Manufacturing of high entropy alloy in the Ni-Nb-Co-Fe-Cr system by rapidly solidification method for oxide ceramic brazing

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Abstract. This paper presents results of research of high-entropy alloys of the Ni-Nb-Co-Fe-Cr system in the as-cast state and after rapid quenching from the melt. The results of experiments on obtaining a brazed joint of aluminum-oxide ceramics with using the filler metal of this system and the results of a studying this joint are presented. Differential thermal analysis (DTA), X-ray diffraction analysis (XRD), scanning electron microscopy (SEM), energy-dispersive X-ray microanalysis (EDX) and measurement of microhardness were used as experimental research methods. The liquidus and solidus temperatures of high-entropy alloy Nb$_{0.73}$CoCrFeNi$_{2.1}$ were determined. The phase composition of alloys of the Ni-Nb-Co-Fe-Cr system was studied. It was shown, that alloys of this system can be used as filler metal to create a joint between ceramics. The microhardness of the brazed seam was studied. Based on these results the brazing mode for samples of aluminum-oxide ceramics with using high-entropy alloy Nb$_{0.73}$CoCrFeNi$_{2.1}$ as a filler metal was chosen.

1. Introduction

In modern technologies, there is often a need to create joints with between two or more structural elements. One way to create one-piece joints is brazing. Brazing is the process of connecting materials in a solid state with filler metal that wets the joined surfaces at the brazing temperature, fills the gap between them and forms a brazed joint during crystallization [1]. One of the important advantages of brazing is the ability to connect dissimilar materials. Brazing is also a group processing method, which allows using it for simultaneous connection any number of parts [2].

Rapidly quenched filler metals in amorphous and nanocrystalline states are often used for brazing of various materials [3]. By means of such filler metals, brazed joints are obtained in different fields such as rocket engineering that requires high-stress joints with great heat-resistance [4]. As it was mentioned above, the brazing allows to connect different materials such as ceramics and metal or metals that have properties that highly differs to each other. For example, these filler metals can be used to get a brazed a joint between tungsten with steel and vanadium alloys [5]. Properties of such brazed joints are strongly affected by microstructure and composition of brazed seam. In this field, it is important to choose carefully the composition of filler metal. Many tasks of creation joints between different materials in modern technologies that still do not have a solution. Due to it is also important to search for new alloys can be used as filler metals.

During the development of micro- and macro-alloying technologies, the first works on the creation and comprehensive study of new so-called multicomponent high-entropy alloys (HEA), including up
to 5-6 basic elements, each in high concentration (from 5 at.% to 35 at.%), appeared. Alloys of the FeCrNiMnCo system were studied as the first candidates for such materials, since such alloys form a simple FCC structure and have good mechanical properties [6].

These materials, along with the typical characteristics of metal alloys, have unique and unusual properties inherent, for example, cermets: high hardness and resistance to softening at high temperatures, dispersion hardening, positive temperature hardening coefficient, high wear resistance, corrosion resistance and a number of other properties [7], [8].

It is assumed that HEAs are attractive for using in various fields, and there are studies in which they were used as filler metal [9], [10]. HEA can be used for brazing heat-resistant alloys, refractory metals, ceramics, due to their high melting point and good mechanical properties. HEA with a solid solution or eutectic structure can be obtained for brazing, having a good balance of hardness and ductility, with a melting point in the same range as the currently used filler metals, but without adding components that greatly reduce the melting temperature.

A non-equilibrium structure forms in HEAs due to the following effects present in such alloys: high mixing entropy effect; sluggish diffusion kinetics; severe lattice distortion; the cocktail effect that is the dependence of the material properties on its constituent elements and the interaction between these elements [10].

This study presents the results of researching high-entropy alloys of the Ni-Nb-Co-Fe-Cr system in the as-cast state and after rapid quenching from the melt. The results of experiments on obtaining a brazed joint of aluminum-oxide ceramics with using the filler metal of this system and the results of a studying this joint are presented.

