

Calculation of Thermodynamically Optimized Temperature-/Time-Cycles in Nickel-Based Brazing Joints

Optymalizacja temperatury/cykli czasowych w lutowaniu twardym poprzez obliczenia termodynamiczne

Abstract

Brazing with nickel-based filler materials is an established joining process. In this context the formation of brittle phases in the joint is a significant difficulty. An increased proportion of these phases influences the mechanical properties of the joints negatively. This effect gains strong influence if a continuous band of brittle phases is formed. In order to avoid formation of brittle phases, small brazing gaps are necessary. Subsequent heat treatment is partially able to reduce the proportion of brittle phases. In this paper thermodynamic simulations are applied in order to calculate phase transformations and diffusion processes during brazing of commonly used materials. The simulations are performed by using Thermo-Calc and TC Dictra, as well as an analytical model. Different temperature-/time-cycles are examined in order to characterize their influence on the formation of brittle phases. Additionally, experiments were executed with the materials of interest. Nanoindentation is used to determine local values of YOUNG's modulus and indentation hardness. Miniature tensile tests are applied to examine the tensile strength. The evaluated data is used to specify correlations between the properties of brittle phases in the joint and of its global mechanical properties.

Keywords: brazing; nickel-based filler materials; brittle phases; heat treatment; calculations and theoretical simulations; investigations of joints properties

Streszczenie

Lutowanie materiałów z wykorzystaniem lutów na osnowie niklu jest już procesem znanym i opanowanym. W tym kontekście tworzenie się w złączu kruchych faz jest istotnym problemem. Wzrastająca ilość tych faz wpływa negatywnie na własności mechaniczne połączenia. Efekt ten zwiększa się jeżeli lut produkuje się w postaci taśmy i ilość kruchych faz jest wyraźnie większa. Uniknięcie formowania się kruchych faz zmusza do stosowania małych szczelin lutowniczych. Stosowana dodatkowo obróbka cieplna również częściowo redukuje ilość kruchych faz. W przedstawianej pracy zastosowano symulację termodynamiczną w celu określenia przemian fazowych i procesu dyfuzji w złączu lutowanym. Symulacje wykonano przy pomocy Thermo-Calc i TC Dictra oraz modelu analitycznego. Sprawdzano różne cykle temperatura/czas aby ustalić ich wpływ na tworzenie kruchych faz. Wykonano dodatkowo wybrane badania dotyczące interesujących nas materiałów. Zastosowano metodę pomiaru nanowgłębienia do określenia lokalnego modułu Younga oraz pomiaru twardości. Badanie wytrzymałości na rozciąganie wykonano na próbkach miniaturowych. Wyniki pozwoliły ustalić wpływ ilości kruchych faz w złączu na własności mechaniczne całego połączenia.

Słowa kluczowe: lutowanie twarde; luty na osnowie niklu; kruche fazy; obróbka cieplna; obliczenia i symulacje teoretyczne; badania własności połączeń

Introduction

High temperature brazing with nickel-based filler materials is widely applied in various sectors, e.g., aviation and aerospace engineering, medical technology and refrigeration industry. Tensile strengths of more than 500 MPa are achievable. The brazing process is performed in vacuum

and inert gas furnaces at temperatures above 900 °C. High temperature brazing has been subject of scientific investigation since the 1970's [1-7]. The most significant obstacle is the occurrence of brittle phases in the brazing gap, which can influence the mechanical properties of the joint nega-

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tively. This effect is reinforced in case of continuous, band-shaped brittle phases, cf. Fig. 1., i.e., the tensile strength can be reduced to values less than 50 MPa. In order to avoid the formation of brittle phases, the width of the brazing gap must not exceed a critical value. This requires a precise and therefore cost-intensive manufacturing of the components to be brazed. It is the objective of this work to propose temperature/time-cycles which avoid the formation of brittle phases in larger brazing gaps. This is obtained by thermodynamic simulations. Therefore the diffusion processes during brazing can be analysed for commonly used filler materials, namely Ni 620, Ni 650 and B-Ni60CrPSi-980/1020. Base materials are usual steels. At first, the commercial software packages Thermo-Calc and TC Dictra are examined for simulation capability. Here, many difficulties occur due to limitations of the available databases. Their applicability to the required simulation processes is currently unfortunately strongly restricted. Therefore, another simulation approach is used, which is based on an analytical solution of FICK's diffusion equation. Diffusion coefficients are obtained from EDX-linescans and ARRHENIUS' equation is used to take temperature dependence into account. For examination of the mechanical properties of the joints, miniature tensile tests and nanoindentation tests are performed.

