

# Research trends in brazing and soldering

## Trendy badawcze w procesach lutowania miękkiego i twardego

### Abstract

Brazing has a long tradition at the Institute of Material Science and Engineering of the University of Chemnitz, Germany. During the last years, comprehensive and innovative knowledge in brazing and soldering technologies were generated. Originating from high-temperature brazing, topics like metal-ceramic and light metal brazing, ultrasound assisted joining processes through to brazing of metal matrix composites were examined. In addition, new topics like joining by nanoparticles or corrosion behavior of brazed heat exchangers are in the focus of research. Prof. Bernhard Wielage managed the institute for 22 years. Today, Prof. Guntram Wagner introduces new topics like friction stir welding and continues the activities in brazing.

**Keywords:** brazing; soldering; heat exchangers; brazing of metal-ceramic joints; soldering with diamond particles

### Streszczenie

Tradycje związane z tematyką lutowania twardego w Instytucie Materiałoznawstwa i Inżynierii Uniwersytetu w Chemnitz (Niemcy) są długie. W ciągu ostatnich lat wygenerowano kompleksową i innowacyjną wiedzę dotyczącą technologii lutowania miękkiego i twardego. Zajmowano się problematyką badawczą wywodzącą się od lutowania wysokotemperaturowego, taką m.in. jak: lutowanie twarde metali lekkich z ceramiką i wspomaganie procesu spajania ultradźwiękami w lutowaniu kompozytów metalowych. Obecnie przedmiotem badań są nowe zagadnienia, takie jak: spajanie nanocząsteczkami oraz zachowanie odporności korozyjnej wymienników ciepła lutowanych na twardo. Profesor Bernhard Wielage zarządzał Instytutem przez ostatnie 22 lata. Obecnie, nowy Dyrektor Instytutu Profesor Guntram Wagner zajmuje się takimi zagadnieniami, tjak np. zgrzewaniem tarciovym z wymieszaniem materiału zgrzeiny (FSW) i kontynuuje prace badawcze związane z lutowaniem twardym.

**Słowa kluczowe:** lutowanie twarde; lutowanie miękkie; wymienniki ciepła; lutowanie materiałów różnoimiennych metal-ceramika; lutowanie miękkie z cząstkami diamentu

## Introduction

This work gives an overview of the research fields in Brazing and Soldering at the Institute of Material Science and Engineering of the University of Chemnitz, Germany. In the last years, scientists were dealing with brazing of aluminum heat exchangers, brazing of metal-ceramic joints, soldering with diamond particles, magnesium soldering etc. Innovative and suitable joining technologies are a key factor to enlarge fields of application of modern materials or material combinations. In industrial applications, brazed components have to meet increased requirements such as mechanical, thermal, corrosive resistance under specific operating conditions. This leads to different tendencies in filler and process development. One requirement on high strength joints is the rise of service temperatures, for example

for turbine components, and, as a consequence, a rise of the brazing temperatures. On the contrary extreme low joining temperatures as necessary in electronic equipment are needed. Therefore, nowadays topics like high-temperature brazing of Co-based superalloys, arc brazing of aluminum matrix composites (AMC), induction brazing of dissimilar materials and joining by nanoparticles are in the focus of research. Additionally, the investigation of the corrosion behavior of brazed heat exchangers is a special field of interest. To verify corresponding properties, investigations with application-related test methods are available. This is shown by the testing bench for brazed heat exchanger in portable and industrial water. All the previously mentioned investigations are described in more detail in this work.

**Dr Sebastian Weis, Vasilii Fedorov, Michael Elssner, Dipl.-Ing. Thomas Uhlig, Dr Susann Hausner, Prof. Guntram Wagner, Prof. Bernhard Wielage** – Chemnitz University of Technology.

Autor korespondencyjny/Corresponding author: [guntram.wagner@mb.tu-chemnitz.de](mailto:guntram.wagner@mb.tu-chemnitz.de)

## High-temperature brazing with newly developed Co-based fillers

The main requirements on the Co superalloys are good high-temperature strength as well as resistance against corrosion and creep [1÷3]. To produce complex structures, it is necessary to join these alloys. Especially in case of gaps exceeding a thickness of 50÷80 µm, the nickel based fillers form brittle intermetallics in the center of the joint. Because of their higher tolerance on gap geometry, expensive noble metal based fillers are preferred in some industrial processes [4÷6]. Nevertheless, especially gold-based fillers behave disadvantageous due to erosion effects at the grain boundaries of the base materials and the local difference in electrochemical potential [7]. The use of brazing fillers of the same base material improves the corrosion resistance and the homogenization of mechanical properties within the joints. Therefore, alternative Co-based brazing fillers were developed [8]. The alloying concept is based on results of Shurin et al. from the 1990s [9,10]. The published data indicates that there is the lowest melting composition within the quasi-ternary system Co-ZrCo<sub>0.81</sub>-TaC<sub>0.82</sub> at 1250 °C. The alloys are prepared by melting in an electric arc furnace and the melting behavior is investigated by DSC (Differential Scanning Calorimetry). The near eutectic composition with a carbide content of 9 wt% (Zr,Ta)C melts at 1350 °C, figure 1 [8].

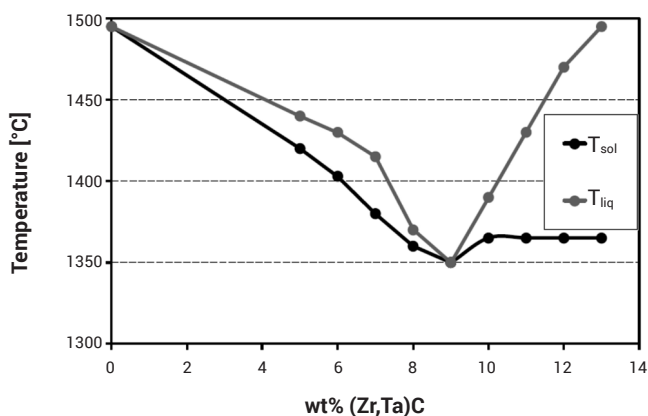


Fig. 1. Melting behavior of CoZrTaC-alloys as a function of carbide content, determined by DSC [8]

Rys. 1. Temperatura topnienia stopów CoZrTaC w funkcji zawartości węglków Zr i Ta, określona metodą DSC [8]