2. Materials and Experimental Methods

The high entropy alloy Nb_{0.73}CoCrFeNi_{2.1} was obtained from components with a purity 99.95 wt.% or more, with using pure metals Cr, Fe, Co, and Ni and NiNb ligature (52 wt.% Nb, 48 wt.% Ni). The as-cast ingot was remelted five times to achieve a homogeneous chemical composition.

One part of the ingot was used to obtain samples for further studying of the structure and properties, and the other to obtain rapidly quenched ribbon. The alloy Nb_{0.91}Co_{1.16}Cr_{1.05}Fe_{1}Ni_{2.11} was melted in a similar manner. Obtaining the rapid quenched ribbon was carried out on the special installation "Crystal-702". In this installation, melt cooling rates to 10^{3} – 10^{6} K/s are achieved. As a result, a rapidly quenched ribbon with a width of about 10 mm and a thickness of about 30 μm was obtained. Compositions of obtained HEAs are presented in the Table 1.

| HEA                  | Nb    | Co    | Cr    | Fe    | Ni    |
|----------------------|-------|-------|-------|-------|-------|
| Nb_{0.73}CoCrFeNi_{2.1} | 19.0  | 16.5  | 14.5  | 15.6  | 34.4  |
| Nb_{0.91}Co_{1.16}Cr_{1.05}Fe_{1}Ni_{2.11} | 22.2  | 17.6  | 14.0  | 14.4  | 31.8  |

To determine the temperature range of melting and crystallization of the studied alloys, differential thermal analysis was carried out using differential thermal analysis (DTA). Samples of an ingot and a rapidly quenched ribbon weighing about 100 mg were prepared for measurement. The measurements were carried out at a heating rate of 10 °C/min.

The microhardness of the samples was measured on a microhardness tester model HVS-1000 under a load of 100 g for 30 s.

X-ray phase analysis was carried out on a DRON-3.0 diffractometer with the Bragg-Brentano focusing scheme using Kα characteristic radiation of copper anode. The angular velocity of the detector is 1 degree per minute.

Annealing and brazing of the samples were carried out in a vacuum furnace with resistive heating. The design of the furnace allows to achieve vacuum of 1.3 · 10^{3} Pa at temperatures up to 1600 °C. Annealing of the sample of rapidly quenched ribbon was carried out for 8 hours at a temperature of...
1000 °C in a vacuum for homogenization of the composition and elimination of the dendritic structure formed during rapid quenching.

The samples of an aluminum-oxide ceramics XC22 were prepared for brazing. This XC22 ceramic has the next composition: 94.4 wt.% Al₂O₃; 2.76 wt.% SiO₂; 0.49 wt.% Cr₂O₃; 2.35 wt.% MnO. These samples are 1 mm thick plates with an area of about 1 cm². During the brazing the samples were fixed in a clamp. The brazing was carried out according to the mode, which includes heating to 1300 °C, holding for 20 minutes and step cooling.

3. Results and discussion

3.1. Calculation

The following quantities, that characterize the behavior of atoms, were calculated for HEA Nb₀.₇₃CoCrFeNi₂.₁: the atomic size difference δ, the mixing enthalpy ΔHₘᵢₓ and the mixing entropy ΔSₘᵢₓ. These quantities are δ = 4.8; ΔHₘᵢₓ = −12.2 kJ/mol; ΔSₘᵢₓ = 12.8 J/(K·mol).

It is shown [11], [12] that solid solution is formed if these values are in the ranges: 0 ≤ δ ≤ 8.5; −22 ≤ ΔHₘᵢₓ ≤ 7 kJ/mol; 11 ≤ ΔSₘᵢₓ ≤ 19.5 J/(K·mol). Amorphous alloys are formed when these parameters are in the following ranges: δ ≥ 9; −35 ≤ΔHₘᵢₓ≤−8.5 kJ/mol; 7≤ΔSₘᵢₓ≤14 J/(K·mol). However, this range may be wider if the alloy contains components with a high tendency to form an amorphous phase. With other values of the parameters, in most cases, the alloy structure contains some kind of intermetallic phase.

