Development of rapidly quenched nickel-based non-boron filler metals for brazing corrosion resistant steels

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Abstract. Corrosion-resistant steels are stably applied in modern rocket and nuclear technology. Creating of permanent joints of these steels is a difficult task that can be solved by means of welding or brazing. Recently, the use rapidly quenched boron-containing filler metals is perspective. However, the use of such alloys leads to the formation of brittle borides in brazing zone, which degrades the corrosion resistance and mechanical properties of the compounds. Therefore, the development of non-boron alloys for brazing stainless steels is important task. The study of binary systems Ni-Be and Ni-Si revealed the perspective of replacing boron in Ni-based filler metals by beryllium, so there was the objective of studying of phase equilibrium in the system Ni-Be-Si. The alloys of the Ni-Si-Be with different contents of Si and Be are considered in this paper. The presence of two low-melting components is revealed during of their studying by methods of metallography analysis and DTA. Microhardness is measured and X-ray diffraction analysis is conducted for a number of alloys of Ni-Si-Be. The compositions are developed on the basis of these data. Rapidly quenched brazing alloys can be prepared from these compositions, and they are suitable for high temperature brazing of steels.

1. Introduction
Nowadays the structure having lower performance because of the presence of heterogeneities, which can lead to the degradation and destruction of the joint structures during operation, is forming in the brazed joints while using filler metals containing boron [1]. Therefore, an important task is to develop non-boron filler metal.

Currently the system Ni-Si-Be is poorly studied. The action of beryllium in nickel alloys in many ways similar to the action of boron; but in contrast to boron, it is highly soluble in nickel, forming an eutectic with the beryllium content of 23.8 at.% melting at 1150 °C and consisting of a solid solution Ni (α) and low ductile intermetallic BeNi (β) [2]. The intermediate phases, worsening properties of the compound will not form in iron during brazing because of high solubility of Be, as is the case with boron. Therefore, nickel alloy containing Be, are promising for brazing steels on a par with containing boron alloys. Studies of various alloys containing beryllium, showed that they have a high specific strength and corrosion resistance [3].

Analyzing all the advantages and disadvantages of the impact of beryllium on the properties of the brazed joint, can be concluded that the study of nickel alloys containing this element is extremely important field and can solve a number of problems that arise when working with boron filler metals,
and therefore the purpose of research is to develop filler metals based on Ni-Si-Be system for brazing stainless steels.

2. Experiment and methods
The microstructure of the samples and elemental composition alloys of Ni-Si-Be, which were pre-annealed for 6 hours at 950 °C in a vacuum of 10⁻⁴ Torr, was investigated by the scanning electron microscope JEOL JSM-6610LV. The study of alloys containing beryllium by techniques of electron microprobe microanalysis is difficult, because Be – can’t be detected by EDX.

Differential thermal analysis, which was performed on the thermal analyzer SDTQ600, was used to determine the intervals of melting alloys Ni-Si-Be. This thermal analyzer allows record the change in mass of the sample (thermal gravimetric analysis) and processes, accompanied by the release or absorption of heat simultaneous.

X-ray diffractometer Bruker D8 Discover with international X-ray data base ICDD PDF-2 was used to determine the quality of the phase composition of samples.

Determination of Vickers microhardness was performed on digital micro durometer models Future-Tech FM-800. The rate of load 50 m/s, the load time of 20 seconds, the accuracy in accordance with GOST 9450 (government state). The measurement was carried out by indentation in the test material the Vickers diamond tip with a square base, four-sided pyramid, providing a mechanical and geometric similarity of fingerprints for the deepening of the indenter under load.

3. Results and Discussion

3.1 Study of the structure alloys Ni-Si-Be
Eutectic alloys in the Ni-Si-Be system, which have low melting points and better fluidity as compared to non-eutectic alloys, are most interesting alloys for the creation of filler metals.

We can assume by analyzing the binary systems Ni-Si and Ni-Be that most fusible alloys (eutectic) are close to the composition of Ni- (4..6)Si- (3..5)Be. To study the effect of alloying beryllium and silicon on the structural-phase state of nickel alloys were selected the compositions containing different amounts of silicon and beryllium (Table 1).

| Table 1. Nickel alloys with various contents of Si and Be. |
|----------------------------------------------------------|
| 1  | Ni-4Si-(2; 3; 3.5; 4)Be |
| 2  | Ni-5Si-(2; 3; 3.5; 4)Be |
| 3  | Ni-6Si-(2; 3; 3.5; 4; 5)Be |
| 4  | Ni-7Si-(4; 5)Be |
| 5  | Ni-8Si-4Be |

These alloys are selected in such way as to capture supposed area amounted to approximately the ternary eutectic.

To investigate influence of the Be and Si amount on the structural-phase state of nickel alloys, the microstructure of the samples was studied and carried out differential thermal analysis (DTA). The effect of silicon and beryllium content on the structure of nickel alloy was studied based on this data. Figure 1 shows the results of metallographic analysis.

