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SUBJECT: Explosion of EBWR Alloy in Boiling Concentrated Nitric Acid

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ABSTRACT

An explosion which occurred while dissolving EBWR core alloy (93.5% U-5.0% Zr-1.5% Nb) in boiling concentrated nitric acid is described.

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1.0 INTRODUCTION

On July 3, 1958, a chemist in the ORNL Chemical Technology Division received minor cuts when an explosion occurred while dissolving EBWR fuel alloy (93.5% U-5.0% Zr-1.5% Nb) in boiling concentrated nitric acid. This is believed to be the first case of an explosion of this alloy in nitric acid, and was totally unexpected since previous attempts to purposely produce such an explosion had failed.

Included below is a detailed account of the incident and a brief discussion of the possible cause.

2.0 DESCRIPTION OF THE INCIDENT

The experiment was being performed to determine the rate of dissolution of the EBWR fuel alloy in concentrated nitric acid. Apparatus for the experiment, which was assembled in a hood, consisted of a 100-ml Pyrex beaker which was clamped in place on a tripod and further supported by wire gauze. The beaker was heated with a Meker burner.

The first step in the experiment was removal with 9 M HF of the Zircaloy-2 cladding from a 12-g section of EBWR plate. The core alloy was then washed with 8 M HNO_3 and dissolved in 15.9 M HNO_3 for 73 minutes. The residual alloy was removed and left in air overnight (16 hr). The next morning, when the alloy was returned to refluxing nitric acid, the reaction was so vigorous that an attempt was made to remove the sample with long-handled, metal tweezers. At this point the explosion occurred.

The force of the blast shattered the beaker and sprayed glass and nitric acid over the interior of the hood. The chemist received a small cut on the right forearm and a second small cut on the chest from flying glass. The chemist's right arm and laboratory coat were also spattered with concentrated nitric acid. Immediate use of a safety shower prevented noticeable nitric acid burns. After treatment at the dispensary, the chemist returned to work.

All previous experiments with the EBWR alloy and nitric-acid were performed in a closed hood with an additional transparent shield between the hood window and the dissolver vessel. However, neither the hood window nor the shield were in place at the time of the explosion since the previous experiments had indicated that the alloy would not explode in nitric acid.

3.0 PREVIOUS EXPERIMENTS

Several previous experiments were performed to determine whether or not 93.5% U-Zr-Nb alloys formed explosive surface films on contact with nitric acid. For these tests both the actual EBWR core alloy, 1.5% Nb, and specially prepared alloys containing 1 and 2% Nb were used. Tests on the special alloys, prepared by the ORNL Metallurgy Division, were made with both annealed and quenched specimens. In these experiments, the specimens were dissolved in various concentrations of nitric acid until a thick, black surface coating had formed. The tendency of this coating to explode was determined by striking the alloy with a metal rod and/or sparking it with a Tesla coil. In no case was an explosion produced. However, in these experiments, the specimens were never in prolonged contact with air.

Several additional tests were made using HNO_3-HF mixtures as the dissolvent. Surface deposits were observed at mole ratios of fluoride to dissolved zirconium (F/Zr) of less than 4, but no explosions were produced.

In an experiment which simulated the one in which the accidental explosion occurred, an explosion was readily initiated with a Tesla coil after another piece of the same EBWR fuel plate was contacted with nitric acid for 30 minutes. This experiment was performed in a manner similar to those described above where no explosions occurred, and differed from that in which the accident occurred only in that the specimen was in contact with air for a very short time (1-2 minutes).

Formation of a surface coating has never been observed when the F/Zr mole ratio was greater than 4 in the absence of other metal ions. However, in a recent experiment,[1] an explosion occurred at a F/Zr ratio of 4.3. In this experiment, the fluoride was very dilute (0.076 $\underline{M}$) and complexed by equimolar quantities of aluminum ion, and the nitric acid was present in great molar excess (5.0 $\underline{M}$).

4.0 CONCLUSIONS

The potentially explosive surface deposit appears to be an intermetallic phase which dissolves much more slowly than does the matrix material. Prolonged exposure of the surface deposit to oxygen is not necessary for explosive conditions. Maintaining a F/Zr mole ratio of 4 may not prevent formation of an explosive surface deposit if other ions capable of complexing fluoride, e.g., Al^{+3} are present. Consequently, dissolution of the EBWR core alloy in nitric acid, in HNO_3-HF mixtures where the F/Zr mole ratio is less than 4, and in HNO_3-HF solutions containing additional ions which can complex fluoride, must be considered hazardous until further information is obtained. There is also some evidence that, although a F/Zr ratio of 4 is maintained in the absence of additional metal ions, large excesses of nitric acid can lead to the formation of explosive surface deposits.

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