Because of the discrepancy to literature data, it is necessary to reduce the melting temperature of the Co-based brazing fillers. Hence, alloying with the elements Al, B, Sn and Ti was carried out [11]. Alloying with Ti leads to the most promising results. An almost linear decrease of the liquidus temperature and solidus temperature occurs with increasing Ti-content without influencing the near eutectic texture. The wide melting range of these alloys indicates that a liquidus temperature below 1200 °C can be reached. This is achieved by additional adjusting of the Zr-, Ta- and C-contents. The adapted composition CoTi<sub>8</sub>Zr<sub>8</sub>Ta<sub>4</sub>C<sub>0.16</sub> has a melting temperature of 1163 °C. Further improvement of the mechanical properties is achieved by alloying the filler with Sn and Ni. The Sn alloyed composition CoTiZrTaC-Sn with an about 20 K lower melting temperature affects the wetting and flow behavior positively. The Ni alloyed composition CoTiZrTaC-Ni is used to generate a partial austenitic lattice structure according to the binary system Co-Ni [12]. This leads to a better ductility of the joint. The commercially available filler B-Co1, containing high amounts of Si and considerable

amounts of B, is used as a benchmark [13]. All joints are produced by induction brazing in vacuum at a pressure of  $< 10^{-2}$  Pa, a temperature of 1225 °C and a holding time of 120 s. MAR M 509 is used as a base material [14]. At room temperature the rupture stresses of the Ni-alloyed filler CoTiZrTaC-Ni reach values comparable to the commercially available filler B-Co1 as well as the base material, figure 2. The better ductility of the joint, caused by the austenitic lattice structure of the filler, is the reason for the significantly higher attainable stress levels. Joints brazed with fillers CoTiZrTaC and CoTiZrTaC-Sn fail at much lower stresses. This can be explained by the hcp lattice of these two fillers at room temperature, which leads to a brittle failure during the tensile tests.

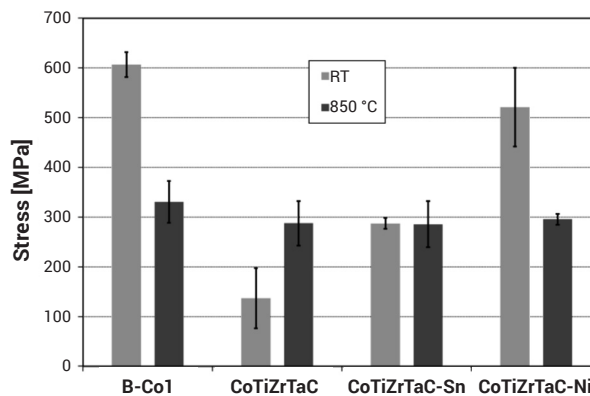


Fig. 2. Rupture stresses of filler alloys determined by monotonic tensile tests at room temperature (RT) and elevated temperature of 850 °C [11]

Rys. 2. Pęknięcia naprężeniowe stopów kobaltu wyznaczone w statycznej próbie rozciągania w temperaturze pokojowej i podwyższonej temperaturze 850 °C [11]

At temperatures of 850 °C, which is within the application range of Co-based superalloys, all investigated fillers exhibit similar strength values of about 290 to 320 MPa, figure 2. The lowest deviation occurs when the filler CoTiZrTaC-Ni is used. The rupture stresses of the joints are close to literature data about the yield strength of MAR M 509 in this range (290 MPa at 870 °C) [15]. The strong difference of strength values at the room temperature and high temperature can be explained by the lattice structure of Co. The transition of  $\epsilon$ -Co (hcp) to  $\alpha$ -Co (fcc) occurs at 422 °C [12] for pure Co and can be influenced by the Ni-content. At the testing temperature of 850 °C all joints passed this transition. Independent on the composition their lattices are in the ductile austenitic (fcc) state. As can be seen in the room temperature tests, this leads to a higher tolerance against rupture.

## Arc brazing of aluminum matrix composites using AlAgCu filler

In the automotive industry or heat exchanger industry, the requirements in lightweight design lead to an increasing demand to combine dissimilar materials like aluminum alloys and stainless steel. High performance materials like aluminum matrix composite (AMC) are used to provide new solutions for engineering applications. In comparison to conventional aluminum alloys, the AMC have a higher specific strength, an increased wear resistance and a lower coefficient of thermal expansion [16÷18]. The thermal stability

of the AMC is limited by the solidus temperature of the aluminum matrix. In addition, the interface of matrix and particles is affected by the heat input. The consequence is a thermal induced damage that leads to ineligibile porosities and inhomogeneities [19]. Furthermore, the formation of IMC can occur so that the properties of these joints can be insufficient [20]. Therefore, a suitable joining technique is required. In comparison to welding, brazing offers the possibility to reduce the joining temperature because of the lower liquidus temperature of the fillers. A filler based on the ternary system Al-Ag-Cu with the eutectic composition of 40 wt% Al, 40 wt% Ag and 20 wt% Cu (named Al40Ag20Cu) is developed. The melting temperature of the filler, measured by differential scanning calorimetry (DSC), is 506 °C [21]. Mixed joints of AMC and stainless steel are produced by arc brazing an inert atmosphere (Ar) using a TIG welding source with an alternating current (AC) of 40 A [21,22]. The microstructures of the arc brazed joints are observed at the AMC / braze metal and the stainless steel / braze metal interface.

An additional alloying of the eutectic filler Al40Ag20Cu with 1.5 wt% Si improves the wetting on stainless steel and prevents the formation of IMC. The liquidus temperature is 498 °C [22]. Before brazing, the eutectic filler consists of the phases  $Ag_2Al$ ,  $Al_2Cu$ , a solid solution of Al and additional Si, analyzed by XRD. An alloying of the braze metal takes place, figure 3. As a result the braze metal is enriched with Al. The phases  $Ag_2Al$ ,  $Al_2Cu$  and a solid solution of Al are detected using XRD analysis. The content of Ag (up to 5 at%, measured by EDXS) in the solid solution of Al is higher than the solubility in Al in equilibrium state ( $< 2$  at%) [23]. Therefore, the hardness increases in direction to AMC due to the precipitated Ag-rich intermetallics [24]. No cracks can be detected at the interface to AMC. Furthermore, the influence of this alloying on the mechanical properties of the joint will be investigated.