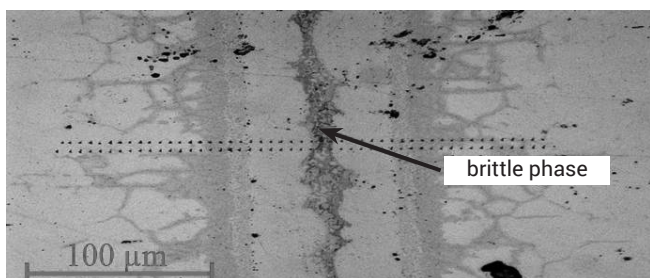


Fig. 1. Brazed joint, brazing gap 100 μm, base material: X5CrNi18-10 (1.4301), filler: Ni 620, 90 min, 1050 °C

Rys. 1. Połączenie lutowane, szczelina 100 μm, materiał rodzimy – X5CrNi18-10 (1.4301), lut – Ni620, 90 min, 1050 °C

Thermo-Calc and TC Dictra

Thermo-Calc and TC Dictra are software packages for thermodynamic and diffusion calculations, respectively. Among other things Thermo-Calc can be used to calculate phase and so-called property diagrams for complex alloys. Figure 2 shows a property diagram for the filler material Ni 650 calculated by Thermo-Calc. The calculations are based on experimental data available in a number of databases designed for a specific purpose, e.g., nickel superalloys or steels. Unfortunately there is no database specifically designed for brazing or usual brazing filler materials. Therefore one has to use a database dealing with a similar kind of material. In case of nickel-based filler materials, one can use the database for nickel superalloys with some limitations. These limitations concern the restricted amount of chemical elements that are available. Furthermore one needs to pay close attention to the results of the calculations, if the application is outside of the originally planned range of use of the database. It is possible that the calculations include some phases which are not found in experiments and are therefore not to be expected to occur in the calculations either. In order to deal with this problem, one has to suspend manually the phases in question to get a more realistic result. In addition, some elements, such as boron or phosphorus, can be a reason for unrealistic results. If an element is not represented in the used database it is impossible to include it in the calculation. This leads to

