM examination of a UO₂ fuel base irradiated to 4.5% burnup at maximum 260 W/cm linear power, which had been further subject to power increases up to 420 W/cm for 60 hours. The base irradiated fuel had a uniform population of very small fission gas bubbles with average diameter 8 nm, linked to metallic precipitates with the same size distribution. The average bubble-metallic precipitate density was $1.2 \cdot 10^{16}$ cm⁻³ at the periphery and $1.9 \cdot 10^{16}$ cm⁻³ at the pellet centre. After the power transient, spherical metallic particles of Mo, Pd, Tc, Ru, Rh ranging in size from 10 nm to 0.5 μ m could be observed at the fuel centre.

Kleykamp (1990) and Adachi et al. (1990) performed dissolution studies of PWR fuels in nitric acid and analyzed the properties of insoluble residues. Kleykamp (1990) reports the mass of residues following dissolution in nitric acid as 0.6 % of the fuel and the residue fraction to increase faster than proportional with burnup. Adachi et al. state "Noble metal FPs such as ruthenium, rhodium and palladium are expected to exist as metals in low oxygen potential atmospheres and form metallic precipitates in the matrix UO₂ phase. These metals together with Mo and Tc are apt to form a hexagonal ruthenium alloy, which is difficult to dissolve in nitric acid solution when it forms a large particle". The absence of observation of oxide hydrates of noble metals reported by Kleykamp (1990) is explained by Adachi et al. (1990) by the use of less concentrated nitric acid (3 M instead of 7 M) and shorter acid contact times (3 h instead of 5 h).

Cui et al. (2012) extracted metallic particles by non-oxidative dissolution of the UO₂ matrix via complexation with hot phosphoric acid and performed EXAFS, SEM and TEM analyses, detecting particles a few nanometres in size of a well ordered homogeneous alloy of pure metals.

In summary, the metallic precipitates formed in fuel are usually a hexagonal ϵ -phase alloy containing mainly Mo, Ru, Tc, Rh, Pd. In FBR fuels at higher temperatures, Pd rich cubic α -phase formation is also reported. The particle sizes detected by TEM are 1-8 nm at the rim and the particles become

larger when fuel temperatures becomes higher, e.g. towards fuel centre or if the fuel is ramped. At the rim of the fuel pellet, differences in metal particle composition due to the different Pu fission yields are also reported (Cui et al. 2012, Adachi et al. 1990). With increased burnup, the yield of the components of metallic particles increases and the amount of metallic particles also increases. From the yield of fission metal particles during nitric acid dissolution, it can be deduced that a large part of these particles are extremely small (a few atoms), hence easily dissolved by the acid.

2 Long term stability

Due to their high content of noble metals, ϵ -particles are resistant to water corrosion. They resist also dissolution by concentrated nitric acid and are discussed to be used as a potential waste form (Crum et al. 2013). The release of the various metal components from synthetic inactive metal particles was reported to be proportional to the metals oxidation potentials, i. e. the metals are released from the particles as Mo>Tc>Ru>Rh>Pd (Cui et al. 2001). Tests of metallic particles extracted from fuel by dissolving the UO₂ matrix in phosphoric acid in presence of Ar+10% H₂ indicated very low releases of all metal components and a reduction of oxidized states of Mo, Tc and U (Cui et al. 2004). Hence the metallic particles are expected to be stable towards dissolution as compared to the fuel matrix also under reducing conditions.

On the other hand it is well known that noble metal catalysts, as e.g. Pd are poisoned by dissolved sulphide ions in the water solution. Sulphide ions form strong surface complexes with the metal surface (Chaplin et al. 2012, Angeles-Wedler et al. 2010). The effect of sulphide ions on radiation-induced dissolution of spent fuel has been investigated by the use of simplified model systems (Yang et al. 2013). The reaction between sulphide and hydrogen peroxide is rapid; and three to four hydrogen peroxide molecules are consumed per oxidized sulphide. Experiments with gamma radiolysis in the presence of sulphide show that release of radiolytically oxidized uranium decreases with the concentration of sulphide in solution. Sulphide also reduces uranium (VI) in anoxic solutions. The effect of sulphide on uranium (VI) reduction by noble metal particles in the presence of hydrogen shows that sulphide does not affect the rate of reduction of uranium (VI) by the palladium-hydrogen system. No poisoning of the palladium catalyst can be detected in the presence of relatively high concentrations of sulphide (1 mM). According to Yang et al. (2013), this may be due to the high concentration of dissolved hydrogen, which causes desorption of sulphide from the palladium surface.

