Thermal fatigue damage of steel joints brazed with various nickel filler metals*

M. A. Penyaz, *Post-Graduate Student[1], Department №9 "Physical problems of materials science", e-mail: mapenyaz@mephi.ru*
A. A. Ivannikov, *Senior Lecturer[1], Department №9 "Physical problems of materials science", e-mail: ivannikov7@rambler.ru*
B. A. Kalin, *Professor[1], Department №9 "Physical problems of materials science", e-mail: bakalin@mephi.ru*
P. S. Dzhumaev, *Associate Professor[1], Department №9 "Physical problems of materials science", e-mail: psdzhumaev@mephi.ru*

[1]National Research Nuclear University MEPhI (Moscow Engineering Physics Institute), Russia, Moscow.

Demands on the properties of constructions are constantly being increased and the technology of producing permanent joints is crucial for advancement of the high-tech industry. This investigation focuses on thermal fatigue of austenitic steel joints, brazed with nickel filler metals based on Ni – Cr – Si system. This type of fatigue has nonmechanical origin and arises from the cyclic variation of thermal stresses with temperature changes. For investigation selected temperature range is: from room temperature to 450 °C (low-cycle fatigue). Due to inhomogeneous thermal expansion or compression during thermal fatigue, thermal stresses and deformation arise and lead to microstructural changes in the joint zone. This can have a strong effect on the mechanical characteristics of the joint. Therefore, it is important to investigate the properties of the brazed seam after thermal cycling. In this work samples brazed various filler metals before and after thermocycling were evaluated using various methods. The microstructures were investigated and analysis by energy-dispersive *X*-ray spectroscopy (EDS) of the diffusion zone was carried out using electron microscope. The main regularities of the structure-phase state formation studied using electron backscatter diffraction (EBSD). Standard tests for the tensile strength of the samples were carried out. The result of this research is the prediction of the durability and reliability of brazed steel constructions operating under conditions of low-cycle temperature changes.

Key words: joint, diffusion brazing, filler metal, BNi-2, EBSD, heat-resistant steel, nickel, boron.
DOI: 10.17580/nfm.2019.01.06

Introduction

Nowadays, the effect on the thermal fatigue properties of the complex structure of borides arising in steel joints [1–3] obtained using industrial boron-containing nickel filler metals has been poorly studied. Studies of borides effect on fatigue mechanisms in the brazed seam by the action of temperature cyclic changes will help to optimize the filler metal compositions, based on Ni – Cr – Si – B system, and obtain the most homogeneous structure. The general trend of increasing the fatigue characteristics of joints can be illustrated by works [4–5]. The resistance of materials, including joints, to fatigue damage is increasingly of interest from the point of view of tests that simulate operating conditions. High operating temperatures and resistance to thermal cyclic loads are a mandatory requirement for many energy-stressed units operating under temperature change conditions [6–9] In such products as rocket nozzles, heat exchangers, gas turbine engine blades, pistons of internal combustion engines, components of atomic technology and energy turbines – the efficiency depends on the operating temperature. Thermal cycling test allows to establish the dependence of thermal fatigue and destruction mechanisms on the microstructure [10–12]. This method is suitable for the qualitative assessment of factors affecting the strength, including fatigue, such as, for example, the elemental composition of the filler metal, the parameters for obtaining a joint or the distribution of stresses. Thus, this method based on a small number of tests may allow an assessment of the fatigue processes and the development of damage in the brazed joint.

Thermal fatigue is a destruction of the internal stresses created by cyclically changing the temperature field in the material. Thermal fatigue is possible both in total with external loads and without it. Stresses arise from the irregularity of heating or cooling over the cross section with changes in operating temperature. Stresses can also be structural, as a result of phase transformations and phase hardening.

In massive structures heated from the surface, thermal deformations are localized in the surface layer, where the crack grows. Thin-walled structures are destroyed by thermal fatigue where they are tougher: near the corner joints,

*The article was attended by the staff of the Department №9 "Physical problems of materials science" NRNU MEPhI – Sevryukov O. N., Suchkov A. N., Fedotov I. V.

stiffeners, in places of brazed joints. Thermal stresses from heating-cooling, for example, when the engine is started / stopped, induce low-cycle thermal fatigue of the turbine disk. And the cracks on the edges of the blades are caused not only by these slow temperature cycles, but also by high-frequency ones from the pulsation of the gas flow.

Until now, there are no full-scale studies of the thermal fatigue of brazed joints, obtained using boron filler metals, and solving the problem associated with the heterogeneous structure of these joints.