Thus, the calculated parameters δ, ΔHₘᵢₓ и ΔSₘᵢₓ predict the formation of a solid solution in the Nb₀.₇₃CoCrFeNi₂.₁ HEA and the impossibility of achieving an amorphous state. However, the experimental results obtained by observing the microstructure of the alloy show its pre-eutectic structure, consisting of two structural components: a solid solution and a eutectic. It will be shown below that an intermetallic compound is also in the alloy structure, which was not predicted by the calculation. In addition, the amorphous state was not achieved in the rapidly quenched ribbon.

3.2. Microstructure

The microstructure of cast ingot and rapidly quenched ribbon of HEA Nb₀.₇₃CoCrFeNi₂.₁ was studied. Figure 1 shows the microstructure of cast ingot. It has a pre-eutectic structure consisting of two structural components: solid solution and eutectic. To clarify the chemical composition, an EDX analysis was performed using SEM, the result of which is shown in Figure 2 and in Table 2.

![Figure 1. Microstructure of the cast ingot of the HEA Nb₀.₇₃CoCrFeNi₂.₁.](image)
Figure 2. Microstructure of the cast ingot of the HEA Nb$_{0.73}$CoCrFeNi$_{2.1}$; the chemical compositions of areas 1 – 3 are shown in Table 1.

Table 2. X-ray microanalysis of the cast ingot of HEA Nb$_{0.73}$CoCrFeNi$_{2.1}$ (values are shown in wt.%).

| Area | Cr  | Fe  | Co  | Ni  | Nb  |
|------|-----|-----|-----|-----|-----|
| 1    | 12.5| 12.9| 19.2| 30.8| 24.7|
| 2 and 3 | 21.3| 20.0| 18.2| 35.8| 4.7 |

Figure 3 shows the microstructure of the rapidly quenched ribbon of the same HEA. It has the thickness about 30 µm. In general, the microstructure of the ribbon has the same character as the microstructure of the cast ingot. Dendritic growth mainly occurred in the direction of heat dissipation. Near the contact surface of the ribbon the highest cooling rate was achieved that caused formation of an ultrafine structure in this area.

Figure 3. Microstructure of the rapidly quenched ribbon of the HEA Nb$_{0.73}$CoCrFeNi$_{2.1}$.

3.3. X-ray diffraction phase analysis
To determine the phase composition of the Nb$_{0.73}$CoCrFeNi$_{2.1}$ HEA, an X-ray diffraction analysis of the annealed rapidly quenched ribbon was carried out (Figure 4). By comparing the results with the results of the analysis of the chemical composition carried out using SEM, it became possible to conclude that the alloy contains two phases: a solid solution based on Ni with Co, Fe and Cr dissolved in it; NbNi$_3$ intermetallic compound with FCC lattice.

A similar analysis of the alloy Nb$_{0.93}$Co$_{1.16}$Cr$_{1.08}$Fe$_{1}$Ni$_{2.11}$ showed that it contains the same two phases.
3.4. Differential thermal analysis
Thermal curves obtained as a result of DTA of samples of the HEAs Nb$_{0.73}$CoCrFeNi$_{2.1}$ and Nb$_{0.93}$Co$_{1.16}$Cr$_{1.05}$Fe$_{1}$Ni$_{2.11}$ are shown in Figures 5 and 6, respectively. With using these results, liquidus and solidus temperatures of HEAs were determined:

- Nb$_{0.73}$CoCrFeNi$_{2.1}$: $T_L \sim 1260$ °C, $T_S \sim 1180$ °C;
- Nb$_{0.93}$Co$_{1.16}$Cr$_{1.05}$Fe$_{1}$Ni$_{2.11}$: $T_L \sim 1240$ °C, $T_S \sim 1180$ °C.