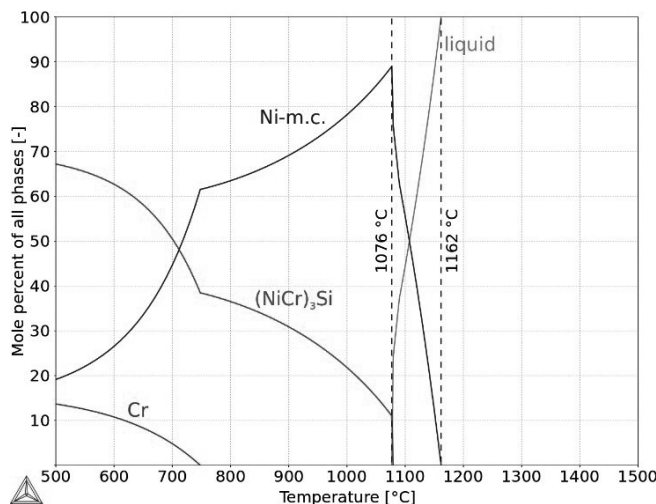


Fig. 2. Property diagram of Ni 650

Rys. 2. Wykres własności Ni650

a change of alloy composition and therefore the result cannot give insight into the real problem. Another point one has to take into account is the amount of the single elements in the composition. Especially the boron content in nickel-based filler materials is critical. If one considers these limitations of the software one obtains diagrams containing important properties of the filler material, i.e., solidus and liquidus temperature. On the other hand TC Dictra offers insight into the dynamics of the brazing process. With the help of this software, one can perform diffusion calculations using experimental thermodynamic and mobility data in specific TC Dictra databases. Nonetheless some databases are shared between Thermo-Calc and TC Dictra. Therefore some of the crucial points mentioned above have to be considered in TC Dictra calculations as well. Furthermore another conflict arises concerning the combination of base and filler materials studied in this paper. Since all base materials of interest are steels which are brazed using nickel-based filler materials one has to decide which database fits best. In contrast to the calculations with Thermo-Calc one should use the steel database in TC Dictra so that the process of diffusion in the steel is represented as best as possible in the calculation. As a result of TC Dictra calculations one obtains the composition in the joint as a function of space and time, cf. Fig. 3. This data can be analysed and used as new input data for Thermo-Calc allowing for the possibility to calculate which phases are present in every point in space and time. With this information one is able to determine which temperature and holding time is needed during the brazing process in order to avoid brittle phases in the joint. These temperatures and holding times are the base for new temperature-/time-cycles. However, even if one considers all of the points mentioned above there are some obstacles which are unsolvable using Thermo-Calc and TC Dictra. Most notably it is not possible to calculate any type of phase or property diagram for the filler material B-Ni60CrPSi-980/1020 due to the high phosphorus content. Phosphorus is not available in the nickel databases of Thermo-Calc and TC Dictra. One could use the steel database since it allows the usage of phosphorus which is recommended to be in the order of magnitude of parts per million. Since the filler material contains about 6 wt.-% of phosphorus it is impossible to obtain any realistic results from Thermo-Calc or TC Dictra if this material is involved. Additionally the filler material Ni 620 needs further analysis. Some of the phases calculated by Thermo-Calc are not found in experiments. This results in solidus and liquidus temperatures that are higher than expected for this material. If one

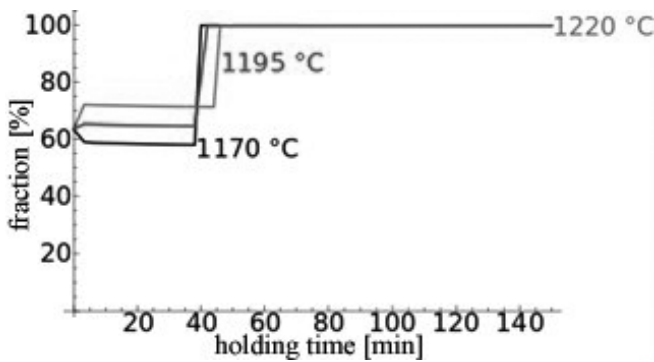


Fig. 3. Fraction of nickel mixed crystal in 16Mo3/Ni650 at 800 °C, 20 μm distance from the middle of the brazing gap
Rys. 3. Frakcja wymieszanych kryształów dla 16Mo3/Ni650 w 800 °C, odległość od środka szczeliny lutowniczej - 20 μm

excludes these phases from the calculation, the solidus and liquidus temperatures are lower but still differ from the expected value by about 100 °C. Due to this fact the results need to be interpreted carefully. In order to do research on these materials we needed to find a way of calculation without using Thermo-Calc and TC DICTRA. Therefore we started to use an experimental method based on energy dispersive x-ray analysis (EDX) and Fick's laws of Diffusion.

Fick's laws of diffusion

Fick's first law of diffusion is an empirical equation correlating the flux j and the concentration gradient. The second law, the continuity equation, is a balance equation for the concentration. By combining Fick's first and second law, one gets the diffusion equation under the assumption that $D = \text{const}$.

$$\frac{\partial c}{\partial t} = D \frac{\partial^2 c}{\partial x^2} \quad (1)$$

where D and c are the diffusivity and the concentration, respectively. In order to use Equation (1) in brazing we have to formulate a proper mathematical problem. Since we are only interested in joints where the base material is the same on both sides, there is a symmetry to be used in the formulation, cf. Fig. 4.

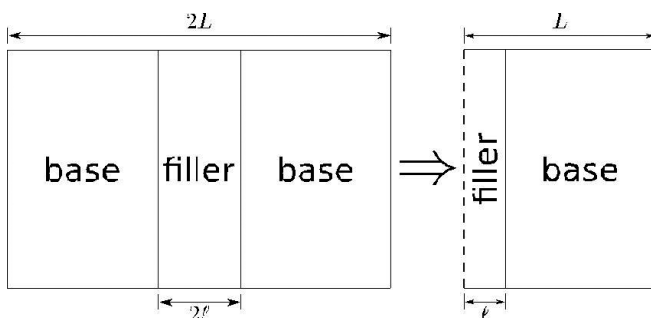


Fig. 4. Geometric model with and without using symmetry
Rys. 4. Symetryczny i asymetryczny model geometryczny