Table 1
Chemical composition of base material

Material	Mark		Chemical composition, wt.%					
	Russian	International	C	Cr	Si	Mn	Ni	Ti
Austenitic steel	12Cr18Ni10Ti	AISI 321	0.12	18	0.8	<2	10	0.5

Table 2
Chemical composition of filler metals

Filler metal	Analogue	Chemical composition, wt.%					
		Ni	Cr	Si	Fe	B	Be
*1301®	BNi-2	bal	7	4.5	3.5	2.6	–
Ni-7	–	bal	7	7.5	4.0	1.5	–
Ni-20	BNi-5a	bal	20	7.5	4.0	1.5	–
Ni-22	–	bal	22	7.5	4.0	1.5	–
Ni-0	–	bal	7	5	–	–	3

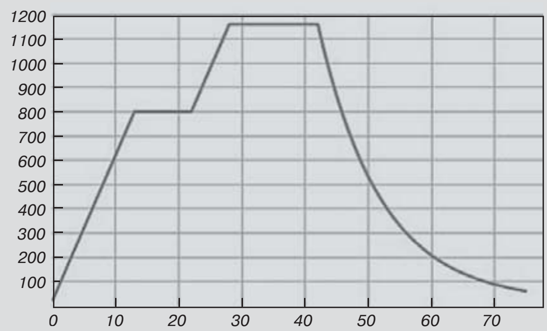
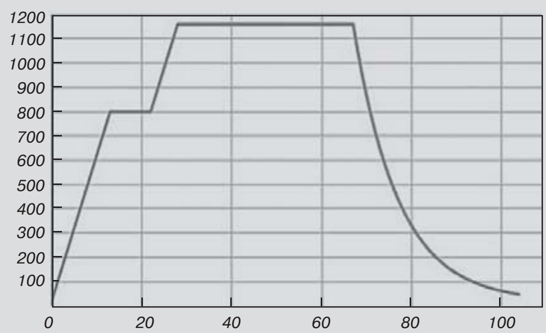
*STEMET® 1301 — Russian industrial filler metal.

Material and methods

Austenitic steel in the form of a rod with a grain size of 7–10 μm was used as initial materials. The nickel filler metals were used in the form of amorphous (nanocrystalline) thin (40–50 μm) films, manufactured according to the ultrafast melt solidification technology. Tables 1 and 2 show the compositions of the materials used and their correspondence to generally known analogs. Development of experimental filler metal Ni-0 is considered in the work [13].

The samples were brazed in a vacuum furnace with resistive heating. The optimal braze modes were chosen, taking into account the temperature characteristics of all the filler metals used, Table 3. The filler metals Ni-7, Ni-20, Ni-22 and Ni-0 have a high liquidus temperature and due to this the high temperature of brazing was chosen. For the filler metal 1301® the temperature is such high in order to grain size when

Table 3
Braze mode

Base material	Filler metal	Braze mode	
12Cr18Ni10Ti	1301®	800 °C, 10 min 1160 °C, 15 min	
	Ni-7	800 °C, 10 min 1160 °C, 40 min	
	Ni-20		
	Ni-22		
	Ni-0		

using it will be the same, as in the case of the use of alloys Ni-7, Ni-20, Ni-22 and Ni-0. It is known that this steel has recrystallization temperature near 1100 °C. With an increase in the holding temperature, the final grain size grows exponentially [14]. The increase in the duration of holding time also leads to an increase in grain size, however, the growth occurs according to a logarithmic law. For this reason temperature is the determining factor in grain growth and it is chosen the same for all samples, because different grain size can effect on result of resistance to thermal fatigue.

The gap between the part of materials corresponded to the thickness of the filler metal. Filler metal is placed in one layer on the ground side of steel sample and fixed with the help of spot capacitor electric welding. Then the steel is laid with the ground side to the filler metal and the assembly is fixed in a special conductor, so that during the thermal brazing cycle a uniform pressure is ensured over the entire surface of the samples. After brazing, samples are prepared for metallographic analysis or for testing.

Cylindrical brazed samples of austenitic steel with a height of ~ 6 mm and a diameter of ~10 mm were used for metallographic investigation (type 1). The cylinders were cut using a diamond disc into pieces, which were investigated using metallographic analysis (Fig. 1).

Strength properties under uniaxial tension of the samples (type 2) were determined according to Russian State Standard (GOST) 28830–90 (working part with a diameter of 6 mm) [15].

Two types of thermal cycling modes were tested. The first mode: thermal cycling of the samples was carried out in a metal flask, which was placed in a preheated muffle furnace. The samples were heated to 450 °C and then cooled to 60 °C with cooling rate 80 °C/min by immersing the flask in cold water. 50 cycles were performed. Only type 1 samples were investigated.

The second mode: thermal cycling of the samples was carried out in a special box, which was placed in a preheated muffle furnace. The samples were heated to 450 °C and then cooled to 60 °C with cooling rate 40 °C/min on the air (outside the furnace) with forced air circulation fan. Also 50 cycles were performed. Type 1 and 2 samples were investigated. Temperature control was carried out using a chromel-alumel thermocouple placed in a flask with samples.

For a more accurate study of the microstructure, a scanning electron microscope (SEM) was used. An *X*-ray microanalysis of the elemental composition will be carried out using an energy dispersive spectrometer (EDS) and wave dispersive spectrometer (WDS). An analysis of the phase composition was studied using a backscattered electron diffraction detector (EBSD).