For both alloys, there is no significant difference between the rapidly quenched tape and the cast ingot. Considering this, the experiment with HEA Nb$_{0.93}$Co$_{1.16}$Cr$_{1.05}$Fe$_{1}$Ni$_{2.11}$ was only managed for as-cast ingot. After crystallization with further cooling down to the room temperature, no curve peaks are observed, which indicates the absence of polymorphic transformations of the studied alloys, since no processes associated with the release or absorption of a heat have been recorded.
Figure 6. DTA curve for the sample of cost ingot of the HEA Nb\textsubscript{0.93}Co\textsubscript{1.16}Cr\textsubscript{1.05}Fe\textsubscript{1}Ni\textsubscript{2.11}.

The HEA with optimized composition Nb\textsubscript{0.93}Co\textsubscript{1.16}Cr\textsubscript{1.05}Fe\textsubscript{1}Ni\textsubscript{2.11} contains a smaller amount of the solid solution primarily releasing during crystallization than the Nb\textsubscript{0.73}CoCrFeNi\textsubscript{2.1} alloy. Therefore, one can conclude that the alloy Nb\textsubscript{0.93}Co\textsubscript{1.16}Cr\textsubscript{1.05}Fe\textsubscript{1}Ni\textsubscript{2.11} is closer to the eutectic composition than Nb\textsubscript{0.73}CoCrFeNi\textsubscript{2.1}. This explains its lower liquidus temperature that approximately equals 1240 °C. Based on the experiments, one can say that the crystallization of the studied alloys proceeds as follows: at a liquidus temperature of T\textsubscript{L} \textasciitilde 1240 – 1260 °C, precipitation of crystals of a solid solution based on Ni with Co, Fe and Cr dissolved in it begins; as the temperature decreases a number of precipitates grows and when the solidus temperature T\textsubscript{S} \textasciitilde 1180 °C is reached, a eutectic forms consisting of the same solid solution and NbNi\textsubscript{3} intermetallic compound.

3.5. Brazing of the aluminum-oxide ceramics

The rapidly quenched ribbon of HEA Nb\textsubscript{0.93}Co\textsubscript{1.16}Cr\textsubscript{1.05}Fe\textsubscript{1}Ni\textsubscript{2.11} was used as a filler metal to obtain a brazed joint of aluminum-oxide ceramics 22XC. The chosen mode with step cooling provides the minimum amount of residual thermal stresses in the brazed seam, which is important for maintaining the integrity of the joint. With the right cooling mode, cracks in the joint can be eliminated. Figure 7 shows the microstructure of the brazed joint.

Figure 7. Microstructure of the brazed joint 22XC/22XC with microhardness data, filler metal is HEA Nb\textsubscript{0.93}Co\textsubscript{1.16}Cr\textsubscript{1.05}Fe\textsubscript{1}Ni\textsubscript{2.11}, brazing temperature is 1300 °C for 20 min with step cooling.

An analysis of the microstructure shows that the original composition of the filler metal was saved in the brazed seam. The seam has a pre-eutectic structure and consists of a solid solution based on Ni with Co, Fe and Cr dissolved in it and a eutectic (solid solution + NbNi\textsubscript{3} intermetallic compound). The
formation of a connecting oxide layer is clearly visible (area 2, Figure 8). Presumably, the oxide layer mainly consists of oxides of aluminum, chromium and manganese, as well as niobium oxide.

**Figure 8.** Microstructure of the brazed joint 22XC/22XC, filler metal is HEA Nb_{0.93}Co_{1.16}Cr_{1.05}Fe_{1.11}. brazing temperature is 1300 °C for 20 min with step cooling. The results of chemical analysis in areas 1 – 6 is shown in Table 3.

### Table 3. X-ray microanalysis of the brazed seam 22XC/22XC, areas 1 – 6 are shown at Fig. 8 (values are shown in wt.%).