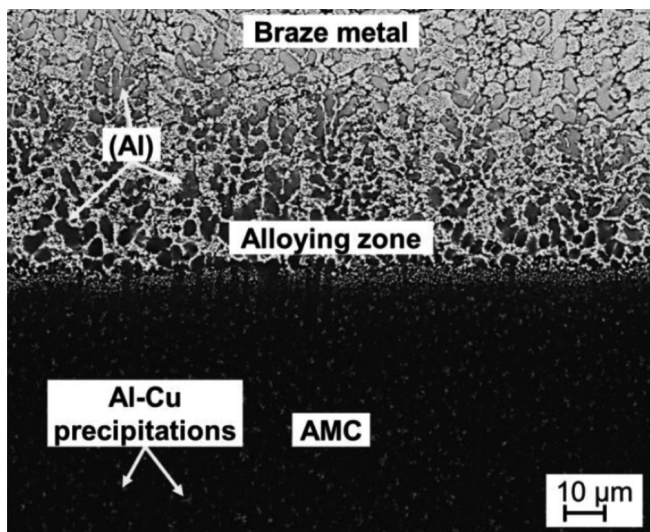


Fig. 3. Interface of AMC / braze metal (SEM) [22]  
Rys. 3. Struktura AMC / lutowina (SEM) [22]

At the interface to the stainless steel the microstructures of the diffusion zone and the braze metal appear differently in comparison to that of the AMC, figure 4. The eutectic part of the filler is not recognizable anymore in the braze metal. The EDXS shows a reduction of the content of Al in the reaction zone from the braze metal to the stainless steel. The increased hardness in this zone is probably a result of the formation of intermetallics of the system Fe-Al. The highest hardness (870 HV0.005), which occurs at the interface

between reaction zone and braze metal, indicates the presence of  $FeAl_3$  (892 HV1) [24,25]. Near to the stainless steel, the hardness and EDXS results indicate the formation of  $AlFe$  (470 HV1) [25]. Cracks in the joints of aluminum and stainless steel mainly occur in the brittle intermetallics. In some cases, cracks can be observed in the area between  $FeAl_3$  and  $AlFe$ . In a previous work, which deals with the wetting behavior, a smaller reaction zone consisting of different layers was detected [22]. Therefore, the aim of the future work is the improvement of the joining process to reduce the amount of IMC.

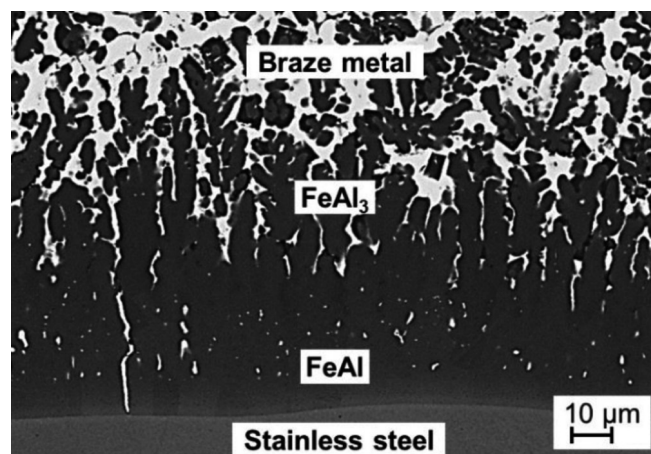


Fig. 4. Interface of stainless steel / braze metal (SEM) [22]  
Rys. 4. Struktura na granicy połączenia stal nierdzewna / lutowina (SEM) [22]

## Induction brazing of aluminum / stainless steel mixed joints

Another approach to join dissimilar materials is the induction brazing of aluminum to stainless steel. To avoid erosion and to improve the mechanical properties of the joints, cold rolled interlayers are used. The roll bonding process is carried out to clad the base material with a filler. In operating conditions, the joints should be able to endure high pressures in a corrosive environment. The use of filler clad stainless steel improves the corrosion resistance of the components [26,27]. The joint design requires the knowledge of mechanical properties, especially the fatigue behavior. Thus, the potential lifetime of the aluminum / stainless steel and stainless steel / stainless steel joints produced by induction brazing using a filler cladding on the stainless steel is determined. The microstructure of the aluminum / stainless steel brazed joints is shown in figure 5. The resulting braze metal consist of a primarily solidified solid solution of Al and an eutectic. Additionally, an IMC layer is formed at the interface to the stainless steel due to the diffusion and the reaction of Fe, Al and Si. The results of the EDX analyses indicate that the IMC layer correlates the  $Al_7Fe_2Si$  phase. The thickness of this IMC layer is about 1 µm. This thin IMC layers are the results of the short brazing time and the local heat input into the joint during induction brazing [28].

In further investigations, the mechanical properties of the joints are examined by tensile tests. For aluminum / filler clad stainless steel mixed joint, the achieved joining strength is 83 MPa. For stainless steel / filler clad stainless steel joint, a joining strength of 96 MPa was determined. After the monotonic tensile test, fatigue tests were carried out up a fatigue limit of  $2 \times 10^6$  cycles. All tests were performed at a load ratio of  $R = 0.1$  [29]. The aluminum / stainless

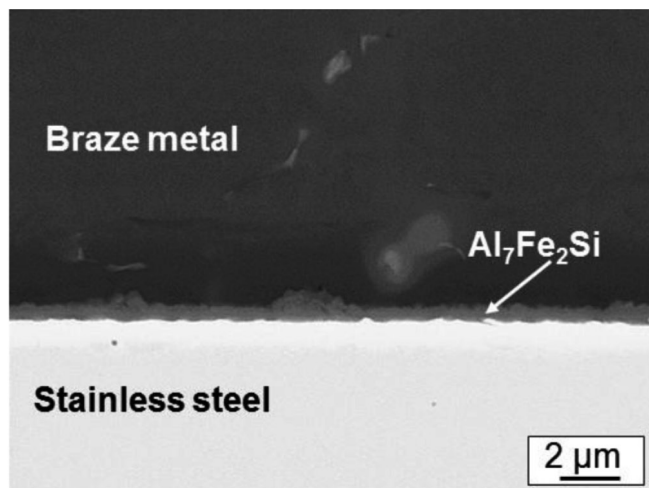
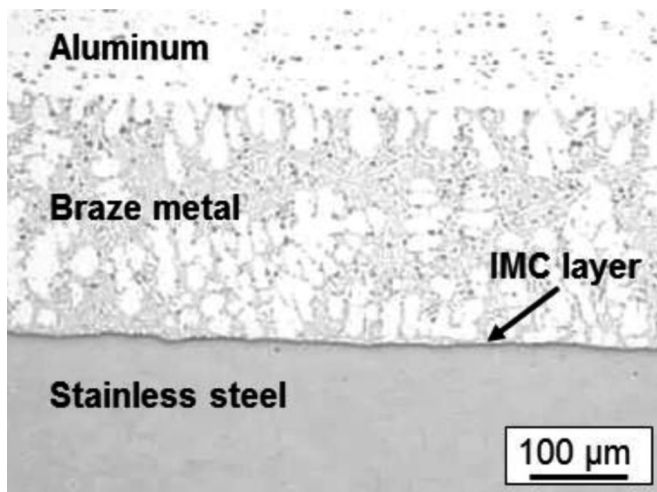


Fig. 5. a) Microstructure of the brazed aluminum / stainless steel joint (OM),  
b) Interface to stainless steel (SEM) [29]

Rys. 5. a) Mikrostruktura złącza lutowanego aluminium / stal nierdzewna (OM), b) struktura na granicy stali nierdzewnej (SEM) [29]

steel brazed joints reach the fatigue life of  $2 \times 10^6$  cycles at a stress amplitude of 6.5 MPa. The stainless steel / stainless steel brazed joints reach the fatigue life of  $2 \times 10^6$  cycles at a stress amplitude of 4.5 MPa [30]. In further investigations, the initiation and the propagation of cracks depending on the number of cycles will be observed.

