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# 合金元素及水化学对铝合金耐 腐蚀性能影响的研究

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# **The Effect of Alloy Elements and Water Chemistry on the Corrosion Resistance of Zirconium Alloys**

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**Major:** Materials Science

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## 答辩委员会对论文的评语

锆合金作为核燃料包壳材料，它的耐腐蚀性能直接影响着核电的安全性、可靠性和经济性。论文选题结合我国核电发展的需求，不仅有较高的学术意义，而且具有很好的现实应用前景。

作者采用各种方法，研究分析了  $\text{LiOH}$  高温水溶液明显加速锆合金腐蚀速度的现象，提出了新的机理。这一机理很好地解释了其他碱溶液、锂的盐溶液和熔融的  $\text{LiOH}$  并不能明显加速锆合金腐蚀速度的现象；也可说明锆合金在  $\text{LiOH}$  水溶液中腐蚀时吸氢量明显增加的原因。作者还研究了合金元素对锆合金在  $\text{LiOH}$  水溶液中耐腐蚀性能的影响，以及热处理制度对  $\text{Zr-Sn-Nb(Fe)}$  合金显微组织和耐腐蚀性能的影响，得出了一些很有价值的规律和结论，对今后发展新锆合金和优化锆合金的热加工制度都有指导意义。

论文书写条理清晰，文字流畅，内容丰富，数据真实可靠。对实验结果的理论分析与探讨有一定深度，答辩过程中回答问题正确。这些都表明了刘文庆同学具有扎实的理论基础与创新的研究能力。该论文是一篇具有较高实用价值和理论价值的博士论文。

## 答辩委员会表决结果

经答辩委员会表决，全票同意通过刘文庆同学的博士学位论文答辩，建议授予工学博士学位。

答辩委员会主席：**林栋樑**

2002年7月3日

## 摘 要

锆合金是水冷核动力反应堆中的燃料元件包壳材料. 无论从保障核反应堆的安全性、可靠性还是从核电的经济性考虑, 都对锆合金的性能提出了更高的要求. 特别是当要求降低核电的成本, 需要提高核燃料燃耗和延长核燃料的换料周期时, 改善燃料元件包壳水侧的耐腐蚀性能就变得尤为迫切. 由于压水堆一回路中采用添加  $\text{H}_3\text{BO}_3$ , 用  $^{10}\text{B}$  作可燃毒物, 所以需要添加  $\text{LiOH}$  调节 pH 值, 但添加  $\text{LiOH}$  后对锆合金的耐腐蚀性能产生有害作用. 近年来, 核材料专家们一直在努力提高锆合金在  $\text{LiOH}$  高温水溶液中的耐腐蚀性能. 本文作者主要在以下三个方面开展研究, 探索提高锆合金在  $\text{LiOH}$  高温水溶液中耐腐蚀性能的方法:

第一个方面研究了  $\text{LiOH}$  水溶液影响锆合金耐腐蚀性能的机理. 通过比较 Zr-4 合金样品在不同水化学条件下的耐腐蚀性能, 用扫描电镜(SEM)、扫描探针显微镜(SPM)和透射电子显微镜(TEM)等实验手段观察腐蚀样品氧化膜的内外表面形貌、显微组织和晶体结构, 用二次离子质谱(SIMS)测定相关离子在腐蚀样品氧化膜剖面上的分布. 得到以下结论: 锆合金在一定浓度  $\text{LiOH}$  高温水溶液中腐蚀时, 氧化锆的生长是一个  $\text{OH}^-$  从膜的外表面向内扩散, 并与锆反应生成氧化锆的过程; 足够量的  $\text{OH}^-$  进入氧化膜与四方结构氧化锆中氧空位反应, 将加快四方结构氧化锆( $\text{t-ZrO}_2$ ) 转变为单斜结构氧化锆( $\text{m-ZrO}_2$ )的速度; 在  $\text{t-ZrO}_2$  转变为  $\text{m-ZrO}_2$  的过程中导致氧化膜中出现孔洞和裂纹, 孔洞和裂纹

的出现一方面松弛了氧化膜中的压应力, 另一方面破坏了氧化膜的完整性, 使氧化膜降低了保护能力. 所以锆合金在一定浓度的 LiOH 水溶液中腐蚀时, 腐蚀转折会提早发生, 转折后的腐蚀速度加快.

要使  $\text{OH}^-$  进入氧化膜, 与其对应的阳离子也应同时进入, 否则会因为阳离子堆积在氧化膜表面产生静电力的作用而妨碍  $\text{OH}^-$  进入氧化膜.  $\text{Li}^+$  半径较小, 容易进入氧化膜, 而  $\text{K}^+$  的半径远大于  $\text{Li}^+$  半径而难于进入氧化膜内层, 所以在 LiOH 水溶液中腐蚀时  $\text{OH}^-$  容易进入氧化膜, 而在 KOH 水溶液中腐蚀时  $\text{OH}^-$  难以进入氧化膜. 因此 KOH 水溶液对锆合金耐腐蚀性能的恶化作用没有相同浓度的 LiOH 水溶液大. 在压水堆一回路的冷却剂中用 KOH 代替 LiOH 来调节 pH 值是一种合理的选择.

