Structure and phase composition of material based on vanadium alloy V-4.9Ti-4.8Cr and ferrite steel 17Cr-12Ni-Fe

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Abstract. Three-layer materials consisting of the V-4.9Ti-4.8Cr/ferrite steel 17Cr-12Ni-Fe /V-4.9Ti-4.8Cr were obtained in the paper. Phase composition and microstructure of the transition zone of the three-layer material of vanadium alloy V-4.9Ti-4.8Cr and ferrite steel 17Cr-12Ni-Fe were considered. The use of the method of direct laser growing allowed obtaining a three-layer material with qualitative interconnection of layers, as well as decreasing a multistage nature of deformation and thermal operations used when obtaining a three-layer material in earlier works. Additional thermal treatment of a three-layer alloy led to growth of matrix grains up to 100 μm of the vanadium alloy. A uniform distribution of main elements V, Ti, Cr was observed in the transition zone both before and after annealing. A zone of interdiffusion of the metals amounted to 250-350 μm .

1 Introduction

At present, materials for nuclear power engineering have limited operational characteristics, which do not allow one to maximally fully realise the potential of power plants of new generation [1, 2]. The material of shells of heat-producing and other responsible elements of the active zone of fast neutrons reactors of new generation, working in mode of the closed nuclear fuel cycle, must provide their reliable and safe operation during maximal fuel burn-out up to 20% of heavy atoms with a damaging dose up to 180...200 dpa at temperatures of 370...700 °C and have the long-term strength of $\sigma_{10000\ 600} \geq 100$ MPa. Obtainment of materials, meeting the mentioned characteristics, namely possessing high heat resistance simultaneously with high radiation and corrosion resistance, is a relevant practical task. Works [1-3] demonstrated that the most promising material for fast neutrons (hereinafter FN) reactors was alloys based on vanadium, titanium and chromium. Enhanced operational characteristics (high strength and radio-resistance) belonged to alloy V-4.9Ti-4.8Cr, obtained by the method of powder metallurgy [3,4] and recommended for using in nuclear power engineering. To enhance corrosion resistance and stability of HPEL in reactors, it was proposed to additionally apply a protective layer on the vanadium alloy. Papers [5-7] showed that when applying steel 17Cr-12Ni-Fe as a protective coating on the vanadium alloy, it became possible to increase significantly the running time and stability of HPELs in the reactors' zone. The drawbacks in obtaining a two- and three-layer material when using methods applied in works [7, 8], during application of a

protective coating by the cladding method, was a multistage nature of deformation and thermal processes leading to long-term time and material expenditures. In paper [8], it is proposed to use an alternative method of heterophase powder metallurgy, namely direct laser growing (hereinafter DLG) of an article. Obtainment of material by DLG does not demand additional isostatic pressing or thermal treatment. Replacement of casting technology and mechanical treatment by the growing technology during application of the protective layer of steel 17Cr-12Ni-Fe onto the vanadium alloy could lead to a significant reduction of prime cost of the article and ensured obtainment of strong materials with enhanced functional characteristics. When using a multilayer material based on the vanadium alloy and steel, an important role belonged to a transition, diffusion layer providing maximal interaction between layers of the vanadium alloy and steel. The research of the transition zone composition of the two layers is a relevant task. The purpose of this paper was to establish the relation of the elemental and phase composition of the transition zone and the method of formation of three-layer material vanadium alloy V-4.9Ti-4.8Cr/ferrite steel 17Cr-12Ni-Fe.

2 Materials and methods

Samples of the three-layer material were obtained from vanadium alloy V-4.9Ti-4.8Cr and from the powder of ferrite corrosion resistant steel 17Cr-12Ni-Fe with the composition presented in the Table 1.

To obtain a vanadium alloy V-4.9Ti-4.8Cr it was used powder of metallic vanadium, titanium and

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chromium in the appropriate ratio of components. It was used two-stage heating of the samples at 350 °C and at 1700 °C. Disks with the thickness of 5 mm were cut out of work pieces from the vanadium alloy of the V-4.9Ti-4.8Cr composition, on which a layer of steel 17Cr-12Ni-Fe was applied by the method of heterophase powder metallurgy (methods of direct laser growing [8]) bilaterally (Fig. 1). Surfacing with ferrite corrosion steel was carried out using the plant of direct laser growing [8]. The average particle size of the steel powder was 75±25 µm. The powder of steel 17Cr-12Ni-Fe was preliminary dried in the vacuum cabinet at a temperature of 150-200 °C during 1 hour. Disks with a height of 3 mm were cut out of the blanks of the vanadium alloy. The sample of the vanadium alloy was placed in the working chamber; the chamber was filled with argon; the pressure of 0.5-1 bar was created.

Table 1. Chemical composition of initial alloys.