## Low temperature joining of copper using Ag nanoparticles and steel by Ni nanoparticles

Due to their large surface-to-volume ratio, nanoparticles exhibit a reduced melting and sintering temperature with decreasing particle size in comparison to the corresponding bulk material. After melting and sintering of the particles, the material behaves like the bulk material (Gibbs-Thomson effect) [31,32]. Thus, high-strength and temperature-resistant joints can be produced at low temperatures, which is of great interest for various joining tasks. Previous publications are mostly concerned with joining of components in power electronics. Especially the joining of copper with Ag nanoparticles as a substitute for soldered joints was investigated [33-39]. With low joining temperatures, structural damage, e.g. abnormal grain growth or undesirable phase transformation, can be avoided. Consequently, it would be also of great interest for the joining of materials with different coefficients of thermal expansion such as carbide-metal joints and ceramic-metal joints, to reduce the often critical thermally induced residual stresses of the joints [40,41]. There is also an increasing demand for novel hybrid compound joints, for example between fiber-reinforced composites and metals, where low joining temperatures are required. For the joining of power electronics components, it is important to reduce the temperature and the necessary pressure, because they only have a limited thermal and mechanical loading capacity. In previous publications, only the parameters temperature, pressure, holding time and particle size were varied and investigated. However, the quality of joints is influenced by a complex interplay of much more process parameters, most of which are systematically. The strength behavior as a function of the mentioned parameters and other process parameters like heating rate, thickness of paste application, surface pre-treatments of the substrates, a pre-drying process and a subsequent heat treatment are investigated [31].

For joining with nanoparticles, the nanoparticles are suspended in solvents and through the addition of dispersing agents surrounded with an organic shell [31,32]. This shell leads to repulsive forces between the particles, so that agglomerations can be avoided [42,43]. A commercially available Ag nanopaste of the company Harima Chemicals, Inc. (Japan) is used for the experiments [44,45]. The particle size distribution has a maximum at  $6 \div 7$  nm, figure 6 [31]. A paste application of  $20 \mu\text{m}$  was applied for the joining experiments.

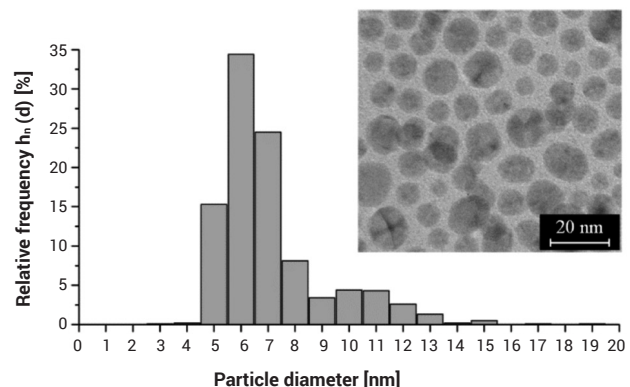


Fig. 6. TEM image of the nanoparticles and particle size distribution of the Ag nanopaste [32]

Rys. 6. Obraz TEM rozkładu nanocząsteczek i wielkość cząstek w nanopaste Ag [32]

A modified hydraulic press was used for the joining experiments. The heating of the samples was carried out in air by means of induction. The desired pressure was applied on the entire joining surface of the sample with a punch. The investigations of the strength behavior show, that it is possible to produce joints even at lower temperatures (of approx.  $300 \text{ }^\circ\text{C}$ ) with good strength properties and high temperature stability. The variation of the process parameters reveals that in particular the joining pressure exerts an essential influence on the achievable strengths. Without pressure, the strengths are even lower than the strengths of soldered joints. With increasing pressure, the strength increases significantly, figure 7. In addition, temperature, holding time and thickness of paste application have a considerable effect on strength behavior. In contrast, the pre-drying process, heating rate, surface pre-treatment and subsequent heat treatment exhibit hardly any influence on joint strength [31].

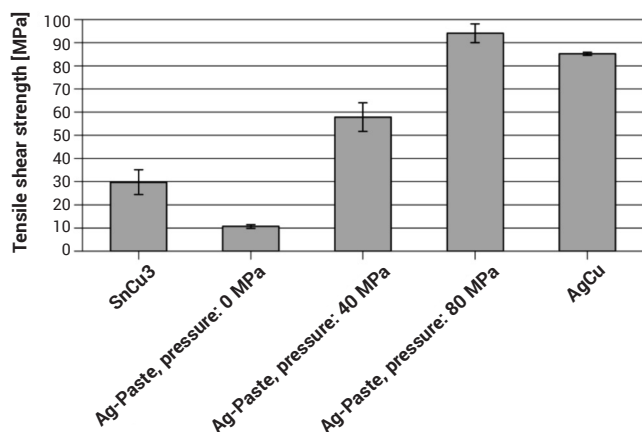
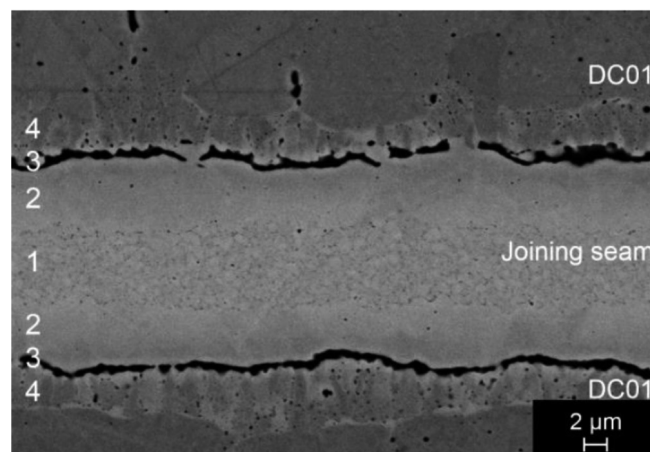