Results and discussion

Initially, the microstructure of the brazed joints was analyzed before thermal cycling tests. Fig. 2 shows the microstructure of the joint for filler metals according the Table 2.

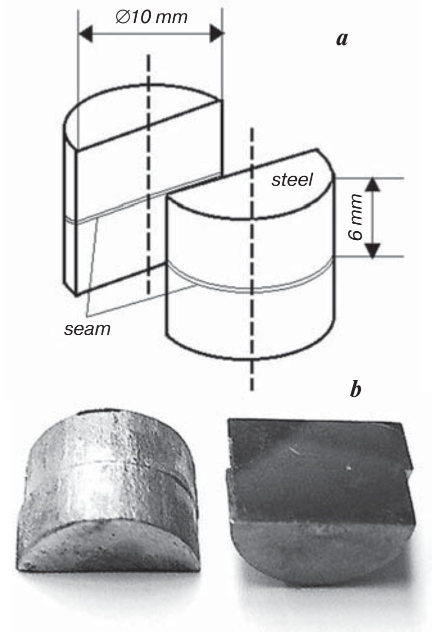


Fig. 1. View of samples for thermal cycling test.
a — geometry of samples for thermal cycling tests;
b — cut brazed sample for thermal cycling testing

Decreasing in boron content and increasing in silicon content, in case of Ni-7 (Fig. 2, *b*), compared with industrial filler metal 1301® (Fig. 2, *a*) positive influence on microstructure of diffusion zone: the amount of borides decreases. With different chromium content the following is observed. With an increase in chromium from 7% to 20% (Fig. 2, *c*) the amount of borides in the diffusion zone visually decreases.

According to WDS-analysis boride in the diffusion zone has a composition of 33Fe – 33Cr – 33B at.%, i.e. it is a complex compound FeCrB. It is formed mainly during isothermal dwell, and not during cooling, due to the grain-boundary diffusion of boron into steel. With an increase in chromium of more than 20% in the case of Ni-22 (Fig. 2, *d*), isothermal solidification does not occur fully and chromium borides Cr2B (according to WDS-analysis and [16]) remain in the center of the seam. In the case of boron-free Ni-0 (Fig. 2, *e*), beryllide nickel BeNi is formed in the center of the seam and a small amount of eutectic γ-Ni + Ni_3Si is present.

Degradation of the structure and an additional formation of intermediate phases were not detected using SEM investigations for all joints after thermal cycling tests (according mode 1 and 2). Fig. 3 shows the microstructure of the brazed joint 1301®/12Cr18Ni10Ti 1160 °C 15 minutes before and after thermal cycling on mode 1.

The diffusion zone was investigated using the EBSD method. Fig. 4 shows a phase map of the 12Cr18Ni-10Ti\1301® and 12Cr18Ni10Ti\Ni-0 brazed joint before

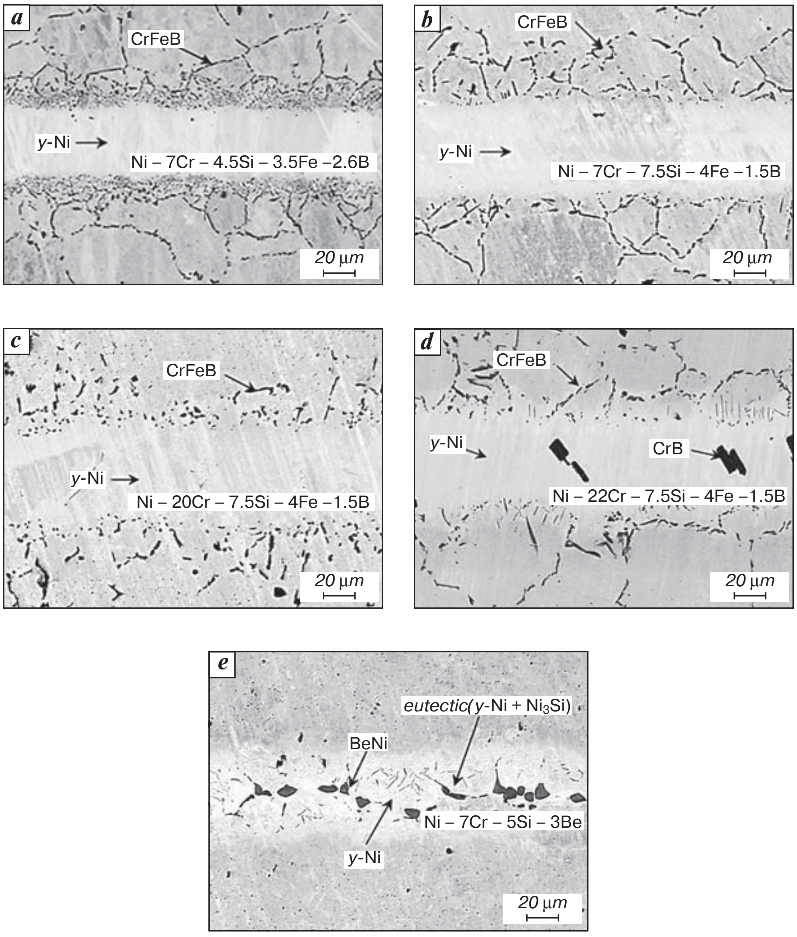


Fig. 2. Microstructure of brazed joints steel 12Cr18Ni10Ti.
a – 1301®; b – Ni-7; c – Ni-20; d – Ni-22; e – Ni-0