Alloy	Content of elements, wt. %					
	Fe	V	C	Cr	Ti	other
V-4.9Ti-4.8Cr	-	base	0.010-0.015	4.9	4.8	N ≤ 0.02; O ≤ 0.025
17Cr-12Ni-Fe	base		0.08-0.17	17	≤ 0.08	Ni ≤ 2.5; Si ≤ 0.1; S, P, Ca ≤ 0.2; O ≤ 0.35

Experimental studies of deposition processes were carried out at the Institute of Laser and Welding Technologies (Russia) using experimental setup based on 5kW IPG fiber laser YLS-5000, 5D CNC machine, Sultzer Metco Twin 10-C powder feeder and HighYAG BIMO processing head. Laser growing was conducted using the powder of chrome-bearing steel (50...100 µm) with a diameter of the beam equal within 1.6...2.0 mm and radiation power of 950-1200 W. The powder consumption was 20-25 g/min; the growth rate was 15-25 mm/s at a temperature of 1500-1800 °C. Then the sample was turned over and the operation was repeated under the same conditions. Figure 1 shows the scheme of the obtained three-layer material.

The thickness and the size of the samples were conditioned by the minimal size of experimental samples, required for the study of radiation and corrosion stability of vanadium alloys.

After application, the steel layer was 2 mm. The obtained three-layer material was additionally subjected to thermal treatment in the vacuum furnace at a temperature of 1200 °C (the rate was 30 °C/min) for 2 hours as proposed in [9]. Annealing temperature of 1200 °C was maximum permissible for checking thermal stability of the alloy and did not exceed the critical temperatures of alloy decomposition. Only one maximum possible temperature regime of treatment, which demonstrated the material stability and

contributed to maximum diffusion of the elements, was considered in the present paper.

Fig. 1. Scheme of three-layer material

The transition region between vanadium alloy V-4.9Ti-4.8Cr and steel 17Cr-12Ni-Fe was investigated in detail. The phase composition and the microstructure of the samples of all layers of the material were studied before and after thermal treatment. The used method of laser surfacing of steel on the vanadium alloy allowed obtaining a three-layer material with improved integration of layers. Direct study of the composition, the structure and localization of the elements in the transition region between the layers was the most significant.

The research of the phase composition of the samples was conducted using the X-ray structural analysis method using diffractometer Shimadzu XRD 6000 at a voltage of 30 kV with automatic scanning of the X-ray beam at an 18-150-degree interval of angles in filtered monochromatized Cu-K_α radiation. Before X-ray phase analysis, mechanical grinding of the samples was carried out.

The studies of the transition zone of the obtained two-layer samples in the contact region of dissimilar materials were undertaken by the Scanning Electron Microscopy (SEM) method with application of a scanning electron microscope QUANTA 200 3D FEI with an accelerating voltage of 35 kV and operating magnifications of 50-10000 times. The SEM method with elemental analysis provided necessary data for assessing homogeneity of the transition region and quantitative evaluation of elements distribution throughout the layer.

SEM studies of the two-layer material allowed qualitatively and quantitatively researching the microstructure, gauging thickness of the transition layer, as well as assessing the quality of the compound (interdiffusion depth, presence of pores and cracks).

3 Results and discussion

SEM studies of the microstructure of the vanadium alloy shows that matrix grains represent a solid solution of chromium in vanadium with an average grain size of 5-10 µm (Fig.2a). In addition, throughout the entire volume along the boundaries of matrix grains, there were dendrite interlayers (3 µm thick) representing regions containing fine crystals of the solid solution of

chromium in vanadium (Fig.2). The size of the grains was around 100-300 nm (Fig.2). Titanium was present as separate particles in the matrix grains and also in the intergranular space localizing predominantly along the boundaries of coarse matrix grains (Fig. 2a).

Fig. 2. Microstructure of alloy V-4.9Ti-4.8Cr a) before thermal treatment ; b) after thermal treatment at 1200 °C for 2 h. Spectral analysis of distributed elements: c)Ti; d)V; e)Cr; on vanadium alloy volume after thermal treatment.

A steel layer represents a fine-crystalline material with an average grain size up to 0.5 μm (Fig.3). During heterophase application, the particles of powder 17Cr-12Ni-Fe interacted with the vanadium alloy, forming a stable intermediate region. Figure 3 presents an area of interconnection of the vanadium alloy and the steel before annealing.

Fig. 3. Region of connection of two layers: V-4.9Ti-4.8Cr/17Cr-12Ni-Fe before annealing with magnification x 200 on left and x 500 on right.

The presence of titanium “tails” is due to thermo-diffusion of the titanium.

Conspicuously, the structure of the vanadium alloy after application of the steel layer did not change (Fig.2), which implied its preservation of original functional properties. The contact region of the two layers (vanadium alloy/steel) represented an area with a uniform distribution of all chemical elements (V, Cr, Ti, Fe). In the transition zone, there was a uniform distribution of iron and vanadium in depth. The transition zone is presented in Figure 4.