Fig. 7. Tensile shear strength of soldered and brazed joints in comparison to samples joined with Ag nanopaste at different pressures (temperature: 300 °C, holding time: 10 min) [32]

Rys. 7. Wytrzymałość na ścinanie połączeń lutowanych na miękko i na twardo w porównaniu z próbkami lutowanymi nanopastą Ag przy różnych ciśnieniach (temperatura 300 °C, czas wygrzewania 10 min) [32]

This demonstrates the great potential of joining with nanoparticles for highly stressed structural components as an alternative for brazing processes. A possible application is the joining of high-performance materials respectively materials with an adapted and optimized microstructure. High joining temperatures can result in undesirable structural damages and therefore to a loss of the previously optimized properties. For example, grain growth of fine-grained steels or recrystallization of monocrystalline Ni-based superalloys lead to strong losses of strength and toughness [46,47]. However, brazing of copper and steel can result in strength losses by grain growth [48,49]. In this context, a reduction of the joining temperature using a Ni nanopaste, investigated by Hausner et al., is of great interest to retain the initial microstructure. The nanopaste was produced by themselves. The particle size of Ni nanoparticles is about of 10 nm to 100 nm. The joining processes were carried out on the same experimental device like for the joining of copper using Ag nanoparticles. Two different steels were used as substrates: the unalloyed quality steel DC01 (EN: 1.0330) and the stainless steel X5CrNi18-10 (EN: 1.4301). For the joining experiments, the influence of the process parameters joining temperature and joining pressure on the strength behavior and the resulting microstructure of the joints was investigated. Furthermore, different surface treatments respectively the application of coatings on the stainless steel were examined to achieve an improved adhesion. The variation of the process parameters joining pressure and joining temperature shows, that the joining temperature exerts a significantly stronger influence on the achievable strengths in comparison to the joining pressure. A comparison with results for the joining of copper with an Ag nanopaste [31,32], where the pressure has a much greater influence on the strength behavior than the temperature, shows that it is not possible to transfer the results of one material system to another when joining with nanosuspensions. The investigations shown that high tensile shear strengths can already be achieved at temperatures between 650 °C and 850 °C [50]. In comparison to the joints with the substrate DC01, the strengths joints with the austenitic stainless steel are significantly decreased. This may be a result of the passivating oxide layer of the stainless steel. The oxide layer presumably limits the diffusion of Ni into Fe (and vice versa). Pronounced diffusion zones can be observed between

the joining seams and the substrates, which were not expected for the low temperatures, figure 8 and figure 9. It is interesting that the diffusion behavior differs for both steels. When using the unalloyed quality steel DC01, in particular Fe diffuses into the Ni joining seam, figure 8. At the beginning of the joining process, the seam has a nanoporous structure (high number of defects) which is compacted during the joining process (sintering process). Nevertheless, the resulting sintered structure inevitably exhibits lattice defects. An increasing number of defects results in an increasing diffusion coefficient [51] so that the large numbers of defects lead to the diffusion of Fe into the seam.



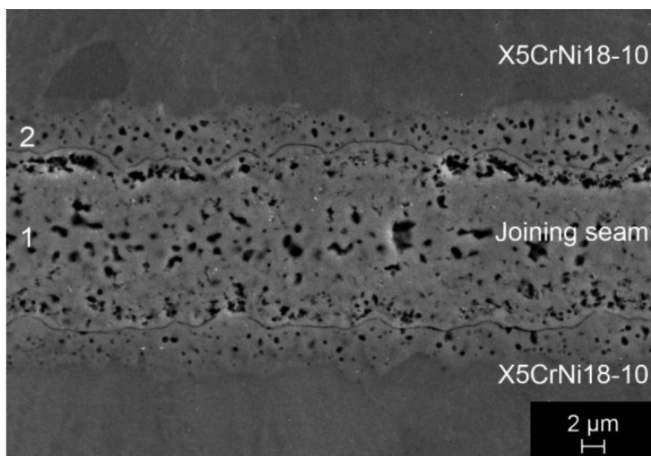
Element [wt%]	Ni	Fe	Mn	O
1	87	13	–	–
2	54	46	–	–
3	5	74	2	19
4	3	96	1	–

Depth [μm]	Fe content inside the joining seam [wt%]	Ni content in the substrate [wt%]
2	46	3
10	13	0

Fig. 8. Microstructure (SEM) and EDX analyses of a joint with DC01 at a joining temperature of 850 °C and a joining pressure of 20 MPa (holding time: 10 min) [50]

Rys. 8. Mikrostruktura (SEM) i analiza EDX złącza DC01 w temperaturze spajania 850 °C i ciśnieniu 20 MPa (czas wygrzewania: 10 min) [50]

In contrast, when using the stainless steel X5CrNi18-10, Ni exhibits a significantly higher diffusion coefficient into the Fe substrate than vice versa, figure 9. This can be attributed to the different structural modifications of the steels: Also [52] determined a much higher diffusion coefficient of Ni in austenite than in ferrite. For a more detailed explanation of this phenomenon, which is probably a complex interaction of many factors, further studies are required.



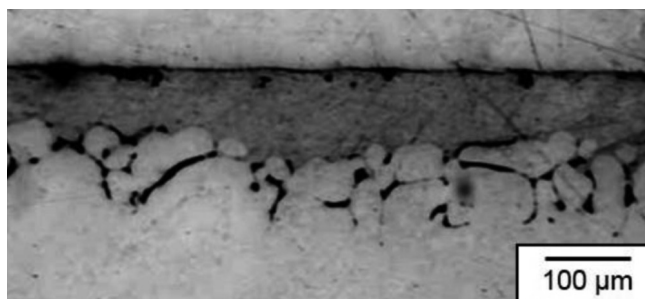
Element [wt%]	Ni	Fe	Cr
1	93	5	2
2	65	28	7

**Fig. 9.** Microstructure (SEM) and EDX analyses of a joint with X5CrNi18-10 at a joining temperature of 850 °C and a joining pressure of 20 MPa (holding time: 10 min) [50]

**Rys. 9.** Mikrostruktura (SEM) i analiza EDX złącza X5CrNi18-10 w temperaturze spajania 850 °C i przy ciśnieniu 20 MPa (czas wygrzewania: 10 min) [50]