By considering the differential equation, i.e., Fick's second law, as well as proper initial and boundary conditions a well posed mathematical formulation of the problem can be derived

$$\frac{\partial c}{\partial t} = D \frac{\partial^2 c}{\partial x^2}, \quad c(x,0) = \begin{cases} c_1, & 0 \leq x < l \\ c_2, & l \leq x \leq L \end{cases}, \quad \frac{\partial c}{\partial x}(0,t) = \frac{\partial c}{\partial x}(L,t) = 0 \quad (2)$$

Due to the fact that in typical brazing processes $l \ll L$, one need to be careful when solving the boundary value problem stated in (2). In order to avoid mistakes due to the large scale variation a dimensionless problem statement is proposed. In order to do so we solve the dimensionless problem and transform the solution back to its dimension containing form. By applying the separation method the following solution can be derived

$$c(x,t) = \frac{lc_1 + (L-l)c_2}{L} + 2(c_1 - c_2) \sum_{n=1}^{\infty} \left[\frac{\sin(n\pi L^{-1})}{n\pi} \exp\left(-\frac{n^2\pi^2 D}{L^2} t\right) \cos\left(\frac{n\pi}{L} x\right) \right] \quad (3)$$

Note that neither the geometric l and L nor the physical parameters c_1 , c_2 and D are known in this point. In order to calculate D , one has to make estimates for the other parameters.

Calculation of diffusivities

Due to the fact that diffusivities are usually not available for complex materials like steels or filler materials in brazing, we aim to calculate diffusivities for our materials of interest. In order to do so, we use data by an energy dispersive x-ray analysis unit (EDX) which gives us the local composition of a specimen. We used actual brazing joints for the sake of calculating diffusivities under the real conditions in the joint. This enables us to calculate the timely change in composition for all material combinations of interest. The calculation needs to be done numerically, since the diffusivity should ensure that the resulting concentration curve fits the measured data points in an optimal manner. We developed a corresponding algorithm which is illustrated in Fig. 5. The process of calculation starts by importing the data from the linescan into mathematical software and make estimates for all uncertain (geometric and physical) parameters but not for the diffusivity itself. In order to find these estimates one should read out the initial concentrations and the geometric parameters from the EDX data. These estimates are combined with the solution of Fick's second law. The remaining free parameter, the diffusivity, is now calculated using a numerical optimization technique to ensure that the data is fitted as good as possible. If the data is not fitted well enough, new estimates have to be made, the afore-mentioned steps have to be repeated. In case that the data is fitted well enough, one can derive the temperature dependency of the diffusivity based on Arrhenius' equation,

$$D(T) = D_0 \exp\left(-\frac{Q}{RT}\right) \quad (4)$$

However, to apply this equation one would need specimens which were brazed using two different temperatures in the brazing process since there are two unknown parameters to be determined, i.e., activation energy and frequency factor. It can be shown, that Eq. (4) can be approximated by

$$D(T) \approx D_1 \frac{T_1}{T} \quad (5)$$

where D_1 is a known diffusivity at a temperature T_1 . This approximation is valid if the chosen temperature T differs not to

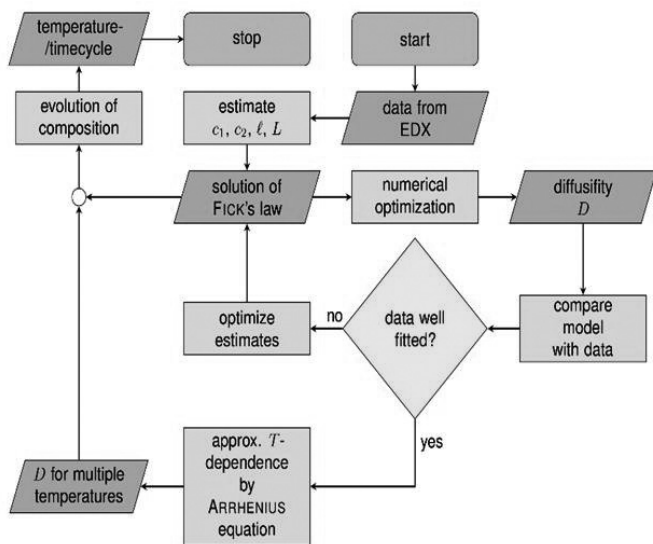


Fig. 5. Flow chart of the algorithm for calculation of diffusivities
Rys. 5. Schemat blokowy algorytmu do obliczania dyfuzyjności

much from T_1 . With the presented method one is able to calculate all parameters needed in FICK's second law to predict the composition of the materials in the joint as a function of time. Furthermore, one is not restricted to the temperature which was used brazing the specimen from which the diffusivity was calculated due to the shown approximation of ARRHENIUS' equation. This is the foundation for the derivation of temperature-/time-cycles for joints with similar as well as dissimilar materials by changing the geometrical model shown in Fig. 4.