| Area | O  | Mg | Al  | Si | Cr | Mn | Fe  | Co | Ni | Nb |
|------|----|----|-----|----|----|----|-----|----|----|----|
| 1    | 46.9 | 0.0 | 52.3 | 0.0 | 0.4 | 0.0 | 0.0 | 0.0 | 0.4 | 0.0 |
| 2    | 33.2 | 0.4 | 20.5 | 0.3 | 13.9 | 16.2 | 2.1 | 3.2 | 4.6 | 5.6 |
| 3    | 0.0  | 0.0 | 0.0  | 1.7 | 6.9 | 0.9 | 11.9 | 18.7 | 24.7 | 35.2 |
| 4    | 0.0  | 0.0 | 0.0  | 0.0 | 12.8 | 1.7 | 19.9 | 18.8 | 39.5 | 7.3 |
| 5    | 0.0  | 0.0 | 0.0  | 0.8 | 10.3 | 1.3 | 16.3 | 18.7 | 34.8 | 17.8 |
| 6    | 29.3 | 0.0 | 35.3 | 1.4 | 14.8 | 19.2 | 0.0 | 0.0 | 0.0 | 0.0 |

3.6. Microhardness of the brazed joint
The microhardness of the brazed joint 22XC/22XC and the microhardness of the cast ingot are given in Table 4. It is noticeable that the microhardness of the brazed seam is slightly higher than the initial cast ingot of the HEA Nb_{0.73}CoCrFeNi_{2.1}.

**Table 4.** Microhardness of the brazed joint 22XC/22XC, the ceramic and the brazed seam.

| Sample          | Microhardness, HV_{0.1} | Error, % |
|-----------------|--------------------------|----------|
| Cast ingot HEA  | 520                      | 12       |
| Ceramic 22XC    | 1800                     | 12       |
| Brazed seam 22XC/22XC | 700                  | 14       |

4. Conclusions
Based on the research of HEAs of the Ni-Nb-Co-Fe-Cr system, the following conclusions can be made:

The following values were calculated for the HEA Nb_{0.73}CoCrFeNi_{2.1}: the atomic size difference are $\delta = 4.8$; the mixing enthalpy $\Delta H_{\text{mix}} = -12.2$ kJ/mol and the mixing entropy $\Delta S_{\text{mix}} = 12.8$ J/(K·mol).

The liquidus and solidus temperatures of HEAs were determined:

- $\text{Nb}_{0.73}\text{CoCrFeNi}_{2.1}$: $T_L \sim 1260 \degree C$, $T_S \sim 1180 \degree C$;
- $\text{Nb}_{0.93}\text{Co}_{1.16}\text{Cr}_{1.05}\text{Fe}_{1.11}$: $T_L \sim 1240 \degree C$, $T_S \sim 1180 \degree C$.

The X-ray diffraction analysis results show that alloys $\text{Nb}_{0.73}\text{CoCrFeNi}_{2.1}$ and $\text{Nb}_{0.93}\text{Co}_{1.16}\text{Cr}_{1.05}\text{Fe}_{1.11}$ contain two phases: a solid solution based on Ni with Co, Fe and Cr...
dissolved in it and NbNi$_3$ intermetallic compound with FCC lattice. The alloys have a hypoeutectic structure consisting of a solid solution based on Ni and a eutectic (solid solution + NbNi$_3$ intermetallic compound).

Based on DTA results the brazing mode for samples of aluminum-oxide ceramics 22XC is chosen: filler metal is HEA Nb$_{0.93}$Co$_{1.16}$Cr$_{1.05}$Fe$_1$Ni$_{2.11}$, brazing temperature is 1300 °C for 20 min with step cooling. The brazed seam 22XC/22XC has a hypoeutectic structure consisting of the solid solution based on Ni with Co, Fe and Cr dissolved in it and the eutectic (solid solution + NbNi$_3$ intermetallic compound). Presumably, the oxide layer mainly consists of oxides of aluminum, chromium and manganese, as well as niobium oxide.

The brazed seam 22XC/22XC has a microhardness 700 HV$_{0.1}$ that is slightly higher than the microhardness of the initial cast ingot of the HEA Nb$_{0.73}$CoCrFeNi$_{2.1}$.

As a result, it was shown that HEA Nb$_{0.93}$Co$_{1.16}$Cr$_{1.05}$Fe$_1$Ni$_{2.11}$ can be used for brazing the aluminum oxide ceramic in which the brazed seam is qualitative and has no defects.

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