In the transition zone between the vanadium alloy and the steel, iron and vanadium interdiffused between layers and were at the ratio of 55/45% at a depth up to 200 μm from the beginning of the fusion zone towards steel (Fig. 4, Fe and V-curve). Further there was a gradual decline in the diffusion process of iron and an increase in the vanadium content by 150-180 μm from the beginning of the transition zone towards the vanadium alloy (Fig. 4, Ti, Cr-curve). Thus, iron could penetrate into the vanadium alloy at a depth of 150 μm with a

content up to 40% mass. Vanadium diffused into iron at a depth of 200 μm with a content of 40-45% mass. (Fig. 4, V and Cr-curve). The layer of the mutual interaction amounted to about 250-350 μm (Fig. 4, Ti-curve). According to the distribution of the elements in depth of layers during application, there was interdiffusion of iron and vanadium between layers accompanied by formation of a uniform region. The titanium and vanadium concentration did not exceed 40%. Titanium and chromium preserved the concentration in depth of the layers of no more than 5%. Interdiffusion of the main elements led to formation of new phases in the intermediate zone: Fe₂Ti with a coherent scattering region (CSR) value of 12-14 μm (Table 2). The detected phase was a solid solution of titanium in iron, the formation of which was conditioned by interdiffusion of components. The diffusion of components in the transition zone will lead to formation of solid solutions.

Fig. 4. The distribution of the elements region between two layers: V-4.9Ti-4.8Cr/17Cr-12Ni-Fe

After additional thermal treatment of the three-layer material at a temperature of 1200 °C, there is an intensive growth of matrix grains of the vanadium alloy and an increase in the thickness of the boundary region between the layers. The results of the changing microstructure are connected with reference [10, 11]. The X-ray spectrum analysis of the vanadium alloy microstructure showed (Fig.2,b) that matrix grains of the vanadium alloy also represented a solid solution of chromium in vanadium (Fig.2c,d,e). However, the temperature annealing led to formation of a coarse-grained structure with an average grain size up to 100 μm.

The results of the X-ray spectrum analysis of the vanadium alloy showed that after thermal treatment, vanadium and chromium were distributed uniformly throughout the alloy volume (Fig. 2). After annealing, there was a uniform distribution of titanium throughout the layer volume, but it localized predominantly along the borders of matrix grains (as well as before annealing). Figure 5 presents an interconnection zone of the two layers after annealing.

Throughout the entire interconnection zone of two layers, the transition region broadens, in which presence

of iron and vanadium can be observed. The 17Cr-12Ni-Fe layer obtained by powder layering became more homogeneous (Fig.5). Additional thermal treatment led to a significant reduction of macrodefects in the transition zone between two layers. According to the conducted spectrum analysis of the vanadium alloy, application of the protective coating by the method of direct laser growing with additional thermal treatment led to formation of the diffusion layer containing chemical elements included in the composition of the vanadium alloy and steel. The transition zone had a monotonically changing composition (Fig.4, 6).

Table 2. Phase composition of the three-layer material.

Phases	Type of crystal lattice	Lattice parameters, Å
before annealing		
Fe	Cubic	a = 3.555
FeV	Tetragonal	a = 8.917
		c = 4.61
VCrFe	Cubic	a = 2.904
FeCr	Tetragonal	a = 8.7995
		c = 4.5442
VC	Hexagonal	a = 2.886
		c = 4.573
after annealing		
Fe	Cubic	a = 3.555
FeV	Tetragonal	a = 8.917
		c = 4.61
VCrFe	Cubic	a = 2.904
FeCr	Tetragonal	a = 8.7995
		c = 4.5442
Fe ₂ Ti	Hexagonal	a = 4.785
		c = 7.799
Cr ₂ Ti	Cubic	a = 6.943

Fig. 5. Region of connection of two layers of alloy V-4.9Ti-4.8Cr/X17H2 after annealing with magnification x 200 on left and x500 on right.

From the direction of the steel, there was a phase, which in addition to Fe, Cr and C, contained V and Ti. According to the obtained concentration images in the depth of the material from the surface, the chemical elements (V, Fe, Cr, Ti), diffusing towards each other from the vanadium alloy and steel to the interface, dissolved in each other. In the interconnection of the vanadium alloy and steel after annealing, iron diffused into the vanadium alloy at a depth of 20-40 μm; vanadium and chromium diffused into the steel layer at a

depth of up to 60-80 μm; at that, the concentration of vanadium and iron did not exceed ~ 25% mass (Fig. 6). Thermal treatment contributed to diffusion of chromium and titanium into the steel layer, which enabled formation of new phases of composition Fe₂Ti and Cr₂Ti.

Fig. 6. The distribution of the elements between two layers: V-4.9Ti-4.8Cr/17Cr-12Ni-Fe.

4 Conclusion

The use of the method of direct laser growing allowed obtaining a three-layer material with a qualitative interconnection, as well as reducing a multi-stage nature, deformation and thermal operations used when obtaining a three-layer material. Formation of the transition zone between two layers of the alloys with a uniform distribution of all the elements throughout the thickness of the layers, containing phases of the VFe and VCrFe composition, was established. Thermal treatment contributed to the growth of matrix grains of the vanadium alloy, additional diffusion of Cr and Ti elements and formation of new phases of the Fe₂Ti and Cr₂Ti composition. The obtained sample showed clearly the formed stable zone between two layers. The sample can be recommended as promising materials to manufacture parts applied in nuclear power engineering.

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