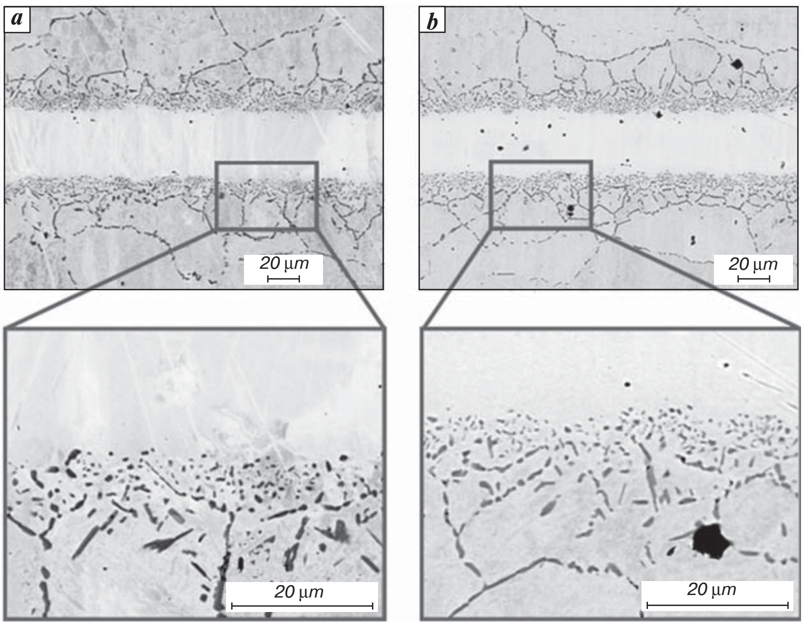


Fig. 3. Microstructure of brazed joints 12Cr18Ni10Ti\1301® 1160 °C 15 min:
a – before thermal cycling tests; *b* — after thermal cycling tests on mode 1

and after thermal cycling on mode 1. The phase map of the 12Cr18Ni10Ti\Ni-20 is the same as 12Cr18Ni10Ti\1301® and for this reason is not given.

Under the action of thermal stresses, deformation martensite is formed [17–18]. Thermal stresses arise due to changes of elastic modulus in different directions of grain. In FCC metals, the elastic modulus increases from 100 to 111. In case of 12Cr18Ni10Ti\1301® (mode 1) martensitic phases reached about 43% after thermal cycling in diffusion zone. In steel far from the brazed seam the amount of formed martensite ranges from 14% to 23%. The complex process of the shear phase transformation $\gamma \rightarrow \alpha'$ occurs in areas with the highest stress density, which accumulates during thermal cycling due to the large number of borides in the diffusion zone in the case of boron-containing filler metals. In case of 12Cr18Ni10Ti\Ni-0 brazed joint, a significant amount of martensite in the diffusion zone has also formed: 15%. It corresponds to the amount, which occurs in the steel, subjected to heat treatment in the same mode. However, for non-boron filler metal the diffusion zone is not significantly accumulated a deformation compared with 12Cr18Ni10Ti\1301® or 12Cr18Ni10Ti\Ni-20.

It was confirmed that the chemical distribution of elements in the brazed joint does not affect the formation of martensite in the diffusion zone. The results of EDS analysis is shown on Fig. 5. The main contribution to the accumulation of deformation during heating and cooling is made by a heterogeneous structure along the seam border.

The selected experimental mode of thermal cycling with a cooling rate of 80 °C/min is too hard. Identical studies were performed on brazed joints thermally cycled in a gentler mode 2 with a cooling rate 40 °C/min. The results for Ni-0 and Ni-20 filler metals are shown on Fig. 6. The phase map of the 12Cr18Ni10Ti\1301® is the same as 12Cr18Ni10Ti\Ni-20.

EBSD analysis demonstrate that the cooling rate huge effects on martensite formation. At rate of 40 °C/min the martensitic phase is formed significantly less, since at such rate smaller stresses were accumulated. In case of 12Cr18Ni10Ti\Ni-0 brazed joint (mode 2) martensitic phases