## Brazing of heat exchangers

Brazed plate heat exchangers (PHE) are used to transfer thermal energy from one fluid to another without a direct contact of the media. They mainly consist of corrugated stainless steel plates that are arranged diametrically opposed creating channels for the liquids. Due to the small sheet thickness and high thermal conductivity of the steel in association with the large surface, these heat exchangers exhibit a very high efficiency. Joining the plates together is carried out by pressing, welding and brazing. In case of pressing there is a need to use rubber sealing gaskets, which limit the applicable pressure. Welding requires lots of process steps due to the many stacks of plates. The advantage of brazing is the possibility to produce all the joints in one process step. This offers the possibility to produce big batch sizes very cost-efficient [53]. The brazing process is commonly carried out in vacuum furnaces. Because of their good formability and the low raw material cost, pure copper foils are used as filler metal [54]. The difference in the electrochemical potentials of copper and stainless steel in contact with electrolytes leads to corrosion effects [55]. Investigations indicate different reasons for leakages and failures: intergranular attack in the braze metal and gap corrosion between braze metal and steel [56]. The chromium oxide layer on the stainless steel surface causes the anodic dissolution of the copper filler [57,58]. Additionally, the brazing process induces the precipitation of chromium carbides at the grain boundaries of the steel, which is known as a sensitization, figure 10. The subsequent reduction of the chromium content of the grains causes further local differences in the electrochemical potential.



**Fig. 10.** LME along the grain boundaries (OM) [58]

**Rys. 10.** LME wzdłuż granic ziaren (OM) [58]

The corrosion behavior is also influenced by the residual stresses within the heat exchanger plates. During the forming process of the corrugated PHE plates, different degrees of deformation emerge depending on the position at the corrugation. When the plates are brazed, the liquid copper can infiltrate the grain boundaries. Cracks mostly occur in the high-deformed areas of the plates originating from the eroded grain boundaries [59]. This phenomenon is known as a liquid metal embrittlement (LME). Furthermore, the dissolution of corrosion products of brazing filler and base material into the water must be taken into account. The migration of heavy metal ions in potable water has to be avoided. Legally fixed maximum values for the concentrations of these ions are existing. Besides the expectable leaching of copper ions, investigations indicate a nickel enrichment of the potable water [60]. This leads to the assumption that the corrosion of the steel plates and the consequent dissolution of the corrosion products in the potable water cause the leaching. With respect to the influence of LME on the corrosion resistance, the so called grain boundary engineering (GBE) is one possibility to improve the properties of copper brazed heat exchangers. This approach is based on a thermomechanical treatment of the stainless steel, which leads to the formation of coincident grains. They form the so called coincidence site lattice (CSL). The grain boundaries in CSL are regarded as low energy grain boundaries. If their frequency is high, the resistance to intergranular corrosion in acids remarkably rises [61,62]. Furthermore, literature data on the LME of stainless steels by copper based brazing fillers and the influence of thermal pretreatments indicate the possibility of reducing the LME [63]. Therefore, the influence of thermomechanical treatments on the liquid metal embrittlement of copper-brazed plate heat exchangers is investigated. Experiments are carried out using steel sheets in the as delivered and normalized condition. During the normalizing process, the grain size increases approximately fivefold. In the normalized state, there is a significant influence of the rolling reduction rate and the heat treatment temperature on the number and the depth of the infiltrations. The lowest values as well as deviations are determined after a heat treatment at 1020 °C. In the as delivered state, the minimum infiltration depth values are determined after heat treatment at 940 °C. In comparison to the normalized state, the number of infiltrations is higher. This can be explained by the smaller grain size, which unavoidably leads to a higher number of grain boundaries. The residual stresses within the sheets in the as delivered state lead to a relaxation at lower temperatures, which decreases the tendency to LME [64]. In further investigations, the possibility to combine the heat treatment with the subsequent brazing process will be considered.

## Conclusions

Newly developed Co-based fillers are developed by decreasing of the melting temperature of the ternary eutectic in the quasiternary system Co-ZrCo<sub>0.81</sub>-TaCo<sub>0.82</sub>. Alloying with Ti and adapting the Zr, Ta and C contents lead to near eutectic composition CoTi<sub>8</sub>Zr<sub>8</sub>Ta<sub>4</sub>Co<sub>1.6</sub> that melts at 1163 °C. Additionally, a Sn containing and a Ni containing composition are used for the brazing experiments. Sn improves the wetting, Ni improves the ductility. The mechanical properties of the joints at room temperature as well as elevated temperature are comparable to the commercially available filler B-Co1 as well as the base material.

During arc brazing of AMC and stainless steel alloying of the filler material takes place. The formation of Al-Fe intermetallics at the interface to the stainless steel occurs. A remarkable diffusion zone emerges at the interface braze metal / stainless steel. The hardness values and XRD analyses indicate the phases FeAl<sub>3</sub> and AlFe. The IMCs may cause cracks during cooling down. The smoother hardness profile at the interfaces of braze metal to the AMC prevents cracks. That is a result of the formation of a solid solution of Al in the braze metal and Cu precipitates in the AMC. The determination of the mechanical properties with respect to process parameters and the resulting microstructure are the purpose of the future work.

The design of brazed joints requires the knowledge of mechanical properties, especially the fatigue behavior. The potential lifetime of the aluminum / stainless steel and stainless steel / stainless steel joints produced by induction brazing using a filler cladding on the stainless steel is determined. The aluminum / stainless steel brazed joints reach the fatigue life of  $2 \times 10^6$  cycles at a stress amplitude of 6.5 MPa. The stainless steel / stainless steel brazed joints reach the fatigue life of  $2 \times 10^6$  cycles at a stress amplitude of 4.5 MPa.

Due to their large surface-to-volume ratio, nanoparticles exhibit a reduced melting and sintering temperature in comparison to the corresponding bulk material. The investigations joints of copper using Ag nanoparticles show that it is possible to produce joints even at lower temperatures (of approx. 300 °C) with good strength properties and high temperature stability compared to conventional brazed joints. It is of great interest for various joining tasks. For joining of steels, a reduction of the joining temperature using a Ni nanopaste is of great interest to retain the initial microstructure and therefore the mechanical properties. The investigations prove that the nanopaste offers a great potential for joining at low temperatures. The high joint strengths can already be achieved at temperatures of 650-850 °C in comparison to conventional Ni-based brazing filler metals.

Copper-brazed plate heat exchangers made of stainless steel can be damaged by corrosion in contact with potable water because of the difference between the electrochemical potential of braze metal and base material. The braze metal infiltrates the stainless steel along the grain boundaries and causes a liquid metal embrittlement. The performed investigations show the possibility to reduce the liquid metal embrittlement of stainless steel by copper filler during thermomechanical treatment, grain boundary engineering. The lowest values as well as deviations are determined after a heat treatment at 1020 °C in the normalized state.