Derivation of temperature-/time-cycles

With the knowledge of the change of composition in time one is able to suggest new temperature-/time-cycles by evaluating phase diagrams. The phase diagrams can be taken from the literature or can be calculated by using Thermo-Calc. Especially good results are obtained from Thermo-Calc if binary phase diagrams are needed. These can be used to determine the possibly occurring brittle phases. If the overall amount for a critical element in the joint is less than needed for the formation of a brittle phase, one can be sure that this phase will not be found in the joint. Fig. 6 shows the evolution of the composition in the middle of the brazing gap in the joint B-Ni60CrPSi-980/1020 – 1.4301. The composition in the joint is evaluated in the middle of the brazing gap since this is the most critical point in the connection.

It is obvious that chromium and silicon reach their satu-

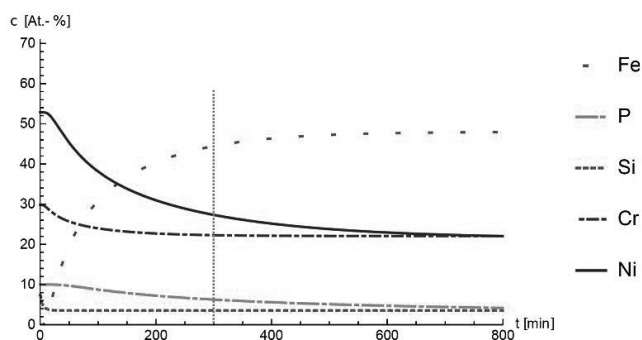


Fig. 6. Evolution of the composition in the middle of the brazing gap, steel: 1.4301, filler material: B-Ni60CrPSi-980/1020, brazing gap: 50 μm , brazing temperature: 1195 $^{\circ}\text{C}$

Rys. 6. Zmiana składu w środku szczeliny lutowniczej, stal: 1.4301, lut: B-Ni60CrPSi-980/1020 szczelina: 50 μm , temperatura lutowania: 1195 $^{\circ}\text{C}$

ration concentration quickly. This is because of the similar amounts in base and filler materials. The change in concentration of phosphorus is nearly completed after five hours. Merely the concentrations of iron and nickel are changing after this point. Since iron and nickel are completely miscible at the brazing temperature, one cannot expect any change in the occurring phases due to the interchange of iron and nickel.

Table I. Proposed temperature-/time-cycles, *calculated only using Thermo-Calc and Dictra

Tablica I. Zaproponowane cykle temperatura/czas, *wg obliczeń z Thermo-Calc i Dictra

filler material	base material	brazing temp. ($^{\circ}\text{C}$)	holding time (min)	brazing gap (μm)
Ni 620	1.2343	1075	60	50
	1.4301	1075	60	50
	1.4404	1075	60	50
B-Ni60 CrPSi -980 /1020	1.4301	1195	300	50
		1220	180	50
		1220	150	50
	1.4404	1195	150	50
		1220	120	50
		1220	105	50
Ni 650	1.4301*	1220	360	50
	16Mo3	1220	270	50

Therefore one should choose the brazing temperature to be 1195 $^{\circ}\text{C}$ with a holding time of five hours if the brazing gap is 50 μm wide. This temperature-/time-cycle ensures the best chances to avoid brittle phases in the brazing gap for this combination of base and filler material. This procedure can be carried out in a similar manner for other combinations in order to derive new temperature-/time-cycles for these combinations. By applying this method we calculated new temperature-/time-cycles for a wide variety of material combinations using a brazing gap of 50 μm . The results are shown in Tab. 1.

