Neutron-absorbing amorphous alloys for cladding coatings

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Abstract. This paper shows developed compositions of neutron-absorbing cladding alloys based on nickel and containing such elements as B, Gd, Hf, and Mn. The techniques for application of coatings from these alloys on the surface of structural steels have been improved. It has been shown that the amorphous neutron-absorbing coating is more uniform than the crystalline one. The experimental data on the adhesion of cladding coatings with a steel substrate and their neutron-absorbing capacity have been obtained.

1. Introduction
One of the instruments to ensure nuclear safety in the transportation of spent nuclear fuel (SNF) is to create a high-strength transport container that will effectively absorb the radioactive radiations of fission products. In this regard, the problem arises of creating of corresponding structural materials. It is known that the corrosion-resistant boron steels with a boron concentration of 1 to 2.4 wt. % are sufficiently technological and have satisfactory physicomechanical properties. The steels alloyed with gadolinium are also prospective absorbing structural materials. However, both the first and the second materials have a number of disadvantages. Firstly, it is a small concentration of the absorbing element and the related need to manufacture containers with thick walls. Secondly, the reduced ductility and impact toughness of these materials due to alloying significantly reduce the manufacturability of the product and create an increased risk of breaking the container during its transportation.

In this connection, it is very promising to use an absorbing metal coating on the surface of a high-strength corrosion-resistant steel that is well developed in the industry. However, ensuring the effectiveness of such a coating is possible only at a high concentration of neutron-absorbing elements in the cladding layer. From this point of view, it seems appropriate to use amorphous metal foils obtained by rapid solidification. This method allows to: a) significantly (up to 2 and more times) increase the concentration of sparingly soluble elements in the metal matrix; b) obtain a thin (10-100 μm) plastic foil from practically non-deformable alloys, which provides a high manufacturability of applying a cladding material on the surface of products of complex configuration. In the light of the above-said, the work was performed on the choice of compositions for cladding, improvement of the technology of obtaining amorphous alloys by rapid solidification, the cladding of corrosion-resistance steel samples, metallographic analysis of the coatings obtained and measurement of the absorbing characteristics of the clad samples.

2. The choice of the compositions of amorphizing cladding alloys
In accordance with the known data and the previous studies [1,2], a boron containing nickel alloy (in wt.%, Ni (basis)-3.0Fe-7Cr-3B-4Si) was taken as a base material for investigations. This alloy easily
becomes amorphous, it is free-running and it well wets the chrome-nickel steels. Its melting point ($T_{m}$) is 975 °C. In accordance with the recommendations, it was proposed to add gadolinium, hafnium and manganese as alloying elements and, moreover, to increase the boron concentration up to 5%. To increase the corrosion resistance of the alloy, the chromium concentration should be increased to 14 wt.%.

Thus, further studies were carried out with the following compositions:

- Ni (basis) - 7Cr - 3Fe - 4Si - 3B;
- Ni (basis) - 7Cr - 4Fe - 4Si - 5B;
- Ni (basis) - 14Cr - 4Fe - 4.5Si - 4.5B;
- 45Fe - 40Ni - 7Cr - 4Si - 4B;
- Ni (basis) - 3Fe-7Cr-4B-4Si-1Gd-2Hf;
- Ni (basis) - 3Fe-7Cr-5B-4Si-5Gd;
- Ni (basis) - 3Fe-7Cr-5B-4Si-4Mn.

Besides the above-listed cladding materials, the concentration of boron in the cladding layer was additionally increased by the ligature Ni + 15% B (NiB). To improve the physicochemical properties of the ligature, it was also obtained in the form of an amorphous ribbon by rapid solidification of the melt. For cladding, a standard amorphous alloy Ni + 7% Cr + 4% Fe + 4% B + 4% Si in the form of a ribbon was used. The alloy was layer-by-layer alternated with a ribbon of the NiB ligature and placed on the surface of a plate. The ratio of the both cladding alloys was of such a value that the total boron content in the combined layer after their application on the surface of the steel was not less than 8-9%.

3. The manufacturing technology of ingots

The following materials were used as the initial charge materials for the production of ingots: Ni of the grade H-0 (GOST 849-70), electrolytic Cr, carbonyl Fe, iodide Hf (TsMTU 05-177-69), distilled Gd, semiconductor Si (GOST 19658-74), Mn of the grade Mr00 (GOST 6008-75), amorphous B, and Ni-powder of the grade PNE1 (nickel electrolytic powder, GOST 9722-71).

To ensure a uniform chemical composition of the ingots, metalloids were added in the form of Ni-15%Si and Ni-10%B ligatures. For convenience of the addition of refractory Hf into the alloy, it was added using the Ni-35%Hf ligature obtained in an arc furnace MEPhI-9 with no less than a sixfold remelting. An ingot of the alloy 85%Gd-15%(Ni+Fe) was also melted in an arc furnace.