## References

- [1] Lechner C., Seume J.: Stationäre Gasturbinen, Springer-Verlag, 2010.
- [2] Adam, P.: Fertigungsverfahren von Turboflugtriebwerken, Birkhäuser-Verlag, 1998.
- [3] Campbell F. C.: Elements of metallurgy and engineering alloys, ASM International, 2008.
- [4] Heikinheimo L., Miglietti W. et al.: Brazing of Co- and Ni-based superalloys using new amorphous brazing filler metals, DVS-Berichte 212, pp. 30-34, 2001.
- [5] Greaves W.: Cost effective repairs for IGT vanes, Proceedings of the 3rd IBSC, pp. 392-394, 2006.
- [6] Falkenberg S., Watermeyer K.: Die Untersuchung des Lötverhaltens von auf Ti-Al-Phasen aufgebauten Hochtemperaturwerkstoffen, Sonderbände der Praktischen Metallographie, pp. 401-404, 1995.
- [7] Donachie M. J., Donachie S. J.: Superalloys: a technical guide, ASM International, 2002.
- [8] Uhlig T., Weis S. et al.: Co-based brazing fillers. Welding Technology Review, pp. 64-67, 2013.
- [9] Shurin A. K., Dmitrieva G. P. et al.: Phase equilibria in Co-Me'C-Me''C alloys. I: Systems with three-phase eutectic equilibrium, Powder Metallurgy and Metal Ceramics, pp. 615-620, 1996.
- [10] Shurin A. K., Dmitrieva G. P. et al.: Phase Equilibria in Co-Me'C-Me''C alloys. II: Systems with four-phase eutectic equilibrium, Powder Metallurgy and Metal Ceramics, pp. 193-196, 1997.
- [11] Uhlig T., Weis S., Schuberth S., Wagner G., Wielage B.: Entwicklung von Cobaltbasisloten zum Hochtemperaturlöten hochfester Cobaltbasislegierungen, Schweißen und Schneiden Band 68, 2016, Heft 5, S. 260-265, ISSN: 0036-7184.
- [12] Ishida K., Nishizawa T.: The Co-Ni (Cobalt-Nickel) System, Bulletin of Alloy Phase Diagrams, pp. 390-395, 1983.
- [13] Sekulic D.: Advances in Brazing: Science, Technology and Applications, Elsevier, 2013.
- [14] Wheaton H. L.: MAR-M 509, a new cast cobalt-base alloy for high-temperature service, Cobalt, 1965, pp. 163-170.
- [15] Davies J. R.: Nickel, cobalt and their alloys, ASM International, 2000.
- [16] Xiu Z., Yang W., Chen G., Jiang L., Mac K., Wu G.: Microstructure and tensile properties of Si<sub>3</sub>N<sub>4</sub>/2024Al composite fabricated by pressure infiltration method. Mat. a. Designs 33, 2012, pp. 350-358.
- [17] Sajjadi S.A., Ezatpour H.R., Parizi M.T.: Comparison of microstructure and mechanical properties of A356 aluminium alloy/Al<sub>2</sub>O<sub>3</sub> composites fabricated by stir and compo-casting processes, Mat. a. Designs 34, 2012, pp. 106-111.
- [18] Qu X-h., Zhang L., Wu M., Ren S.-b.: Review of metal matrix composites with high thermal conductivity for thermal management applications. Progress in Natural Science: Materials International 21, 2011, pp. 189/97.
- [19] Ureña A., Escalera M.D., Gil L.: Influence of interface reactions on fracture mechanisms in TiG arc-welded aluminium matrix composites, Comp. Scien. a. Tech. 60, 2000, pp. 613-622.
- [20] Steiners M., Höcker F.: Einfluss der Beschichtungen beim stoffschlüssigen Lichtbogen-fügen von Stahl mit Aluminium, Mat. u. Werkst. 38, 2007, pp. 559-564.
- [21] Weis S., Elßner M., Grund T., Hausner S., Wielage B., Wagner G.: Lichtbogenlöten von Aluminiummatrix-Verbundwerkstoffen mit AlAgCu-Loten, Werkstoffe und werkstofftechnische Anwendungen 52, 2014, ISBN 978-3-00-046877-3.
- [22] Weis S., Elßner M., Fedorov V., Habisch S., Wagner G., Mayr P.: Innovative joining technologies for mixed joints of stainless steel and aluminum or aluminum based composites, DVS-Berichte, Band 323, 2016, ISBN 978-3-945023-62-4.
- [23] Suzuki T., Effenberg G.: The binary system Ag-Al. MSIT® MSI Eureka in Springer Materials, 1988.
- [24] Elßner M., Weis S., Grund T., Wagner G., Habisch S. and Mayr P.: Microstructure of arc brazed and diffusion bonded joints of stainless steel and SiC reinforced aluminum matrix composite. Werkstoffe und werkstofftechnische Anwendungen 59 (2016), ISBN 978-3-00-052212-3.
- [25] Potesser M., Schoeberl T., Antrekowitsch H., Bruckner J.: The characterization of the intermetallic Fe-Al layer of steel-aluminum weldings, Conference proceedings EPD Congress, 2006, pp. 167-176.
- [26] Sicking R.: Walzprodukte für die Herstellung von Aluminium-Wärmetauschern, Werkstoffwissen-schaftliche Schriftreihe 61, 200, pp. 60-72.
- [27] Nordlien, J. H.: Organically bound braze coatings for header to tube joint formation. In Proceedings 3, International Congress Aluminium Brazing, 2004.
- [28] Fedorov V.; Weis S.; Wagner G.: Mechanical and microstructural behavior of brazed aluminum / stainless steel mixed joints, IOP Conference Series: Materials Science and Engineering, Vol. 118. No. 1. IOP Publishing, 2016.
- [29] Fedorov V., Weis S., Wagner G.: Fatigue behavior of brazed aluminum / stainless steel mixed joints. DVS-Berichte, Band 323, 2016, ISBN 978-3-945023-62-4.
- [30] Fedorov V., Elßner M., Weis S., Wagner G.: Mechanical properties of brazed aluminum / stainless steel mixed joints. Presentation, International Conference LÖT 2016, Aachen, 2016.

