

Basic principles of creating a new generation of high-temperature brazing filler alloys

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Abstract. The development of new materials is based on the formation of a structural-phase state providing the desired properties by selecting the base and the complex of alloying elements. The development of amorphous filler alloys for a high-temperature brazing has its own features that are due to the limited life cycle and the production method of brazing filler alloys. The work presents a cycle of analytical and experimental materials science investigations including justification of the composition of a new amorphous filler alloy for brazing the products from zirconium alloys at the temperature of no more than 800 °C and at the unbrazing temperature of permanent joints of more than 1200 °C. The experimental alloys have been used for manufacture of amorphous ribbons by rapid quenching, of which the certification has been made by X-ray investigations and a differential-thermal analysis. These ribbons were used to obtain permanent joints from the spacer grid cells (made from the alloy Zr-1% Nb) of fuel assemblies of the thermal nuclear reactor VVER-440. The brazed samples in the form of a pair of cells have been exposed to corrosion tests in autoclaves in superheated water at a temperature of 350 °C, a pressure of 160 MPa and duration of up to 6,000 h. They have been also exposed to destructive tests using a tensile machine. The experimental results obtained have made it possible to propose and patent a brazing filler alloy of the following composition: Zr-5.5Fe-(2.5-3.5)Be-1Nb-(5-8)Cu-2Sn-0.4Cr-(0.5-1.0)Ge. Its melting point is 780 °C and the recommended brazing temperature is 800°C.

1. Introduction

The development of new materials and the improvement of the existing ones is a complex process, of which the purpose or the main task is the directed formation of an element composition, a phase state and a structure in the volume of a material and (or) in its surface layers, i.e. formation of a predetermined structural-phase state (SPHS). At that, an important task is to ensure the stability of this state in the operating conditions of the material (the product) [1].

The development of materials for a specified product is based on an analysis of the operating conditions of the product in the construction under development, an analysis of a single-item and combined action of structural components of the product, determination of a manufacturing technology of individual parts and the construction in general, knowledge of the achievements in the corresponding field of materials science.

An analysis of all these factors ends by formulation of characteristics of the developed material and drawing up requirements to the main and auxiliary properties of the developed material.

The development of such functional materials as high-temperature brazing filler alloys has its own features that are due to the limited life cycle and the production method. Solders obtained by rapid



quenching of the melt are called rapidly quenched filler alloys (RQFA). At present, rapidly quenched filler alloys in the form of ribbons with a thickness of 20-80 μm have become widely used in mechanical engineering. Such filler alloys are obtained by ultrarapid quenching of the melt on a rotating disk-refrigerator with a cooling rate of 10^4 - 10^6 K/s. The high cooling rate allows obtaining brazing filler alloys at room temperature with the structure of a supercooled liquid and in the state of a supersaturated solid solution with a uniform distribution of the alloy components over the entire volume, which determines the unique properties (wettability, capillary activity, etc.) of the filler alloy in the process of melting and interaction of the melt with the brazed materials [2].

Features of the application of brazing filler alloys determine the requirements for the structural-phase state of alloys to ensure an amorphous or nanocrystalline state, and chemical and microstructural homogeneity as they determine narrow temperature ranges of melting, a high diffusion activity of atoms, an increased capillary and adhesion activity and an increased flowing of the melt into the gap for providing a high strength and corrosion resistance of the brazed joints, especially for creating permanent joints of dissimilar materials, dispersion-strengthened alloys and steels, beryllium, refractory metals, solid alloys, ceramics, graphite and others [1, 3].

On the example of practical application of RQFAs in the energy-intensive techniques, for example, for the manufacture of the first wall and the divertor of ITER, rocket engine nozzles, the fuel elements of nuclear reactors, it is shown that profound studies of the structural-phase state of developed RQFAs at every stage of their life cycle: developments, manufacture and application, are necessary to ensure the operability of important units. The step of producing alloys at fast (10^4 - 10^6 K/s) quenching rates is crucial for obtaining a homogeneous distribution of components in the alloys with complex composition. Not only the brazing temperature, but also the brazing time requires deep justification in the process of forming a permanent joint [4-7].

In this context, the aim of this report is to present the fundamental materials science investigations that made it possible to obtain specified structural-phase states of both the RQFAs themselves and in the zones of permanent joints of metals and dissimilar materials on the example of development of a new amorphous filler metal based on zirconium alloys.

