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# PROCESS OF DISSOLVING ZIRCONIUM ALLOYS

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This application is a continuation-in-part of application Serial No. 327,656, filed December 23, 1952, now abandoned.

This invention deals with a process of dissolving zirconium alloys, and in particular binary zirconium-uranium alloys.

Zirconium alloys have many uses on account of their high corrosion resistance; for instance, they have been employed as construction material. In some instances the components of the zirconium alloys are to be recovered for reuse, and one way of approaching this problem is by dissolving the alloy and then recovering the metals individually by chemical or physicochemical methods. One other use of zirconium alloys, and more specifically of zirconium-uranium alloys, is in fuel elements of certain neutronic reactors. Also, in this case, it is desirable to separate the components of the irradiated fuel elements, and dissolution of the fuel elements is necessary for this purpose.

Heretofore dissolution of binary zirconium-uranium alloys has been carried out with aqueous hydrofluoric acid; it was considered necessary to use at least 6 moles of hydrofluoric acid per 1 mole of zirconim. However, dissolution by this process was not complete since uranium tetrafluoride was always obtained in the form of a precipitate. This drawback was overcome heretofore by the use of a strong oxidizing agent, such as alkali metal dichromate, in combination with the hydrofluoric acid whereby the uranium was oxidized to its hexavalent state and complete dissolution was accomplished. However, the combination of hydrofluoric acid and dichromate created serious corrosion problems.

It is an object of this invention to provide a process for the dissolution of binary zirconium-uranium alloys in which no highly corrosive materials are used, so that container materials, such as Monel metal, are not attacked.

It is also an object of this invention to provide a process for the dissolution of binary zirconium-uranium alloys by which a complete dissolution is accomplished without the formation of a precipitate.

It has been found that, if the quantity of aqueous hydrofluoric acid is kept close to the stoichiometric amount required with regard to the zirconium (4 moles of hydrofluoric acid per 1 mole of zirconium), complete dissolution of the zirconium and uranium is accomplished without the use of any oxidizing agent. The upper quantity limit for the hydrofluoric acid with which this highly desirable result is obtained is approximately a 10% excess of the stoichiometric quantity. Within this range, the excess quantity of acid is advisably varied in accordance with the uranium content of the alloy, the use of a lower excess being advantageous for a higher uranium content and vice versa. The alloys do not have to be disintegrated prior to dissolution and the whole fuel elements, for instance, can be dissolved by the process of this invention.



Satisfactory results have been obtained with hydrofluoric acid of concentrations ranging between 2 M and about 10 M. The acid can either be added in the proper concentration; or water can be first added to the alloy and concentrated 27 M hydrofluoric acid is then added in a quantity to obtain the proper concentration and amount. The time necessary for dissolving the massive alloys has ranged between 2 and 4 hours. Room temperature is operative, but elevated temperature of approximately 80° C. was found to accelerate the dissolving procedure.

In the following two examples are given illustrating the process of this invention without the intention to limit the invention to the details given therein.

*Example I*

A piece of binary zirconium-uranium alloy weighing 4 g. and containing about 1% by weight of uranium was immersed in 26.8 ml. of 10 M hydrofluoric acid; the zirconium was completely dissolved after about 12 minutes, but the solubility of uranium tetrafluoride was so low as to yield a concentration of 0.0022 M in $UF_4$. Immersion for a longer period of time did not increase the solubility of uranium. When 18.9 ml. of a 10 M hydrofluoric acid were added to a 4-gram piece of the same alloy, the solution obtained contained uranium tetrafluoride in a concentration of 0.014 M. The dissolution process in this instance was somewhat slower; it took about 4 hours. A clear green liquid was obtained. This total dissolution of 100% compares favorably with the run using the 26.8 ml. of hydrofluoric acid, where the molar ratio of HF:Zr was about 6, and less than 20% of the uranium was dissolved.

*Example II*

A fuel element subassembly for a neutronic reactor weighed 16,300 g., 139 g. of which was uranium; the remaining 16,161 g. was zirconium. This fuel element was immersed in 79 liters of water, and 30 liters of 27 M hydrofluoric acid were then added to the water. The fuel element was dissolved after several hours, and a clear solution was obtained.

The solutions obtained by the process of this invention may then be further treated for the recovery of the uranium and zirconium by methods known to those skilled in the art, for instance, by selective solvent extraction.

The process of this invention is satisfactory for zirconium-uranium alloys containing up to about 2% by weight of uranium. It has also been applied satisfactorily to ternary zirconium-uranium-tin alloys; in this instance the zirconium and uranium are also completely dissolved while the tin is found in a residue.

It will be understood that this invention is not to be limited to the details given herein but that it may be modified within the scope of the appended claims.

What is claimed is:

1. A process of completely dissolving zirconium and uranium from massive zirconium-base alloys containing uranium in an amount up to about 2% by weight based on the zirconium content, consisting of contacting said alloys with a solution consisting of water and hydrofluoric acid in a quantity of between stoichiometric amount and approximately 10% excess hydrofluoric acid over the amount stoichiometrically required, said hydrofluoric acid solution having a molarity between 2 M and about 10 M.

2. The process of claim 1 in which the quantity of hydrofluoric acid used is about that stoichiometrically required.

No references cited.