Let us consider the alloys Ni-4Si-2Be, Ni-4Si-4Be, Ni-6Si-4Be, Ni-6Si-5Be for study of the effect of the beryllium and silicon amount on the temperature and melting range. Alloy with the lowest amount beryllium Ni-4Si 2Be has the structure of a solid solution with a small amount of the eutectic. The forming of second phases in the form of needles into the solid solution is observed due to the reduction the solubility of Be and Si in nickel, according to the contrast and shape of these emissions it is the phase with a high content beryllium that is beryllide.
Further increase of the amount of beryllium up to 4 wt. % leads to formation of a new structural component which has a finely dispersed eutectic structure. Its amount increases with the increase of beryllium, and enhanced thermal effect associated with the crystallization / melting of the structural component.

The thermal effect is in the temperature range 885-985°C on the thermograms by increasing the silicon content up to 5 wt. % that indicates the appearance of a new structural component having a low transformation temperature. Thus, as in the case of the alloy Ni-4Si-4Be, new fine eutectic can be observed in the structure. The solidus temperature of this alloy series is practically unchanged and is 1115-1118°C (heating), 1107-1112°C (cooling).

The effect of increasing the melting range is observed in alloys with 5 wt. % silicon by increasing the amount of beryllium from 3.5 to 4%. This is related to a decrease of the amount of binary eutectic (1107-1112°C) and the appearance of the ternary eutectic (880-936°C), while on the border of the ternary eutectic crystallized solid solution, which gives the increase of the melting range.

**Figure 1.** The microstructure of nickel alloys with different contents of Si and Be, (a) – Ni-4Si-2Be; (b) – Ni-4Si-4Be; (c) – Ni-6Si-4Be; (d) – Ni-6Si-5Be.

Figure 2 shows the results of differential thermal analysis for alloys with constant silicon content of 6 wt. % and variable content of beryllium (all DTA curves are offset for clarity). The microstructure of
the alloy Ni-6Si-5Be most interesting as it is fully eutectic and has a needle structure. Analyzing the thermogram it can be compared observed eutectic structure with low-temperature peak in the range of consumable 933-944°C. Supposedly the composition is close to the composition of the low-temperature ternary eutectic. However, large melting range of the solid solution, which is apparently present in the alloy, is still observed on the thermogram.

It may be noted that the same pattern repeats for the alloys with a silicon content of 6 wt. % as for the previous alloys containing 5 wt. % silicon. Specifically, the amount of beryllium has no effect on the solidus temperature. Melting range decreases with increasing of beryllium (3 wt. % and 3.5 wt. % Be), and an eutectic structure becomes larger. And when it reaches content of 4 wt. % of beryllium range begins to increase again, which is associated with the formation of low-temperature and over-eutectic solid solution on its border.

Figure 2. Differential thermal analysis for alloys Ni-6Si-2Be, Ni-6Si-3Be, Ni-6Si-3.5Be, Ni-6Si-4Be, Ni-6Si-5Be.

It was further considered the change of temperature and melting range of alloys with the same amount of beryllium and various amount of silicon. Thermogram was made for alloys with constant content of beryllium and varying content of silicon, and it was found that silicon lowers the temperature of solidus. In alloys with a constant content of beryllium observed effect of the amount of silicon on the eutectic structure.

With the increase of silicon up to 6 wt. % the eutectic structure becomes fine and uniform that is the proportion of the ternary eutectic increases with an increase of silicon. With a high silicon content (7-8 wt. %) the structure of alloys becomes needle, and there are observed silicides (white allocation). The peak corresponding ternary eutectic are clearly defined in the alloy Ni-6Si-5Be due to the high amount of Be and Si, and practically no peaks corresponding binary eutectic (little thermal effect), which were pronounced in the previous alloys containing less of silicon and beryllium.

It was concluded about the influence of Be and Si to nickel alloys on the basis of the thermograms and the microstructures. Increasing the amount of Be and Si in the alloy is accompanied by an increase of the amount of low-temperature ternary eutectic in structure (appearance of the eutectic changes - it becomes fine, and there is an eutectic with larger plates). Also, melting range varies strongly enough with increasing the silicon content - it becomes smaller and decreases the solidus temperature at 10-15°C that is the peaks shifted to the left. The narrowest melting range of all considered alloys
characterized for the beryllium content of 3-3.5 wt. % independently of the silicon content. Also, thermal effect of melting ternary eutectic enhanced, when the silicon content of 6 wt. %.

After analyzing the results of studies it can be concluded that a high amount of silicon in the alloy uniquely effect on its properties. On the one hand adding more silicon which lowers a melting point of ternary eutectic enhanced, when the silicon content of 6 wt. %.

According to the obtained values it can be concluded that an increase the silicon and beryllium content in the alloy increases the value of microhardness. Alloys, which is present as a solid solution in structure, have lower values of microhardness. For example Ni-4Si-2Be, which has the structure: ternary eutectic.