2. Basic requirements to the properties of the brazing filler alloy

The requirements are determined by the appointment of a brazing filler alloy. For example, the fuel elements and other details of fuel assemblies of the thermal neutron reactor active zone must meet the following basic requirements for a high-temperature brazing of details made from zirconium alloys [8]:

- the brazing filler alloy must be compatible with brazed materials, i.e. not to induce a significant chemical erosion and not to form chemical compounds;
- it must have a low melting point and a small brazing time to prevent the formation of intermetallic compounds in the brazed seam and changes of the structural-phase state of brazed materials; with respect to this work, the brazing temperature should be below the temperature range of the existence of a two-phase area in zirconium alloys, i.e. the melting point of the alloy should be below 800°C and, in this case, the brazed alloy should be in a single-phase area during the brazing;
- the brazed joint should have an unbrazing temperature no less than 1200 °C (this is a stability condition of the fuel assembly at a complete loss of the coolant, accidents of the LOCA type - Loss of Coolant Accident);
- should have a minimum thermal-neutron capture cross-section and an absence of the formation of relatively long-lived radioactive nuclides;
- must provide a corrosion resistance of the brazed product and the brazed seam for the entire operation period (3-6 years);
- should provide a predetermined resistance of the brazed seam to radiation creep;
- must provide a production of a brazing filler alloy in the amorphous state.

3. Principles of the choice of the composition of zirconium brazing filler metals

The developed alloy should have such a composition and a structural-phase state that will provide the required level of properties and characteristics. Studying the experience of the development of brazing filler metals based on zirconium showed that the following compositions and brazing temperatures were tested in experiments: (80–91)Zr–(5.5–15)Fe–1.5Ge–(1–3)Cr–2.5Be (the brazing temperature is 960–1030 °C), Zr–12.5Cu–2.5Be (brazing at the temperature of 1130 °C), Zr–5Be (the brazing temperature is 965 °C) and others [8]. The main disadvantage of the developed brazing filler metals is their high brazing temperature resulting in a significant oxidation of the brazed seams during tests in reactor conditions.

When selecting the alloy composition, a classic scheme of synthesis containing the following main stages was developed:

- choice of the alloy *base*, of which the state corresponds to the basic requirements to its properties;
- choice of *alloying elements* and identification of harmful impurities;
- choice of a *complex* and a composition of alloying elements with regard to all the requirements to the properties of the alloy;
- *obtaining* (smelting) of an alloy;
- obtaining of an amorphous ribbon by rapid quenching of the melt on the surface of a rapidly rotating disk-refrigerator;
- study of the structural-phase state and the temperatures of phase transformations of the resulting ribbon.

3.1. The choice of an alloy base and alloying elements

In materials science of brazing filler alloys for a high-temperature brazing, in choosing the alloy base it is oriented on known requirements to avoid changes of the state of brazed materials and formation of brittle intermetallic compounds in the brazed seam [9, 10]. In this case, the base element of the brazed composition should be selected as the base of a filler alloy and the filler alloy may include alloying elements of the brazed material. In addition, the experience of the development of filler alloys for brazing of zirconium was taken into account. Therefore, the composition Zr-Nb was selected as the base for the future brazing filler alloy.

Niobium has a number of positive properties, including the formation of a solid solution with β -phase of zirconium. Niobium dissolves in α -phase of zirconium at the monotectoid temperature in the amount of up to 1.5 wt.%, it has a small capture cross section of thermal neutrons, stabilizes the corrosion resistance of unalloyed zirconium, eliminates the harmful effects of small amounts of such impurities as carbon, aluminum and titanium, and effectively decreases the quantity of hydrogen absorbed by the zirconium alloy [11].

When developing the brazing filler alloy composition, two conjugated scientific and technical problems were solved in the first place. The first problem is the choice of the filler alloy composition with a minimum melting point, i.e. with a temperature less than 800 °C. The second one is improvement of the composition content to obtain an amorphous state by rapid quenching of the melt.

3.1.1. The choice of a composition with the minimum melting point

There are no alloys with the melting point less than 800 °C among the known two- or three-component systems based on zirconium. Therefore, the development of the composition of alloying elements was made with taking into account the compositions of existing commercial alloys (Nb, Sn, and Fe) and in the direction of creating a multi-component system with a melting point below 800 °C. Analyzing the composition of known filler alloys mentioned above, it can be seen that Fe, Ge, Cr, Be and Cu were used as alloying elements. In general, a preliminary chemical and physical analysis of potential alloying elements shows that Sn and rare-earth metals are of interest in addition to the above-mentioned elements [8].

Small quantities of iron insoluble in α -zirconium and present in the form of fine-dispersed crystals of intermetallic compounds increase the strength of a zirconium alloy. It should be noted that niobium and iron slightly lower the melting point of zirconium [11].