在锆合金腐蚀过程中, 参加反应的虽然是  $\text{OH}^-$ , 被消耗的却是水分子. 熔融的 LiOH 中没有水分子, 因此过去没有观察到熔融的 LiOH 使锆合金腐蚀加速的现象.

第二个方面研究了合金元素对锆合金在 LiOH 水溶液中耐腐蚀性能的影响. 比较了几种合金的显微组织和它们们在 0.01M LiOH 高温水溶液中的耐腐蚀性能, 观察了腐蚀后氧化膜的内外表面形貌、显微组织和晶体结构, 重点讨论了  $\beta\text{Nb}$  和 Zr-Nb-Fe 第二相粒子对锆合金在 LiOH 水溶液中耐腐蚀性能的影响. 结果表明: 锆合金中 Sn 含量不宜太高, 过高的 Sn 含量会降低氧化膜中  $\text{t-ZrO}_2$  的含量, 使氧化膜中难以形成致密的阻挡层; Nb 元素含量应该不低于 0.4 wt%, 并应有一定量的 Fe 元素, 当有 Cr 元素存在时, Fe 元素含量还应该提高, 以保证得到足够多细小的 Zr-Nb-Fe 第二相粒子; 过多的 Cr 元素会与 Fe 元素形成密排六方结构的  $\text{Zr(Fe, Cr)}_2$  第二相, 减少 Zr-Nb-Fe 第二相粒子的

数量; Nb 的氧化物在 LiOH 高温水溶液中有一定的溶解度, 含 Nb 达 80 wt% 的  $\beta$ Nb 第二相粒子在 LiOH 高温水溶液中腐蚀时, 形成的氧化物被溶解后会破坏氧化膜的完整; 细小的 Zr-Nb-Fe 粒子可能通过保持氧化膜的完整性改善锆合金在 LiOH 水溶液中的耐腐蚀性能.

第三个方面研究了热处理制度对 Zr-Sn-Nb(Fe)合金显微组织和耐腐蚀性能的影响. 结果表明: Zr-Sn-Nb(Fe)合金经  $750^{\circ}\text{C}-0.5\text{ h}$  /冷轧/ $560^{\circ}\text{C}-10\text{ h}$  处理后的耐腐蚀性能最好, 其原因在于: 样品经过这样处理后, 基体  $\alpha$ Zr 中固溶的 Nb 含量较低( $<0.3\text{ wt}\%$ ), 并获得了细小的 Zr-Nb-Fe 第二相粒子, 后者对改善耐腐蚀性能尤为重要. 样品在最终  $560^{\circ}\text{C}$  加热处理之前的冷轧变形, 可以促进  $\beta$ Zr 分解时的形核, 是获得细小 Zr-Nb-Fe 第二相粒子的必要措施.

**关键词** 锆合金, 耐腐蚀性能, 显微组织, 第二相, 合金元素, 变形及热处理

## Abstract

Zirconium alloys have been used as cladding material for nuclear fuel in water-cooled nuclear power reactors, whose performances must be improved to ensure the safety and reliability of reactors and increase economical competition of nuclear electricity. Especially, the improvement of the waterside corrosion resistance of fuel cladding becomes instant because increasing burn-up and prolonging the fuel cycle are demanded for reducing the cost of nuclear electricity.  $^{10}\text{B}$  is taken as burnable poison, so that  $\text{H}_3\text{BO}_3$  is added to primary coolant in the pressurized water reactors (PWRs). To maintain pH value of the coolant,  $\text{LiOH}$  is added and the presence of  $\text{LiOH}$  appears to have a detrimental effect on the corrosion resistance of zirconium alloys. Nuclear material experts have been engaged in the research work for improving the corrosion resistance of zirconium alloys in  $\text{LiOH}$  high temperature aqueous solution for many years. To obtain this goal, three part research works have been done in present study.

In the first part, the mechanism that  $\text{LiOH}$  aqueous solution causes the accelerated corrosion of zirconium alloys was investigated by comparing the corrosion resistance of Zircaloy-4 specimens in different water chemistry, examining the morphology of oxide films at metal /oxide interface and on the surface by means of SEM and SPM, studying the microstructure and crystal structure of oxide films with TEM and determining the penetrations of  $\text{Li}^+$ ,  $\text{K}^+$ ,  $\text{OH}^-$ ,  $\text{Cl}^-$  into

the oxides by SIMS. The results indicated that when zirconium alloys were corroded in LiOH aqueous solution at high temperature with a certain concentration, the growth of oxide film is a process of  $\text{OH}^-$  diffusing from outside of oxide into interface and reacting with zirconium to form  $\text{ZrO}_2$  at the interface. During this process, the reaction between adequate  $\text{OH}^-$  and oxygen vacancy in the tetragonal zirconia would promote the transformation from tetragonal zirconia (t- $\text{ZrO}_2$ ) to monoclinic zirconia (m- $\text{ZrO}_2$ ). The transformation from t- $\text{ZrO}_2$  to m- $\text{ZrO}_2$  would bring some pores and cracks in the oxide and relax the compressive stress in the oxide and degrade the protective ability of oxide films by destroying the integrality of oxide films. So the presence of LiOH causes a reduction in the duration of the pre-transition stage and an enhancement of the corrosion rate in the post-transition stage of zirconium alloys.