For the experiments on rapid solidification, ingots with a mass of 250-800 g were casted in an induction furnace using quartz crucibles and graphite molds.

4. The manufacturing technology of rapidly quenched ribbons

Experiments on the improvement of technological regimes of manufacturing amorphous alloys were carried out, using a high-vacuum installation "Crystal-702", in conditions of a controlled gaseous environment, the temperature regime of casting and the solidification rate of the melt [2, 3]. The installation scheme is shown in figure 1.

5. The results of experiments on rapid solidification

The following materials were used for the investigation.

- Ni-7Cr-3Fe-3B-4Si, Ni-7Cr-4Fe-4Si-5B and Ni-14Cr-4Fe-4.5Si-4.5B alloys; a plastic ribbon made from the alloy Ni-45Fe-7Cr-4Si-4B with a thickness of 50 µm and a width of 20 mm; the structure of the alloy is amorphous; the start melting temperature ($T_{m}$) is 975, 980 and 990 °C, respectively.

- Brittle fragments of a ribbon made from the alloy Ni-7Cr-3Fe-2Hf-1Gd-4B-4Si with a thickness of 50 µm and a width of 10 mm; the alloy structure is amorphous-crystalline; $T_{m} = 980$ °C.

- Brittle fragments of a ribbon made from the alloy Ni-7Cr-3Fe-5Gd-5B-4Si with a thickness of 50 µm and a width of 10 mm; the alloy structure is amorphous-crystalline; $T_{m} = 980$ 0°C.

- A brittle ribbon made from the alloy Ni-7Cr-3Fe-4Si-5B-4Mn with a thickness of 50 µm and a width of 20 mm; the alloy structure is amorphous-crystalline; $T_{m} = 975$ °C.
6. The manufacture of powder alloys
To manufacture amorphous powders containing neutron-absorbing elements, a technological chain was developed. It includes the following steps: embrittlement of a rapidly quenched ribbon without loss of amorphism at the temperature of no more than 500 °C; preliminary grinding of the ribbon into fragments no larger than 5×10 mm²; grinding in a ball mill in an inert gaseous medium (argon); sifting using a sieve with a mesh size of 100 to 20 μm. To remove grease and dust contaminations containing in the resulting powder, it was washed in acetone with a fivefold change of the solvent and dried on filter paper.

Study of the powder fragments using a microscope showed that the powder can be related to the fragment type and the form of its particles is both isometric and needlelike. The particles can reach 1 mm in length. The grinding technique was the same for all the nickel alloys.

7. The cladding of steel samples by rapidly quenched alloys
Plates with sizes of 40×40×5 mm³ made from the stainless steel 12X18H10T were used as the samples for cladding. The surface to be cladded was purified from oxides, made even by grinding and then degreased. The cladding alloy was applied in the form of either a powder or equal segments of the ribbon so that the cladding layer thickness was from 150 to 200 μm. The powder was used in cases when the manufacture of geometrically regular fragments of the ribbon was not possible. After laying the cladding alloy on the surface of a steel plate, the plate was placed into the working chamber of a vacuum electric resistance furnace of the SShV-25 type. The furnace was evacuated to a residual pressure of 10⁻³ Pa and heated to the temperature which was 100 °C above the starting melting temperature Tₘ. The temperature was controlled by chromel-alumel thermocouples that were in contact with the steel plate, as well as visually by the moment of a full spreading over the plate.
surface. The heating rate was ~ 20 °C/min, the holding time at the temperature of a full spreading was 5 min, after which the heaters were turned off and the sample was cooled in the furnace. To estimate the possibility of using the existing technological equipment for applying of coatings, works were carried out on cladding the steel by an amorphous powder at the installation "Kiev-7" under stationary conditions.

Optimal parameters were determined which are necessary to obtain a dense uniform coating with a thickness of ~ 1 mm on a cylindrical sample of the steel 12X18H10T. The spraying distance was 300 mm and the rotation frequency was 50 rev/min. The resulting coating has a good adhesion to the steel [4]. When the sample was treated by a turning lathe, no peeling, flaking or spalling of the sprayed layer was observed. A roughness is marked on the cladding layer surface that is a consequence of the needlelike form of individual particles of the powder that do not have enough time to be melt in the plasma flow. However, the basis part of the coating has a dense microcrystalline structure and a porosity of no more than 10%.

8. The mechanical properties of coatings from rapidly quenched materials

The mechanical tests of ring-shaped samples with applied coatings were performed using the test machine FPZ 10/1. The samples with a width of 10 mm, an inner diameter of 60 mm and an outer diameter of 66 mm (the outer diameter of the coated pipe was 70 mm) were exposed to a compression test.