Results of proposed temperature-/time-cycles

Several specimen were produced using the proposed temperature-/time-cycles. Table II shows the mechanical properties of some specimen brazed with B-Ni60CrPSi-980/1020. The resulting specimen are shown in Fig. 8. The tensile strengths were measured using miniature tensile tests and the indentation hardness was determined by nanoindentation tests with a BERKOVIC pyramid shaped indenter. Note that the columns with temperature 1220 $^{\circ}\text{C}$ show the measurements of two proposed temperature-/time-cycles and the other are used for comparison. Specimen produced using the new cycles achieve considerably higher tensile strengths than the traditional joints. Furthermore the mechanical properties, i.e., YOUNG's modulus and indentation hardness are homogenized across base material, mixed crystal and brittle phase. This yields the higher tensile strengths due to the dissolution of the mismatch in mechanical properties. The more homogenized material properties result in lesser stresses at the boundary layers between the different areas of the joint,

Table II. Mechanical properties of different brazing joints produced using the filler material B Ni60CrPSi-980/1020. Abbreviations m.c. – mixed crystal, b.p. – brittle phase. Tensile strength was measured by miniature tensile tests.

Tablica II. Właściwości mechaniczne różnych połączeń lutowanych przy użyciu lutu B Ni60CrPSi-980/1020. Skrót m.c. – wymieszany kryształ, b.p. – faza krucha; Wytrzymałość na rozciąganie była mierzona na próbkach miniaturowych

base	1.4301			1.4404			
	holding time (min)	20	90	180	20	90	120
temperature (°C)		1090	1090	1220	1090	1090	1220
tensile strength (N/mm ²)		229	246	>320	199	232	261
Young's modulus (10 ³ N/mm ²)	base	190±13	188±13	241±20	193±7	194±10	249±25
	m.c.	195±9	189±17	249±20	197±7	197±7	249±25
	b.p.	211±9	220±25	270±24	225±12	217±7	247±30
indentation hardness (10 ³ N/mm ²)	base	3.2±0.4	3.1±0.5	5±0.46	3.0±0.1	3.2±0.3	4.9±0.47
	m.c.	3.6±0.3	3.6±0.3	4.8±0.4	3.6±0.3	3.3±0.2	4.9±0.5
	b.p.	8.7±0.9	6.8±1.9	7.4±0.6	8.4±0.9	7.6±1.4	6.7±1.3

i.e., base material, mixed crystal and brittle phase. In case of these joints it is not possible to get rid of the brittle phases in general since iron and phosphorus always form the brittle intermetallic Fe₃P. This phase cannot be avoided, cf. Fig. 7.

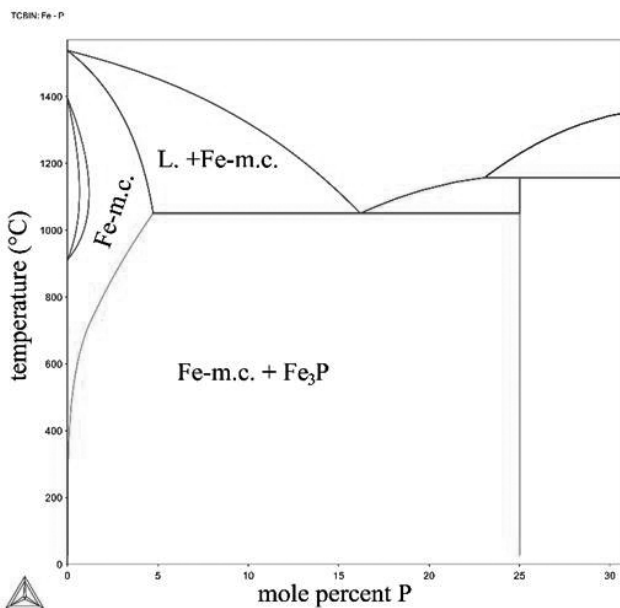


Fig. 7. Fe-P phase diagram
Rys. 7. Wykres fazowy Fe-P

In case of other filler materials brittle phases can be avoided completely by the temperature-/time-cycles presented in this work. Three joints Ni 620 – 1.2343, Ni 620 – 1.4301 and Ni 620 – 1.4404 are depicted in Fig. 9. It can be observed that there are no brittle phases visible in the joint. All three joints were brazed at a brazing temperature of 1075 °C with a holding time of 60 minutes. The microscopic images in Fig. 10 show the joint Ni 650 – 16Mo3, 1220 °C, 270 minutes. The figure depicts both a non-normalised and a normalised specimen. It is clearly observable that without the process of normalisation there is a very coarse grain structure in the base material. In case of the normalised specimen refined grain structure is achieved due to the heat treatment. Note that in both cases the joint is free of brittle phases and is not affected by the heat treatment.