$\text{OH}^-$  diffusing into oxide film would be accompanied by the corresponding cation, otherwise, it will be hard for  $\text{OH}^-$  diffusing into oxide due to static electric field caused by those cation piled up on the surface of oxidation film. It is more difficult for  $\text{K}^+$  diffusing into oxide film than  $\text{Li}^+$  because of its bigger radius, so the  $\text{OH}^-$  diffusing into oxide film will be less during zirconium alloys corroded in KOH aqueous solution. Therefore the degradation effect of KOH aqueous solution on the corrosion resistance of zirconium alloys is slight, and it is a reasonable choice to add KOH into the primary coolant of PWRs instead of LiOH to control the pH value.

It is water molecules that the corrosion reaction consumes, although  $\text{OH}^-$  takes part in the reaction during the corrosion process

of zirconium alloys. The corrosion rate would not accelerate observed in the past when zirconium alloys was corroded in melt LiOH because there was no water molecules in it.

The effects of alloy elements on the corrosion resistance of zirconium alloys in LiOH aqueous solution were studied in the second part. Firstly, the relationship between microstructure of the alloy specimens and their corrosion resistance in LiOH aqueous solution were investigated. Secondly, the microstructure and crystal structure of oxide films and the morphology of oxide films at metal /oxide interface and on the surface were examined. Lastly, the effects of  $\beta$ Nb and Zr-Nb-Fe second phase particles on the corrosion resistance of zirconium alloys in LiOH aqueous solution were discussed. Some results have been suggested: The contents of Sn in zirconium alloys should be lower, otherwise, the contents of t-ZrO<sub>2</sub> would be reduced, so it was difficult to form the compact barrier in the oxide; the contents of Nb should exceed 0.4wt% and there also should be enough Fe in the alloys for forming adequacy of fine Zr-Nb-Fe second phase particles when the alloys contained Cr. Adding Cr caused the formation of hexagonal Zr(Fe,Cr)<sub>2</sub> particles with Fe which might reduce the quantity of Zr-Nb-Fe second phase particles. Since Nb oxide is soluble in high temperature LiOH aqueous solution, the integrity of oxide films would be destroyed when  $\beta$ Nb second phase particles containing 80wt% Nb were corroded and dissolved parts in LiOH aqueous solution. The corrosion resistance of zirconium alloys in LiOH aqueous solution will be improved by fine Zr-Nb-Fe second phase particles containing in zirconium alloys

because which could help to the integrity of oxide films.

In the third part, the effects of heat treatments on the microstructure and corrosion resistance of Zr-Sn-Nb (Fe) alloys have been studied. The results show that the corrosion resistance of specimens treated by 750°C–0.5 h /C.R/560°C–10 h is the best among all specimens adopted in this work. It is concluded that a lower niobium concentration in solid solution in  $\alpha$ Zr matrix and a uniform distribution of fine Zr-Nb-Fe particles are important factors for improving the corrosion resistance significantly, especially, the later one is more important. The cold deformation before the final annealing at 560°C plays an important role in obtaining fine Zr-Nb-Fe particles because which can promote the nucleation during the  $\beta$ Zr decomposition.

**Key words** zirconium alloys, corrosion resistance, microstructure, second phase, alloy elements, deformation and heat treatment

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in the third part, the effects of heat treatments on the microstructure and corrosion resistance of Zr-20Nb-10Fe alloys have been studied. The results show that the corrosion resistance of specimens treated by  $730^{\circ}\text{C}-0.5\text{ h}$ ,  $760^{\circ}\text{C}-10\text{ h}$  is the best among all specimens adopted in this work. It is concluded that a lower niobium concentration in solid solution in  $\alpha\text{-Zr}$  matrix and a uniform distribution of fine Zr-Nb-Fe particles are important factors for improving the corrosion resistance significantly, especially, the latter one is more important. The cold deformation before the final annealing at  $760^{\circ}\text{C}$  plays an important role in obtaining fine Zr-Nb-Fe particles because which can promote the nucleation during the  $\beta\text{-Zr}$  decomposition.

Key words: zirconium alloys, corrosion resistance, microstructure, second phase, alloy elements, deformation and heat treatment

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