The fact that sulphide reacts quickly with hydrogen peroxide also means that the small quantities of sulphide ions that may be present in the groundwater after its contact with copper and iron surfaces of the canister, cannot reach the fuel surface as long as it is producing hydrogen peroxide. This is the case assumed in SR-Site model with an oxidative dissolution rate in the interval 10⁻⁸ to 10⁻⁶/year. However, most of the experimental data show no evidence of oxidative dissolution and in case all peroxide and other radiolytic oxidants are neutralized by hydrogen, sulphide ions can reach the fuel surface and the metallic particles, thus poisoning them by building a Pd-sulphide layer. Extensive sulphide corrosion has been observed in metallic particles from the Oklo site in Gabon (Utsonomiya and Ewing 2006). If this happens with a few thousand years old fuel, experimental data show that under inert atmosphere (N₂) one ppm sulphide is sufficient to neutralise completely the oxidative dissolution of alpha doped pellets simulating a few thousand years old fuel (Ollila 2006). The alpha doped pellets used in the study contained no metallic particles, but sulphide is a reductant which counteracts successfully the oxidative dissolution of the doped pellets. Further, hydrogen peroxide or hypochlorite are used to regenerate Pd-catalysts poisoned by sulphide (Schüth et al. 2004, Munakata and Reinard 2007, Chen and Huang 2013, Wang et al. 2004). In case the radiation field of spent fuel is still high and some sulphide poisoning of the metallic particles occurs, if no other mechanisms contribute to hydrogen activation, the produced radiolytic oxidants should create oxidizing conditions at the surface. Oxidizing conditions at the fuel surface imply that all sulphide will be consumed and the catalyst surface will be regenerated.

In summary the epsilon particles are resistant to water corrosion both under oxidizing and reducing conditions. Sulphide poisoning of Pd is reported not to take place in presence of high hydrogen and

sulphide concentrations. Sulphide corrosion is possible under reducing conditions at the fuel surface, i. e. when the radioactivity of fuel has decayed to negligible levels, as indicated by Oklo data. Given the extremely low solubilities of most metal sulphides, sulphide corrosion does not contribute to releases of ϵ -particle components. Sulphide is a reducing species and it has been shown that at ppm level it counteracts successfully the radiolytic dissolution of a few thousand years old fuel.

3 Effect on oxidation state of the spent fuel

The oxygen content, normally denoted by the O/U ratio for UO₂ fuel and O/M ratio for MOX fuel, is a very important parameter because many fuel properties, as e.g. thermal conductivity, depend on it. The oxygen content of the fuel is related to the oxygen potential of the fuel, which is the partial molar free energy of oxygen $\overline{\Delta G_{O_2}}$ at equilibrium with the fuel. The oxygen potential during pellet fabrication is imposed by the gaseous mixture in the sintering furnace (H₂+1% vol H₂O) to \sim -450 kJ/mol. During irradiation in the reactor, the oxygen content in the fuel increases, because the fission products with valences lower than 4 produced by fission of U and Pu atoms cannot bind all oxygen atoms previously bound to U and Pu. Kleykamp (1985) reports a decrease of the Mo content in metallic particles of FBR fuels, which is converted to Mo (IV) dissolved in the matrix to bind excess oxygen. This is based in the similarity of Mo/MoO₂ oxygen potential to that of slightly hypo-stoichiometric uranium-plutonium oxide fuel. Later, direct measurements of the oxygen potential of low (Une et al. 1991) and high burnup (Matzke 1994) fuels by the solid electrolyte technique confirmed the absence of fuel oxidation. The excess oxygen created during fission is fully neutralized by the oxidation of Mo in the metallic precipitates (Kleykamp 1985) and the inner surface of Zr cladding (Matzke 1995, Kleykamp 1990). Matzke (1995) states: "However, based on a careful X-ray microanalysis of both fuel and Zircaloy clad, Kleykamp (1979) predicted UO₂ fuel operated at high power, hence at high temperatures, to remain essentially stoichiometric since any excess oxygen due to possible hyperstoichiometry of the starting fuel or due to the above formation of excess oxygen by fission would diffuse to the clad and be gettered in a reaction layer". The extensive study of several fuels by Matzke (1995) indicated the oxygen potential of spent fuel changes only slightly from the fabrication value, independently of the burnup. The highest values measured coincide with the oxygen potential of the Mo/MoO₂ couple (\sim -400 kJ/mol), indicating the important role of this abundant fission product in buffering the oxygen potential of the spent fuel. Thus the distribution of Mo between metallic particles and dissolved in the UO₂ matrix as MoO₂ plays an important role in buffering the oxygen potential of the spent fuel. This role of Mo was confirmed recently by implanting Mo-ions in UO₂ and determining the oxidation state by XANES (X-ray Absorption Near Edge Structure). Molybdenum located at the grain boundaries was found both as metallic Mo (0) and at the Mo (IV) oxidation state dissolved in the UO₂ matrix (Martin et al. 2004).

In summary, the oxygen potential of the spent fuel changes only slightly from the fabrication value during fuel burnup in the reactor because of the buffering effect of the abundant fission product molybdenum. The excess oxygen created during fission of U and Pu is fully neutralized by oxidation of Mo in metallic particles to Mo (IV) dissolved in the fuel matrix and by the oxidation of a layer of the inner Zircaloy surface.

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