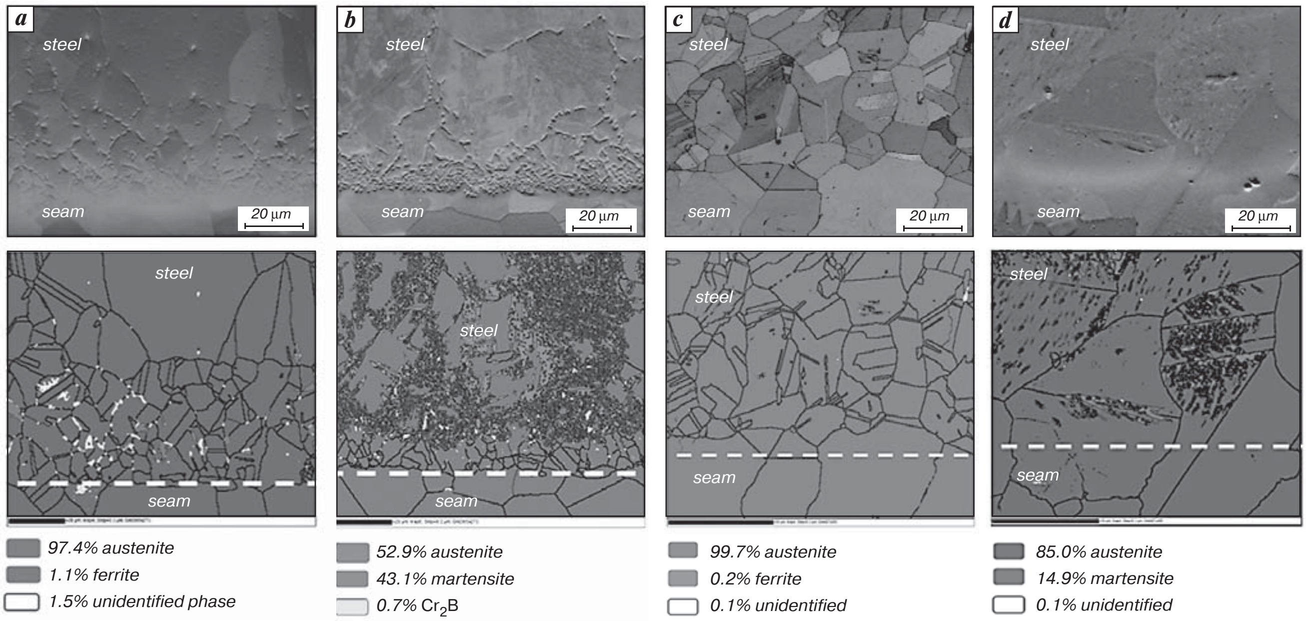


Fig. 4. Phase map by EBSD analysis of brazed joints steel 12Cr18Ni10Ti.
a — 1301®: before thermal cycling tests; *b* – 1301®: after thermal cycling tests on mode 1; *c* — Ni-0: before thermal cycling tests; *d* — Ni-0: after thermal cycling tests on mode 1

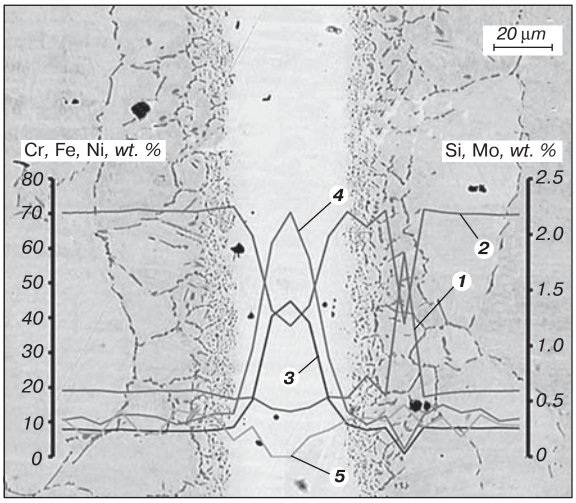


Fig. 5. EDS-analysis of brazed joints 12Cr18Ni10Ti\1301® 1160 °C 15 min:
1 — Cr; *2* — Fe; *3* — Ni; *4* — Si; *5* — Mo

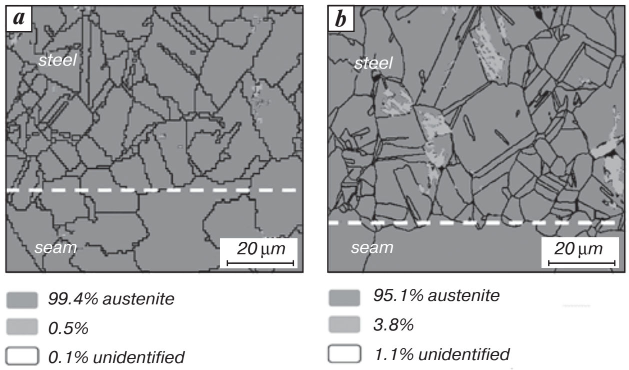


Fig. 6. Phase map by EBSD analysis of brazed joints steel 12Cr18Ni10Ti after thermal cycling tests on mode 2.
a — Ni-0; *b* – Ni-20

reached about 0.5% after thermal cycling in diffusion zone. In case of 12Cr18Ni10Ti\Ni-20 — 3.8%.

It can be concluded that if the brazed construction works for a long time in harsh cooling conditions reaching 80 °C/min and above, the use of 12Cr18Ni10Ti steel is not advisable due to changes in the structural-phase state both in the diffusion region and in the steel itself.