3.2 X-ray diffraction analysis
In addition for the qualitative study of alloys Ni-Si-Be was carried out X-ray analysis of the alloy Ni-4Si-2Be, which has the structure: dominated solid solution and the double eutectic, and Ni-6Si-5Be, which has the structure: ternary eutectic.

According to the results of X-ray analysis of the sample Ni-4Si-2Be present: a solid solution based on Ni, BeNi, Ni5Si. The phases presenting in the sample Ni-6Si-5Be are identical with the phases of the sample-Ni-4Si 2Be.

Analyzing the experimental data, we can conclude that alloys compositions close to: Ni-5Si-3Be and Ni-6Si-5Be, - are interesting for further research. The latter has a low melting point due to the ternary eutectic (brazing temperature of the brazing alloy so 1070°C).

3.3 Measurement of microhardness nickel-based alloys with various contents of silicon and beryllium
In order to evaluate the mechanical properties of the developed filler metals and determine the form in which they will be used (in the form rapidly quenched ribbon or powder) microhardness of the alloys was measured. The microhardness of near eutectic nickel alloys containing boron was measured for comparison. Table 2 shows the measurement results.

If the value of microhardness is too high, then the alloy will not apply some methods of getting the structure of a rapidly quenched. Alloy with high microhardness - not technological, and because of low ductility it can easily evolve microcracks, so that it is can show low performance.

According to the obtained values it can be concluded that an increase the silicon and beryllium content in the alloy increases the value of microhardness. The alloys, which is present as a solid solution and eutectic is high magnitude of the spread of values of microhardness. Alloys, having mainly the solid solution in structure, have lower values of microhardness.

Compared with the boron alloys it should be considered that the ribbon received from the alloy Ni-3.5Fe-7.5Cr-4.5Si-2.6B is amorphous [4, 5] due to the presence of silicon and boron, in contrast to ribbon produced from alloys system Ni-Si-Be with the same cooling rate.

Table 2. The microhardness alloys of the Ni-Si-B and Ni-Fe-Cr-Si-B systems.

| Alloy          | Average microhardness, (GPa) | The mean square deviation (GPa) | Alloy          | Average microhardness, (GPa) | The mean square deviation (GPa) |
|---------------|------------------------------|-------------------------------|---------------|------------------------------|-------------------------------|
| Ni-4Si-2Be    | 3.0                          | 0.5                           | Ni-6Si-3Be    | 4.1                          | 1.2                           |
| Ni-4Si-3Be    | 3.7                          | 0.4                           | Ni-6Si-3.5Be  | 5.7                          | 1.5                           |
| Ni-4Si-3.5Be  | 3.7                          | 0.6                           | Ni-6Si-4Be    | 6.1                          | 1.1                           |
| Ni-4Si-4Be    | 4.0                          | 1.0                           | Ni-6Si-5Be    | 6.4                          | 0.9                           |
| Ni-5Si-2Be    | 3.4                          | 0.7                           | Ni-7Si-4Be    | 6.6                          | 1.1                           |
| Ni-5Si-3Be    | 4.6                          | 0.9                           | Ni-7Si-5Be    | 6.5                          | 0.8                           |
| Ni-5Si-3.5Be  | 4.6                          | 0.7                           | Ni-8Si-4Be    | 6.4                          | 1.5                           |
| Ni-5Si-4Be    | 4.8                          | 1.9                           | Ni-3.5Fe-7.5Cr-4.5Si-1.7B | 6.0                          | 1.5                           |
| Ni-6Si-2Be    | 4.2                          | 1.2                           | Ni-3.5Fe-7.5Cr-4.5Si-2.6B | 6.8                          | 1.6                           |
Therefore the microhardness for 1301A alloy does not affect on the flexibility of the final ribbon, but for alloys with beryllium effect: there are limiting the amount of silicon and beryllium in the Ni-Si-Be, which you can get flexible processing ribbon. On the basis of the data we concluded that to obtain high-quality ribbon the amount of silicon shall not exceed (4.5-5.0) wt. % and the amount of beryllium (3.0-3.5) wt. %.

4. Conclusions
From the analysis of the research of Ni-Si-Be discovered that the system Ni-Si-Be is promising to create of a rapidly quenched filler metal without boron. In the system Ni-Si-Be has been established the presence of two eutectic with melting temperatures \( \sim 1100^\circ C \) and \( \sim 915^\circ C \). With regard to such factors as the melting range, the brazing temperature and microhardness alloys of Ni-5Si-3Be and Ni-6Si-5Be are the most interesting for further studies, the compositions of which are mounted near two eutectics respectively.

Composition of Ni-6Si-5Be is promising because it could be get the filler metal with brazing temperature from 1070°C, but only in the form of powder, therefore, such a composition requires additional alloying increases the ductility of the alloy. In contrast, the alloy composition of Ni-5Si-3Be can be obtained tech flexible ribbon but the temperature of brazing of this filler metal is little bit higher than 1130°C.

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