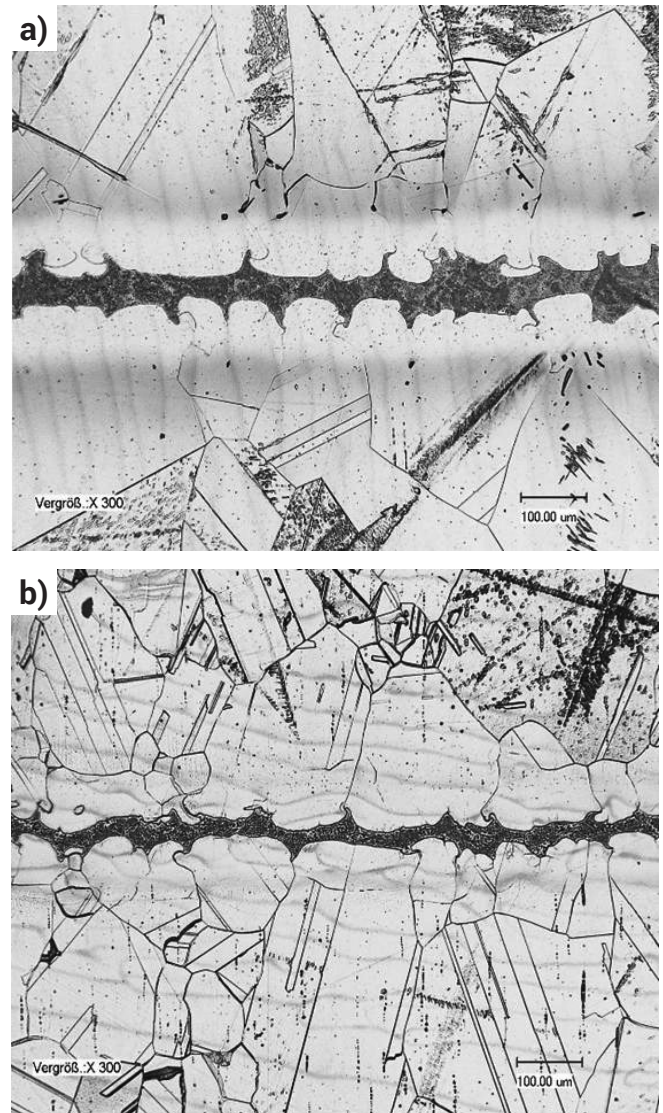


Fig. 8. Microscopic images of two joints brazed with the filler material B-Ni60CrPSi-980/1020 (a) 1.4301, 1220 °C, 180 min, gap > 100 µm, (b) 1.4404, 1220 °C, 120 min, gap 50 µm

Rys. 8. Mikrostruktura dwóch połączeń lutowanych – lut B-Ni60CrPSi-980/1020(a)1.4301,1220°C,180min,szczelina>100µm, (b) 1.4404, 1220 °C, 120 min, szczelina 50 µm