Uniaxial tension tests were performed for the samples (type 2) before and after thermal cycling test on mode 2 with cooling rate 40 °C/min. The results on uniaxial tensile test of the samples demonstrated a decrease in the tensile strength after thermal cycling. Fig. 7 presents the results of tests on uniaxial tension before and after thermal cycling. Ni-7 and Ni-22 samples were rejected, as they showed the worst results after the uniaxial tension test without thermal cycling test. Percentage denotes degradation after thermal cycling. In the case of the yield strength, the reduction is small, no more than 13%. In the case of tensile strength, the results are different. The largest decrease is observed in industrial filler metal 1301® and in the non-boron experimental alloy Ni-0: 30% and 29%, respectively. The tensile strength of steel has not changed significantly. The best heat resistance was shown by the joint 12Cr18Ni10Ti\Ni-20, which is probably related to the structure of the diffusion zone (only 10% reduce of tensile strength and 17% reduce of relative elongation against 60% and 66% for Ni-0 and 1301®, respectively). The smallest amount of borides is formed when brazing with this filler metal. Based on these results, it can be judged that the advantage in strength characteristics of joints obtained by filler

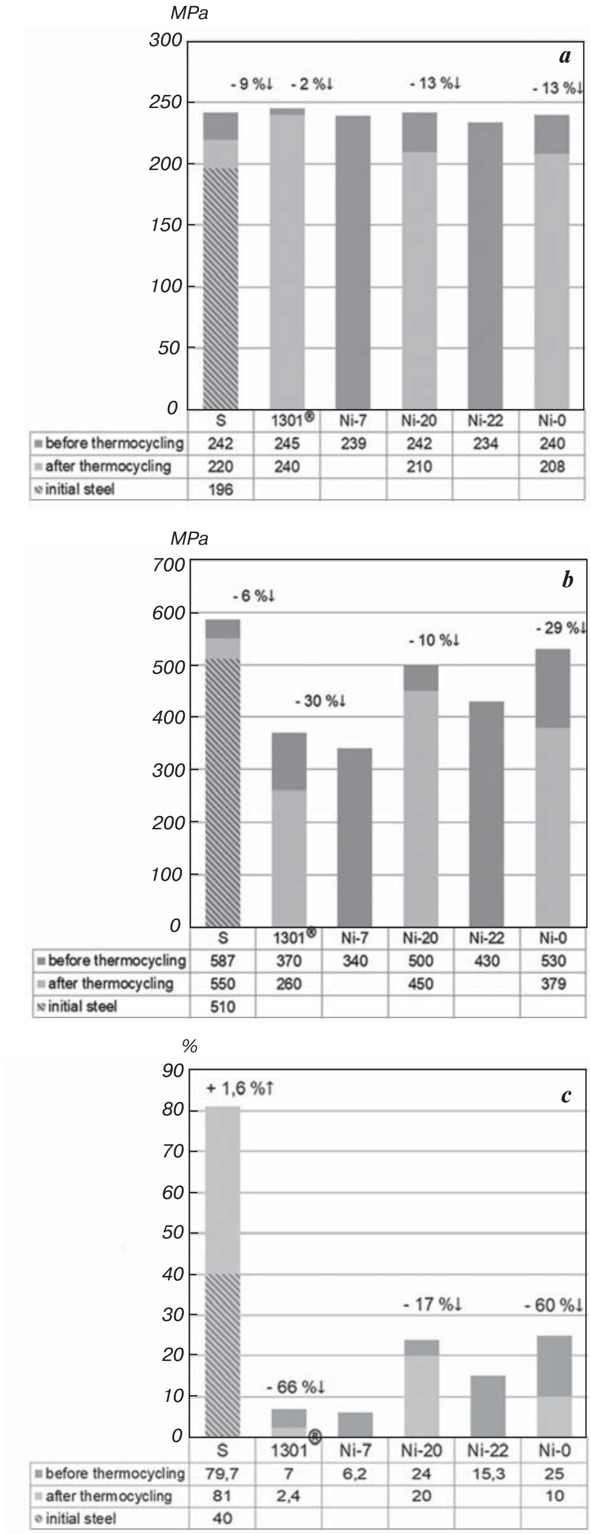


Fig. 7. Uniaxial tensile test results before and after thermal cycling tests. *a* — yield strength; *b* — tensile strength; *c* — relative elongation

metal with a smaller amount of boron and a large amount of chromium is retained even after thermal cycling test. It can be concluded that the formation of martensite is not the main factor that reduces strength, since after thermal cycling Ni-20 showed better strength than non-boron Ni-0 filler metall.