The distance between the grippers \( L_{tr} \) at the time of appearance of a crack in the coating was registered during the loading. The moving rate of the active gripper was 1.0 mm/min. Three samples of each type of the coating were exposed to tests. The results of tests are shown in table 1.

| Number of a sample | Amorphous coating \( L_{tr} \) (mm) | Crystalline coating \( L_{tr} \) (mm) |
|--------------------|------------------------------------|-------------------------------------|
| 1                  | 60.4                               | 68.6                                |
| 2                  | 63.2                               | 67.3                                |
| 3                  | 62.1                               | 67.9                                |

As follows from the data presented, the deformation ability of the coating obtained using an amorphous alloy is significantly higher \( (L_{tr} = 61.9 \text{ mm}) \) than that obtained using traditional crystalline powders \( (L_{tr} = 68.0 \text{ mm}) \).

The microhardness of the coatings and the substrate was measured using a micro-hardness testing machine PMT-3. The measurement results are shown in table 2.

| Alloy composition, wt.% | Microhardness (MPa) |
|-------------------------|---------------------|
| Ni (basis)-3Fe-7Cr-5B-4Si-4Mn |                        |
| Amorphous               | 7500                |
| Crystalline             | 9600                |
| Ni (basis)-7Cr-4Fe-4Si-5B; |                        |
| Ni (basis)-14Cr-4Fe-4.5Si-4.5B; |                |
| 45Fe - 40Ni - 7Cr - 4Si - 4B. |                |
| Steel X18H10T           | 3500                |

Thus, the results obtained show that the coating plasticity when using amorphous alloys is higher than that in case of crystalline ones [5].
9. The test of clad samples on the neutron-absorbing capability

To perform comparative studies, four steel samples (No. 1, 2, 3, and 4) with sizes of 30×30 mm were prepared. The sample No. 1 is a 3 mm thick tube fragment of a corrosion-resistant steel 12X18H10T. The sample No. 2 is a tube fragment with a neutron-absorbing coating about 1 mm in thickness. The sample No. 3 is a sheet steel 12X18H10T with a thickness of 3.5 mm and a volume content of boron of 1.5 wt. %. The sample No. 4 is a sheet steel 12X18H10T with a thickness of 5 mm.

Investigation of the neutron-absorbing capability of materials was carried out using a spectrometric installation consisting of a neutron source (Pu-Be, with an activity of 2.04×10⁶ n/s), a neutron moderator (140 mm thick organic glass), a cadmium filter with a thickness of 0.5 mm, and a semiconductor thermal neutron detector (DTP 2Kh603B Ts23.394, 022TU).

The neutron-absorbing capability of materials was determined by a coefficient of neutron absorption:

\[ k_n = \frac{N_o - N_1}{N_o}, \]  

where \( N_o \) is the number of neutrons recorded without the sample; \( N_1 \) is the number of neutrons recorded with the sample.

The results of determining the neutron absorption coefficients are presented in Table 3 which shows that the samples No. 2 (with coating containing neutron-absorbing elements) and No. 3 (containing boron) have the best neutron-absorbing capability.

| Sample number | 1 (without a coating) | 2 (with a coating) | 3 (a borated sheet) | 4 (a sheet) |
|---------------|-----------------------|-------------------|---------------------|-------------|
| \( k_n \)     | 0.16±0.03             | 0.46±0.05         | 0.54±0.05           | 0.23±0.03   |

It is obvious that the neutron-absorbing layer decreases the penetration of neutrons by several times and, even in the illustrated variant of the cladding alloy (with a boron concentration in the layer of 3.5%), its effectiveness is highly competitive with that of the volume-alloyed stainless steel.

10. Conclusion

- The compositions and the technology for manufacturing of rapidly quenched alloys based on nickel and containing such neutron-absorbing elements as B, Gd, Hf, and Mn have been developed and amorphous and amorphous-crystalline alloys have been obtained.
- The elements of the cladding technology of steel details using both a rapidly quenched ribbon and powders of amorphous alloys with complex composition have been improved.
- The optimum temperature-time parameters of the application of a coating required to obtain a uniform layer with a thickness of 1.0-2.0 mm have been chosen. Special studies have showed that the coating obtained has a good adhesion to the steel.
- It has been shown that the amorphous neutron-absorbing coating is more uniform in comparison with the crystalline one.
- The mechanical compression tests have shown that the deformation ability of the coating obtained using an amorphous alloy is significantly higher than that obtained using traditional crystalline powders.
- It has been shown that the coating with a thickness of no more than 1 mm from the viewpoint of its neutron-absorbing capability is equivalent to 3.5 mm thick borated steel.
- The experimental data obtained on the adhesion strength of cladding coatings with a steel substrate and their neutron-absorbing capability give grounds to speak about the prospects of using of amorphous materials and the technologies developed for cladding of structural elements of the container as an alternative variant of the biological protection from the penetrating radiation of a spent nuclear fuel.
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