- [31] Hausner S.: Potential von Nanosuspensionen zum Fügen bei niedrigen Temperaturen. Dissertaion, Schriftenreihe Werkstoffe und werkstofftechnische Anwendungen 56, 2015, ISSN: 1439-1597.
- [32] Hausner S., Weis S., Wielage B., Wagner G.: Low temperature joining of copper by Ag Nanopaste: Correlation of mechanical properties and process parameters, Submitted for publication: Welding in the world, 2016.
- [33] Calata J.N., Lei T.G., Lu G.-Q.: Sintered nanosilver paste for high-temperature power semiconductor device attachment, International Journal of Materials and Product Technology 34, 2009, pp. 95-110.
- [34] Wang T.; Chen X.; Lu G.-Q.; Lei G.Y.: Low-Temperature Sintering with Nano-Silver Paste in Die-Attached Interconnection, Journal of Electronic Materials 36, 2007, pp. 1333-1340.
- [35] Ide E., Angata S., Hirose A., Kobayashi K.F.: Metal-metal bonding process using Ag metallo-organic nanoparticles, Acta Materialia 53, 2005, pp. 2385-2393.
- [36] Ogura T., Yagishita T., Takata S., Fujimoto T., Hirose A.: Bondability of copper joints formed using a mixed paste of Ag<sub>2</sub>O and CuO for low-temperature sinter bonding, Materials Transactions 54, 2013, pp. 860-865.
- [37] Hu A., Guo J.Y., Alarifi H., Patane G.; Zhou Y.N., Compagnini G., Xu C.X.: Low temperature sintering of Ag nanoparticles for flexible electronics packaging, Applied Physics Letters 97, 2010, pp. 1531171-1531173.
- [38] Alarifi H., Hu A., Yavuz M., Zhou Y.N.: Silver Nanoparticle Paste for Low-temperature Bonding of Copper, Journal of Electronic Materials 40, 2011, pp. 1394-1402.
- [39] Yan J., Zou G., Wu A., Ren J., Yan J., Hu A., Zhou Y. N.: Pressureless bonding process using Ag nanoparticle paste for flexible electronics packaging. Scripta Materialia 66, 2012, pp. 582-585
- [40] Boretius M., Lugscheider E., Tillmann W.: Fügen von Hochleistungskeramik: Verfahren - Auslegung, Prüfung - Anwendung, Düsseldorf: VDI-Verlag, 1995 - ISBN 3-18-401272-7.
- [41] Wielage B., Hoyer I., Hausner S.: Induktives Löten von Metall mit Aluminiumoxid und Zirkonoxid. Schweißen und Schneiden 43, 2012, pp. 656-660.
- [42] Nagasawa H., Maruyama M., Komatsu T., Iso-da S.: Physical Characteristics of Stabilized Silver Nanoparticles Formed Using a New Thermal-Decomposition Method, physica status solidi (a) 191, 2002, pp. 67-76.
- [43] Jiang H., Moon K.-S., Lu J., Wong C. P.: Conductivity Enhancement of Nano Silver-Filled Conductive Adhesives by Particle Surface Functionalization, Journal of Electronic Materials 34, 2005, pp. 1432-1439.
- [44] Mathews N. et al: Printing materials for electronic devices, International Journal of Materials Research, Vol. 101, 2010, 236-250.
- [45] Kim J.-W. et al: Electrical characterization of screen-printed conductive circuit with silver nanopaste, Japanese Journal of Applied Physics, Part 1, Vol. 48, 2009, 06FD14/1-6.
- [46] Fahrenwaldt H.J., Schuler V., Twrdek J.: Praxiswissen Schweißtechnik, Wiesbaden:Springer Vieweg, 2014. - ISBN 978-3-6580-3141-1..
- [47] Cox D.C., Roebuck B., Rae C.M.F., Reed R.C.: Recrystallisation of single crystal superalloy CMSX-4, Materials Science and Technology Conference 19, 2003, pp. 440-446.
- [48] Benninghoff H.: Loeten von Kupfer und Kupferlegierungen, Technische Rundschau 76, 1984, pp. 12-14.
- [49] Müller W., Müller J.-U.: Löttechnik: Leitfadens für die Praxis, Düsseldorf: DVS-Verlag, 1995. - ISBN 3-87155-149-X.
- [50] Hausner S., Weis S., Wagner G.: Joining of steels at low temperatures by Ni nanoparticles, DVS-Berichte Band 325, 2016, pp. 278-284, ISBN 978-3-945023-64-8
- [51] Heumann T.: Diffusion in Metallen. Berlin, Heidelberg, New York: Springer-Verlag, 1992. - ISBN 3-540-55379-7.
- [52] Dean D.C., Goldstein J.I.: Determination of the Interdiffusion Coefficients in the Fe-Ni and Fe-Ni-P Systems below 900 °C, Metallurgical Transactions A (Physical Metallurgy and Materials Science) 17, 1986, pp. 1131-1138
- [53] Oehmigen H.-G.: Produktionstechnik in der Wärmeübertrager-fertigung, Verlag Publico, pp. 6-18, Essen 2009.
- [54] Wielage B., Weis S., Uhlig T., Fedorov V.: Löten von Wärmeübertragern aus Al, Cu und Edelstahl, DVS-Berichte Band 315, pp. 438-443, 2015.
- [55] Baskutis S.: Mechanics and material aspects in serviceability prediction of the heat exchangers, Mechanics 17, pp. 239-245, 2011.
- [56] Stichel W.: Korrosionsprobleme mit gelöteten Plattenwärmetauschern aus nichtrostendem Stahl, IKZ Haustechnik 15, pp. 27-33, 1998.
- [57] Ehreke J.: Messung der Kupfer-Ionenkonzentration in Stagnationswässern aus kupfergelöteten Plattenwärmeübertragern, Materials and Corrosion 49, pp. 195-197, 1998.
- [58] Pajonk G.: Korrosionsschäden an kupfergelöteten Plattenwärmetauschern, 2004.
- [59] Köhler S., Schäden an gelöteten Plattenwärmetauschern bei der Erwärmung von Trinkwasser, Materials and Corrosion 50, pp. 227-232, 1999.
- [60] DVGW W10/01/05: Schwermetallmigration aus Bauteilen der Trinkwassererwärmung, 2009.
- [61] Kurihara K.: Grain boundary engineering of titanium-stabilized 321 austenitic stainless steel, Journal of materials science 46, pp. 4270-4275, 2011.
- [62] Michiuchi M.: Twin-induced grain boundary engineering for 316 austenitic stainless steel, Acta materialia 54, pp. 5179-5184, 2006.
- [63] Shimada M.: Optimization of grain boundary character distribution for intergranular corrosion resistant 304 stainless steel by twin-induced grain boundary engineering, Acta Materialia 50, pp. 2331-2341, 2002.
- [64] Uhlig T., Weis S., Wagner G.: Influence of thermomechanical treatment on the liquid metal embrittlement of copper-brazed plate heat exchangers, DVS-Berichte Band 325, 2016, pp. 278-284, ISBN 978-3-945023-64-8