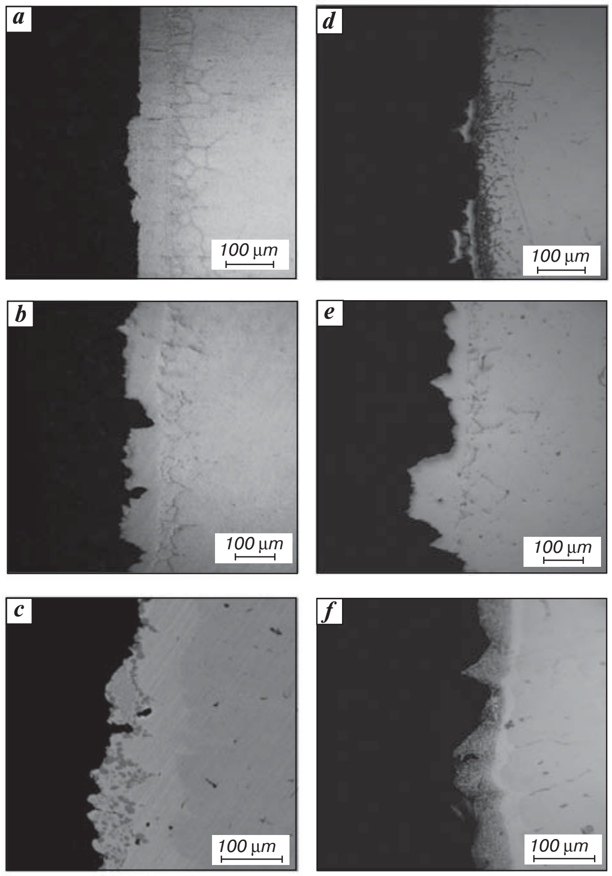


Fig. 8. Fracture area of brazed joints steel 12Cr18Ni10Ti after an uniaxial tensile test.
a — 1301®: before thermal cycling tests; *b* — Ni-20: before thermal cycling tests; *c* — Ni-0: before thermal cycling tests; *d* – 1301®: after thermal cycling tests on mode 2; *e* – Ni-20: after thermal cycling tests on mode 2; *f* — Ni-0: after thermal cycling tests on mode 2

An analysis of the fracture area of the initial and thermal cycled brazed samples showed that the fracture is predominantly brittle-viscous. In this case, the geometry of the joint is broken; the brazed joint is curved, which is explained by the local accumulation of plastic deformations. The crack propagation occurs practically along the straight line separating the area of the seam and brazed steel, with rare tearing out of individual seam grains.

Fig. 8, *a–c* shows the destruction of uncyclized brazed samples. After thermal cycling, the character of the damage is preserved (Fig. 8, *d–f*).

Conclusions

According to the results of thermal fatigue studies for steel joints brazed with various nickel filler metals, the following conclusions can be drawn:

– Under cyclic temperature changes from room temperature to 450 °C with a heating/cooling rate 80 °C/min deformation martensite are formed in the structure of steel 12Cr18Ni10Ti.

– Brazed joints 12Cr18Ni10Ti, obtained with Ni – 7Cr – 4.5Si – 3.5Fe – 2.6B filler metal, have a tensile strength of 370 ± 30 MPa. The tensile strength is reduced by 29% after thermal cycling. This is due to the occurrence of deformation martensite in the diffusion zone when using a high boron filler metal.

– Brazed joints 12Cr18Ni10Ti, obtained using Ni – 20Cr – 7.5Si – 4Fe – 1.5B filler metal, have high strength characteristics and heat resistance. Thermal cycling tests led to a decrease in tensile strength by 10% (from 500 ± ± 40 MPa to 450 ± 30 MPa). Positive trends are due to lower boron content and higher chromium content.

– It can be concluded that the formation of martensite is not the main factor that reduces strength, since after thermal cycling Ni-20 showed better strength than non-boron Ni-0 filler metall.

– Ni – 20Cr – 7.5Si – 4Fe – 1.5B filler metal can be recommended for producing brazed joints that are used in conditions of high thermal cyclic loads.

– EBSD analysis demonstrate that the cooling rate huge effects on martensite formation. At rate of 40 ^{o}C/min the martensitic phase is formed significantly less compared with rate of 80 ^{o}C/min, since at such rate smaller stresses were accumulated. If the brazed construction works for a long time in harsh cooling conditions reaching 80 ^{o}C/min and above, the use brazed joints of 12Cr18Ni10Ti steel considered in this work is not advisable due to changes in the structural-phase state both in the diffusion region and in the steel itself.

Acknowledgment

The reported study was funded by RFBR and DFG according to the research project №19-52-12030.

This work was supported by the MEPhI Academic Excellence Project.

References

1. Liu Z. P., Zhou G.-Y., Tian F. Q., Chen D. Q., Tu S.-T. Experimental Investigation on the Kinetic Parameters of Diffusion Component for Vacuum Brazing SS316L/BNi-2/SS316L Joint. *Procedia Engineering*. 2015. Vol. 130. pp. 497–508. DOI: 10.1016/j.proeng.2015.12.246.

2. Gu X. L., Yang C. J., Chen Z. J., Wu C. D., Feng L. L. Effect of Temperature on Microstructure and Mechanical Properties of 316L Stainless Steel Brazed Joints. *Advanced Materials Research*. 2011. Vol. 418–420. pp. 1494–1497. DOI: 10.4028/www.scientific.net/amr.418-420.1494.