Beryllium greatly lowers the melting point of zirconium and forms a eutectic at a content of 5 wt. %. It has a low capture cross section of thermal neutrons. The data on the corrosion resistance of brazed joints obtained using brazing filler alloys of the system Zr-Be are ambiguous, but it is possible to increase their corrosion resistance by additional alloying elements [11].

Copper was chosen as a depressant, since it most strongly lowers the melting point of zirconium at a content of up to 8 wt.% and decreases the liquidus temperature of zirconium from 1860 to 995 °C at increasing the content up to 21 wt.%. The eutectic reaction $Lq \leftrightarrow CuZr_2 + \beta Zr$ occurs in the binary alloy Zr-Cu at the temperature of 995 °C [11].

To neutralize the possible influence of copper on the deterioration of the alloy's corrosion resistance and additionally strengthen the alloy, it was alloyed by Sn (2%) and Cr (0.4%).

The quantitative composition of the selected alloying elements was clarified in the process of the analysis of binary and ternary phase diagrams of the alloy systems.

The performed physicochemical analysis of alloys of the systems Zr-Be, Zr-Fe, Zr-Nb, Be-Fe, Zr-Cu, Zr-Be-Fe, Zr-Be-Nb, Fe-Nb-Zr and Zr-Fe-Nb-Be made it possible to choose optimal compositions and produce a pilot batch of alloys for the investigation of phase transformations and temperatures of liquidus and solidus. It was taken into account that the system Zr-Be has a eutectic $Lq \leftrightarrow Zr + ZrBe_2$ at the temperature of 965 °C, of which the composition is 95 wt.% (65.2 at.%) Zr and 5 wt.% (34.8 at.%) Be, the beryllium concentration of about 5 wt.% being optimal.

The system of Zr-Fe alloys has a eutectic $Lq \leftrightarrow \beta\text{-Zr} + Fe_2Zr$ at 934 °C. The liquid composition at the eutectic temperature is 16 wt.% Fe, Fe decreasing the polymorphic transformation temperature in zirconium to $735 \pm 5^\circ\text{C}$. The eutectoid concentration is 3.5 at.% Fe.

The system of Be-Fe alloys has two eutectic reactions at 1165 °C (the eutectic liquid composition is 8 wt.% Be) and 1225 °C (the eutectic liquid composition is 77 wt.% Be).

The following reactions are present in the system of Cu-Zr alloys in the copper content range of 0-20 wt. %: a) eutectic: $Lq \leftrightarrow \beta\text{-Zr} + CuZr_2$ at 995 °C (at the zirconium content in phases of 72: 94.7: 66.67 at.%) and b) eutectoid: $\beta\text{-Zr} \leftrightarrow CuZr_2 + \alpha\text{-Zr}$ at $882 \pm 10^\circ\text{C}$ (at the zirconium content in phases of 97.7: 66.7: ~ 99.7 at. %).

In the system of Zr-Be-Fe alloys, the alloys quenched from the temperature of 800 °C are still in a liquid-solid state and contain beryllium and iron in the following proportions:

Fe:Be = 4:1 (Be+Fe) \geq 3%, i.e. Be \geq 0.6% and Fe \geq 2.4%;

Fe:Be = 3:2 (Be+Fe) \geq 2%, i.e. Be \geq 0.8% and Fe \geq 1.2%;

Fe:Be = 2:3 (Be+Fe) \geq 1%, i.e. Be \geq 0.6% and Fe \geq 0.4%;

Fe:Be = 1:4 (Be+Fe) \geq 1%, i.e. Be \geq 0.8% and Fe \geq 0.2%.

From the performed analysis it follows that the eutectic composition of the alloy is approximately the following one: > 5 wt.% Fe and > 2.5 wt.% Be.

In the system of Zr-Nb-Be alloys at the temperature of about 855 °C, there is a eutectic equilibrium $Lq^7 \leftrightarrow \alpha^7_{Zr} + \beta^7_{Zr} + ZrBe_2$ at a composition of the point Lq^7 ~ 5 wt.% Be and ~ 1 wt.% Nb. Thus, there is one more confirmation of the concentration of ~ 1% Nb.

In the system of Zr-Fe-Nb alloys, the following reaction $Lq \leftrightarrow \beta\text{-Zr} + Zr_2Fe + T$ (~ 5 at.% Fe in the liquid composition) taking place at the temperature of 850°C has the lowest temperature of all the possible eutectic reactions.

