

MOSSBAUER SPECTROSCOPY OF ZIRCONIUM ALLOYS

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Zirconium is used in nuclear reactors as a construction material. In Russia, the most widely used alloys are such as E110, E125, E635 having the approximate compositions of Zr-1% Nb, Zr-2.5% Nb, Zr-1% Nb +0.35% Fe-1, 2% Sn, respectively. Abroad such alloys as Zircaloy-2 (Zr-1.2-1.7% Sn-0.07-0.2% Fe-0.05-0.15% Cr), Zircaloy-4, M4, M5 and NSF are used. Thus, in order to improve mechanical and corrosion properties of zirconium alloys they are modified with alloying elements as iron, tin, niobium, nickel, chromium, copper in varying amounts to 1.5 mas.% depending on country of manufacture and conditions of using. Iron and tin have the Mossbauer isotopes and therefore it is possible to carry out a study of their state and their influence on the properties of zirconium alloys by Mossbauer spectroscopy. One can study the state of the atoms in solid solutions and formed intermetallic compounds. The solubility of the iron atoms in the α -Zr is determined. It is 0.015 mas.% at 600 °C. The parameters of the Mossbauer spectra of the solid solution of iron atoms α -Zr at room temperature are $\delta = -0.10 \pm 0.02$ mm/s (isomer shift), $\Delta E = 0.32 \pm 0.02$ mm/s (quadrupole splitting) [1]. Studying of penetration of oxygen in solid solution of iron atoms in the α -Zr showed that the iron atoms leave the solid solution and form intermetallic compounds. This indicates that the iron atoms in the α -Zr are in a state solid solution, since the oxygen atoms form a solid solution taking places of the iron atoms.

With the help of Mössbauer spectroscopy it was experimentally demonstrated the formation of intermetallic compounds Zr_2Fe in the Zr-Fe alloys [2] ($\delta = -0.32 \pm 0.02$ mm/s, $\eta = 0$, $\Delta E = (0.60 \div 0.72)$ mm/s). Aubertin [3] carried out measurements in magnetic fields and stated that in binary Zr-Fe alloys in addition to Zr_2Fe the stable compound Zr_3Fe is formed, whose parameters of Mossbauer spectra differ only by the value of the quadrupole splitting and sign of the electric field gradient ($\delta = -0.32 \pm 0.02$ mm/s, $\eta = 0.6$, $\Delta E = -(0.75 \div 0.90)$ mm/s). Adding other elements (W, Ni, Cu) [4] leads to changing in the values of the quadrupole splitting, or in the case of Cr, Nb - both the values of the quadrupole splitting and isomer shift [5-12]. Reducing the electric field gradient at the ^{57}Fe nuclei indicates the formation of a mixed phase composition on the basis of ZrV_2 $ZrCr_2$ and with the substitution of atoms of vanadium and chromium atoms with iron atoms [7-9]. As to the alloys with niobium, there may be formation of intermetallic compounds of two types - $(Zr_{1-x}Nb_x)_2Fe$, with the spectra parameters ($\Delta E = 0.5 \div 0.75$ mm/s, $\delta = -(0.28 \div 0.34)$ mm/s) and $(Zr_{1-x}Nb_x)Fe_2$ with a smaller quadrupole splitting ($\Delta E = (0.20 \div 0.51)$ mm/s, $\delta = -(0.16 \div 0.28)$ mm/s). During heat treatment the iron atoms in alloys tend to move to the surface and enrich the surface layer of the intermetallic particles. In thin layers (0.1 mm) this

enrichment can reach 5 mas.%, with the initial concentration 0.35mas.% Fe in alloy. Effect of laser irradiation on the enrichment of the surface layers manifests itself differently for the annealed and deformed samples. The reason for this behavior of the iron atoms can be explained both the fast diffusion of iron atoms and the presence of defects in deformed samples of the alloys. In alloys containing iron, tin, and chromium atoms it is found the conversion of one type of intermetallic particles to another type in the surface layers even at room temperature [10]. Irradiation of the surface of zirconium alloys by argon ions leads to the changing of ratio of intermetallic compounds concentrations in near surface layers [12]. The changes were detected for all investigated samples of E635, NSF and Zircaloy-2 alloys. In particular for cold deformed NSF alloy relative increase of compound $(Zr_{1-x}Nb_x)Fe_2$ is noticed. Relative changes of concentration Zr_3Fe in near surface layers aren't observed. For specimens of Zircaloy-2 alloy after the ionic irradiation the substantial growth of concentration of compound with nickel near surfaces of the sample is revealed, i.e. the concentration of $Zr_2(Fe,Ni)$ compound increases and the concentration of $Zr(Fe,Cr)_2$ (C14) decreases.

With regard to the state of tin, which concentration in alloys is 0.5-1.3 mas.%, most researchers find it in the form of a solid solution of Sn atoms in α -Zr and with parameters of Mössbauer spectra $\delta = 1.72 \pm 0.04$ mm/s, $\Delta E = 0.32 \pm 0.02$ mm/s (relative to $BaSnO_3$). In the ternary alloys with Fe and Nb after quenching the lines of β -Sn and compounds Nb_3Sn are visible. Formation of β -Sn is explained due to the occurrence of oxide films on the surface of the quenched samples. In oxide films the particles of metallic tin are formed, which go into α -Zr solid solution in the process of thermal treatment once again.

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