3. Ivannikov A. A., Tukhbatov V. A., Suchkov A. N., Ustyuzhaninov A. L., Bogachev I. A. Rapidly quenched nickel based filler metal for high temperature various constructive elements brazing. *Tsvetnye Metally*. 2014. No. 12. pp. 27–31.

4. Binesh B., Jazayeri Gharehbagh A. Transient Liquid Phase Bonding of IN738LC/MBF-15/IN738LC: Solidification Behavior and Mechanical Properties. *Journal of Materials Science & Technology*. 2016. Vol. 32, Iss. 11. pp. 1137–1151. DOI: 10.1016/j.jmst.2016.07.017.

5. Hartmann T., Marsilius M. Influence of Boron and Phosphor Containing Nickel Based Brazing Alloy on Different Base Materials. *LÖT 2016: 11th International Conference on Brazing, High Temperature Brazing and Diffusion Bonding, June 7th to 9th, 2016, Aachen, Germany*. 2016. DVS-Berichte, Bd. 325. pp. 227–232.

6. Xia C., Sun W., Zhou Y., Xu X. Thermal fatigue damage and residual mechanical properties of W – Cu/Ag – Cu/1Cr18Ni9 brazed joint. *Journal of Alloys and Compounds*. 2018. Vol. 741. pp. 155–160. DOI: 10.1016/j.jallcom.2018.01.151.

7. de Prado J., Sánchez M., Wirtz M., Pintsuk G., Du J., Linke J., Ureña A. Impact of thermal fatigue on W–W brazed joints for divertor components. *Journal of Materials Processing Technology*. 2018. Vol. 252. pp. 211–216. DOI: 10.1016/j.jmatprotec.2017.09.024.

8. Bachurina D., Suchkov A., Kalin B., Sevriukov O., Fedotov I., Dzhumaev P., Ivannikov A., Leont'eva-Smirnova M., Mozhanov E. Joining of tungsten with low-activation ferritic–martensitic steel and vanadium alloys for demo reactor. *Nuclear Materials and Energy*. 2018. Vol. 15. pp. 135–142. DOI: 10.1016/j.nme.2018.03.010.

9. Bachurina D., Suchkov A., Filimonov A., Fedotov I., Savelyev M., Sevryukov O., Kalin B. High-temperature brazing of tungsten with steel by Cu-based ribbon brazing alloys for DEMO. *Fusion Engineering and Design*. 2019. DOI: 10.1016/j.fusengdes.2019.02.072.

10. Das A. Cyclic plasticity induced transformation of austenitic stainless steels. *Materials Characterization*. 2019. Vol. 149. pp. 1–25. DOI: 10.1016/j.matchar.2018.12.002.

11. M. Sistaninia, M. Niffenegger, Fatigue crack initiation and crystallographic growth in 316L stainless steel. *International Journal of Fatigue*. 2015. Vol. 70. pp. 163–170. DOI: 10.1016/j.ijfatigue.2014.09.010.

12. ASM Handbook: Fatigue and Fracture, Vol. 19. ASM International. Handbook Committee, 1996.

13. Ivannikov A. A., Kalin B. A., Sevryukov O. N., Penyaz M. A., Fedotov I. V., Misnikov V. E., Tarasova M. S. Study of the Ni – Si – Be system as a base to create boron-free brazing filler metals. *Science and Technology of Welding and Joining*. 2017. Vol. 23, Iss. 3. pp. 187–197. DOI: 10.1080/13621718.2017.1361668.

14. Metal Science: a manual in 2 vol. Vol. 2. Heat treatment. Alloys. Ed. by V. S. Zolotarevsky. 2nd ed., rev. Moscow : Izdatelskiy dom MISiS, 2014. 528 p.

15. GOST-28830–90. Soldered and brazed joints. Test methods for tension and long-term strength. Publication date: 01.01.92. Moscow: IPK Izdatelstvo standartov, 2005.

16. Rabinkin A. Brazing with (NiCoCr) – B – Si amorphous brazing filler metals: alloys, processing, joint structure, properties, applications. *Science and Technology of Welding and Joining*. 2004. Vol. 9, Iss. 3. pp. 181–199. DOI: 10.1179/136217104225012300.

17. Baak N., Garlich M., Schmiedt A., Bambach M., Walther F. Characterization of residual stresses in austenitic disc springs induced by martensite formation during incremental forming using micromagnetic methods. *Materials Testing*. 2017. Vol. 59, Iss. 4. pp. 309–314. DOI: 10.3139/120.111012.

18. Eskandari M., Najafizadeh A., Kermanpur A. Effect of strain-induced martensite on the formation of nanocrystalline 316L stainless steel after cold rolling and annealing. *Materials Science and Engineering: A*. 2009. Vol. 519, Iss. 1-2. pp. 46–50. DOI: 10.1016/j.msea.2009.04.038 NFM