An analysis of alloys of the system Zr-Fe-Nb-Be showed that the brazing filler alloy composition having the lowest melting point is located in the range of (3-6)% Fe, (2-5)% Be, and (1-3) % Nb. On this basis a filler alloy of the following composition Zr-5.5% Fe-1% Nb-2.5 % Be was selected.

Samples of the alloy were smelted for a complex analytical research and tests of its properties. The samples were used to obtain foils by a spinning technique and then these foils were applied to braze the spacing grid cells of the VVER-440 fuel assemblies using the following regime: the brazing temperature was 850 °C and the holding time at the temperature of 580 °C was 6 h.

The temperature melting ranges of the smelted ingots were determined at the heating rate of 20 K/min by a differential thermal analysis using the installation VDTA-8M3. Tensile tests of the brazed samples showed that the joints have a satisfactory strength. The destruction of the samples took place mainly at the base metal. However, autoclave corrosion tests showed that the brazed joints had an insufficient corrosion resistance. This means that the brazing temperature of 850 °C is overrated and it is necessary to decrease it. To do this, 8 wt.% of Cu was added. To increase the corrosion resistance and additionally strengthen the alloy, 2% of Sn and 0.4% of Cr were additionally added into the alloy. Thus, an alloy of the following composition Zr-5.5Fe-2.5Be-1Nb-8Cu-2Sn-0.4Cr (in wt.%) was smelted. After the spinning technique, this alloy was used to braze cells made from the alloy E110 for corrosion tests.

The brazed joints withstood corrosion tests in a distilled steam-water mixture in an autoclave at the temperature of 350 °C and the pressure of 16.5 MPa for 6,000 h. A further increase of the time resulted in formation of elements of a noticeable corrosion in the zone of fillets of the brazed seam, which indicated the necessity to further decrease the melting point of the alloy and, therefore, the brazing temperature up to 780 °C. A possible reduction of the copper content of up to 5 wt.% was justified. However, decreasing the content of copper is accompanied by increasing the melting point of the alloy (820-830 °C at 5%). To decrease the melting point of the brazing filler alloy, the content of Be was increased up to 3.5 wt.%. The resulting alloy **Zr- 5.5 Fe-3.5Be-1Nb-5Cu-2Sn-0.4Cr (wt.%)** has a start melting temperature of ~ 780 °C.

3.1.2. The refinement of the composition for obtaining an amorphous state by rapid quenching of the melt

The amorphous state is most likely for the elements with polymorphic transformations that are trend to form various phases and have a high degree of anisotropy of the interatomic bond [1]. From this viewpoint, zirconium is the most suitable metal. All the amorphizing metal melts are like in having a quick growth in the intensity of *the covalent component* of forces of the interatomic interaction at decreasing the temperature. The growth in the covalent interaction intensity under supercooling of the melt leads to the binding of components into associative complexes, which, on the one hand, makes the processes of mass transfer more difficult and inhibits crystallization and, on the other hand, creates an ordered state in the liquid phase that has a smaller amount of Gibbs energy in relation to that of the crystal. Thus, the transfer of metal melts into the glassy state at a rapid cooling is completely controlled by the covalent component of the chemical bond of atoms.

The interval of compositions in which this is realized is in the concentration area of a dominance of associative complexes with low *entropy of formation*. For example, the tendency of the Cu-Zr melts to glass formation in wide concentration ranges is predetermined by the fact that all the kinds of associative groups present in them have large negative entropies of formation. It is seen from Table 1 that presents the enthalpy ($-\Delta H$, J/mol) and the entropy ($-\Delta S$, J/(mol×K)) of the formation reactions of associations and data on the concentration ranges of the alloy amorphization [1].

It is the entropy term of the atom association reactions that determines to a decisive extent the values of the dynamic contributions to thermodynamic (configurational entropy and heat capacity) and kinematic (viscosity, the activation energy of crystallization, crystallization rate) properties of the melt that determine its transition to the amorphous state, bypassing the crystallization under decreasing the temperature.

This allows selecting the formation entropy of associative complexes as the main thermodynamic value to estimate the tendency of alloys to amorphization and forecast the compositions of alloys that are the most prone to amorphization.

Table 1. Thermodynamic parameters of association reactions ($-\Delta H$, J/mol and $-\Delta S$, J/(mol \times K)) and data of the concentration ranges of amorphization for a number of alloys

System of elements	Parameter	Parameters for associations		Amorphization interval
Cu–Zr		CuZr	Cu ₂ Zr	0.20 < x < 0.70
	$-\Delta H$	54800	73100	
	$-\Delta S$	40.5	40.3	

At the same time, it is quite convincingly established that the intensity of the interatomic (interparticle) interaction in metal melts, in contrast to the oxide ones, has only an indirect impact on their glass-forming ability.