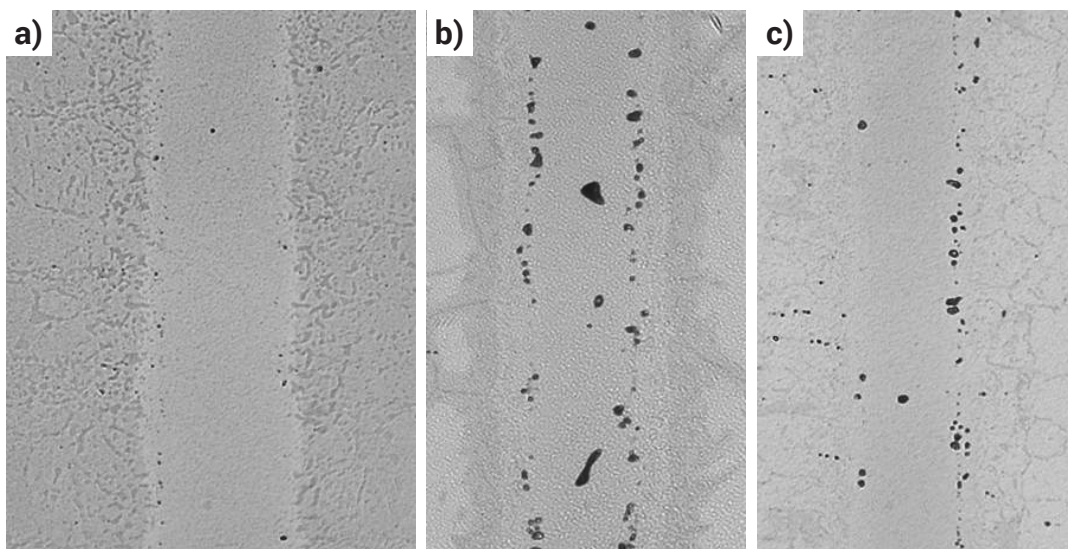


Fig. 9. Microscopic images of three different joints using the filler material Ni 620 and a brazing gap of 50 μm . The base materials are (a) 1.2343, (b) 1.4301 and (c) 1.4404
Rys. 9. Mikrostruktura trzech połączeń lutowniczych – lut Ni 620, szczelina 50 μm . Materiał rodzimy (a) 1.2343, (b) 1.4301 and (c) 1.4404

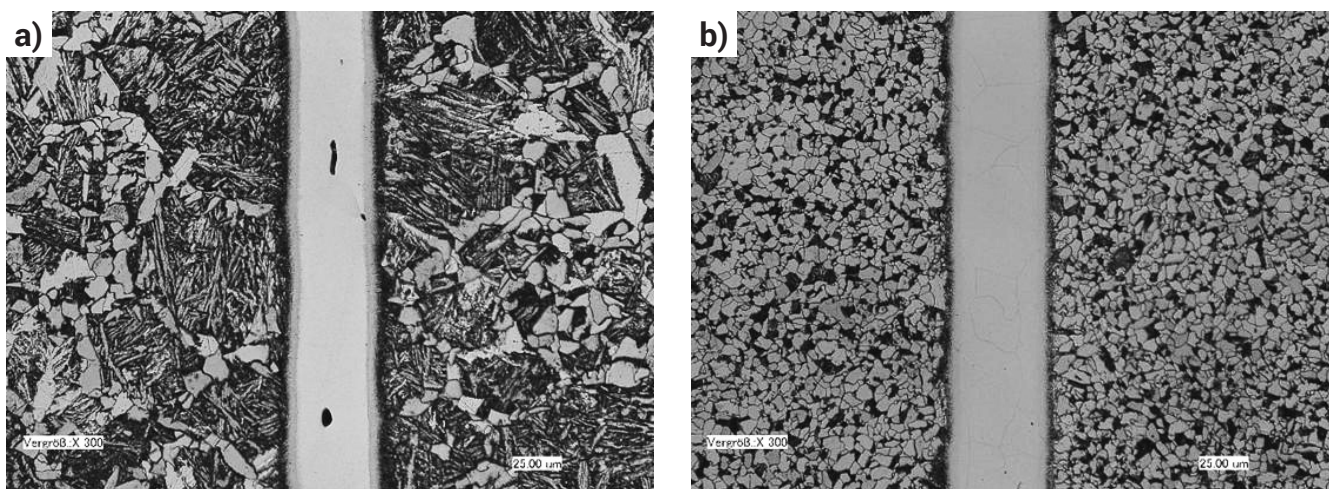


Fig. 10. Microscopic images of etched specimens. Base: 16Mo3, filler: Ni 650. (a) without normalising, (b) with normalising, 930 $^{\circ}\text{C}$, 30 minutes

Rys. 10. Mikrostruktura próbki trawionej. Materiał rodzimy – 16Mo3, lut Ni 650, a) bez normalizowania, b) po normalizowaniu 930 $^{\circ}\text{C}$, 30 min

Summary and outlook

The main objective of this work was the development of new temperature-/time-cycles for brazing with nickel-based filler materials, Ni 620, Ni 650 and B-Ni60CrPSi-980/1020 in order to reduce brittle phases in the brazing gap. By applying the presented method, we were able to propose temperature-/time-cycles for a large variety of material combinations. Furthermore the experimental evaluation of the new cycles showed that it is possible to produce brazing joints using Ni 620 and Ni 650 without any brittle phases. In case of the filler material B-Ni60CrPSi-980/1020 the brittle phase Fe_3P is unavoidable. Nevertheless the proposed cycles produced joints with better mechanical properties than the original brazing process. The presented method proposes the foundation of derivation of temperature-/time-cycles in case of joints using dissimilar materials, i.e., joints with different base materials on both sides of the gap.

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