Beryllium at a concentration of 3.5 wt.% and more significantly lowers the melting point of zirconium and is a strong amorphizer and a strong depressant.

To improve the brazed seam homogeneity, decrease the formation possibility of intermetallic compounds in the brazed zone and thus increase the strength and the corrosion resistance, an addition of germanium at a concentration of 0.5-1.25 wt.% was justified. At that, germanium slightly lowers the melting point of the alloy. Detailed investigations of the microstructure of brazed joints by a scanning electron microscope using 6 alloys containing Ge from 0.5 to 1.25 wt.% at various brazing temperatures ranging from 780 to 860 °C to analyze the distribution of beryllides showed that wedging-out and decreasing the quantity of beryllides until their practically complete disappearance were observed at the concentrations of germanium in the filler metal of 0.75 and 1.0 wt.% and in regulation of the gap between the brazed details. The investigations performed make it possible to conclude that alloying the brazing filler metal by germanium in an amount of 0.5-1.0 wt.% should be considered the most optimal from the viewpoint of the brazed seam structure.

Thus, the following composition of a brazing filler metal, Zr–5.5Fe–(2.5–3.5)Be–1Nb–(5–8)Cu–2Sn–0.4Cr–(0.5–1.0)Ge, for brazing of zirconium alloys of the system Zr–Nb is proposed and patented. Its melting point is 780°C and the recommended brazing temperature is 800°C.

4. The analytical and instrumental maintenance of the development of alloys

Stages of selecting the alloy composition were accompanied by the manufacture of ingots, obtaining a rapidly quenched ribbon of the filler alloy, investigation of the ribbon state, carrying out a pilot brazing of Zr–1Nb plates or brazing the spacing grid cells of the VVER-440 fuel assemblies, studies of the structural-phase state in the brazed seam and performing of corrosion tests and destruction tests of the brazed samples under tensile loads.

Ingots of alloys were obtained using arc and induction melting furnaces. Experiments on improving the technology to manufacture amorphous ribbon-type brazing filler alloys were carried out on the installation Crystal-702 for ultrarapid quenching of the melt at a rate of up to 10⁶ K/s. The experiments performed made it possible to determine the optimum parameters of the process of rapid solidification of the melt for the developed zirconium-based alloy and obtain an amorphous ribbon with a width of 10 mm and a thickness of 40-45 μm. Then, a complex technological problem of obtaining ultrathin AMA-filler alloys (i.e. brazing filler alloys based on amorphous metal alloys) with a thickness of 20-25 μm was successfully solved. The thickness of the filler alloy influences the brazed seam thickness and, accordingly, the structural-phase state in the seam zone. The geometry, the structure and the element composition of the resulting ribbon were investigated. The chemical composition of the ingots and rapidly quenched ribbons was determined by a micro X-ray spectrum analysis using the installation “CamScan-4DV”.

The starting melting point of an amorphous ribbon of the brazing filler alloy was determined by a differential thermal analysis. An X-ray pattern of the ribbon was obtained using the installation DRON-3 that showed the presence of an amorphous structure.

Brazing of the elements of zirconium spacing grids was performed in vacuum furnaces. Then, the brazed joints were exposed to corrosion tests in a distilled steam-water mixture in laboratory autoclaves with a volume of 1 dm³ at the temperature of 350 °C and the pressure of 16.5 MPa for 6,000 h.

The distribution of elements in the area of brazed seams was investigated using the scanning electron microscope “CamScan-4DV” equipped with a wave crystal diffraction spectrometer WDX-3PC.

The unbrazing temperature of the brazed joints was determined in accordance with the previously developed technique [8]. The failure of the brazed joint was shown to start at the temperature above 1400 °C.

The strength of the brazed joints was determined on pairwise brazed cells using the tensile testing machine R-05 with registration of the failure load.

5. Conclusion

The following composition of a brazing filler alloy with a melting temperature of 780 °C and a recommended brazing temperature of 800 °C has been proposed and patented as a result of a physicochemical analysis and an experimental study of a series of zirconium-based alloys: Zr-5.5 Fe-(2.5-3.5)Be-1Nb-(5-8)Cu-2Sn-0.4Cr-(0.5-1.0)Ge.

The developed brazing filler alloy provides the formation of a permanent corrosion-resistant joint of the Zr-1%Nb alloy with a working temperature higher than 1200 °C.

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