Influence of the Titanium Inoculation on the Melting Behavior and Microstructure of Ni 620/X38CrMoV5-1 Brazing Joints

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Since the emergence of the first Ni-based filler metals in the end of the 1940s, the formation of brittle phases due to the metalloids Si, B, and P has been a major challenge. A new approach to selectively manipulate the microstructure of brazing joints with Ni-based brazing alloys is to inoculate the brazing alloy with Ti. The aim of this study is to characterize the influence of Ti on the melting behavior and brazeability in brazed joints consisting of hot-work tool steel X38CrMoV5-1 and inoculated Ni-base brazing alloy Ni 620. For this purpose, the melting behavior of the brazing alloy in the inoculated and noninoculated state is investigated by means of combined differential scanning calorimetry (DSC)/thermogravimetric (TG) analysis. In addition, the flow behavior of the filler metal as well as the resulting microstructure are evaluated by means of acoustic microscopy and scanning electron microscopy on the basis of a special specimen shape. The results show that Ti inoculation has a significant influence on the melting behavior as well as on the flow behavior and the microstructure in this brazing joint.

1. Introduction

The manufacture of high-strength as well as temperature- and corrosion-resistant joints by means of brazing technologies is state of the art in a wide variety of industrial sectors. The groups of Ni-based brazing alloys and iron-based brazing alloys have been particularly successful in this context. The alloying concepts of the Ni and Fe filler metals most commonly used in the industry are typically based on the respective main alloying element, chromium, to improve corrosion resistance and mechanical properties and alloying elements that lower the melting point. The metalloids silicon, boron, and phosphorus are particularly suitable for this purpose. However, in addition to their melting point lowering and in some cases, wetting-promoting properties, these elements have a decisive disadvantage. At supercritical brazing gap widths, these elements form hard and brittle phosphides, borides, and silicides, which often manifest themselves during solidification in the form of brittle phase bands. The critical gap width depends, among other things, on the brazing process, the base material, and the brazing alloy system and usually lies between $w_{krit}$ < 10 μm for P-containing alloy systems and $w_{krit}$ < 35 μm for B-containing alloy systems. The formed brittle phase band deteriorates, in particular, the mechanical properties, and represents a metallurgical notch. If the brazing alloys are used improperly, already residual stresses, for example, caused by cooling after the brazing process, can lead to cracking or immediate failure. Previous strategies for improving the properties of such brazed joints mainly interfere with the diffusion of the metalloids B or Si, for example, by technically limiting the brazing gap width to a subcritical level and thus reducing the metalloid present or using longer dwell times at high temperatures during the brazing process. Subsequent diffusion annealing is also common practice. In the case of P, these strategies are not effective under economic boundary conditions due to the high diffusion coefficient. Due to the long process times, the high energy costs, and the high technical effort required to limit the brazing gap width, the production of high-quality joints based on Ni brazing alloys is cost-intensive, especially compared with significantly lower-cost brazing joints and brazing processes with Cu-based filler metals. The long-lasting high-temperature load on components in the brazing process can also lead to quality losses, in particular, due to the impairment of the base material-like coarse grain formation or distortion. Thus, there is a clear demand for a methodology to selectively manipulate the microstructure without the long process times, high temperatures, or high technical effort to limit the brazing gap width.

A new approach to selectively manipulate the microstructure of brazing joints with Ni-based brazing alloys is to inoculate the brazing alloy with titanium (Ti). In the context of this study, inoculation is defined as the addition of refractory metals in the lower single-digit percentage range with the aim of selectively manipulating the microstructure of the filler metal. Similar approaches...
to improving microstructure and mechanical properties are known from research on Cu and Ni brazing alloys.\textsuperscript{9,10} Other published approaches use the optimization of the temperature–time curve,\textsuperscript{11} the addition of further elements or powdered base material as diffusion sinks or the formation of softer phase bands.\textsuperscript{10,12} In contrast, Ti inoculation aims at splitting and distributing the brittle phase band by directly intervening in the solidification kinetics of the filler metal. Here, the splitting and distribution of the brittle phase band are to be achieved by direct intervention in the solidification kinetics of the filler metal. Initial studies on brazed joints consisting of the austenitic stainless steel X5CrNi18-10 and the high-chromium brazing metal. Here, the splitting and distribution of the brittle phase band were discussed as the reasons for the microstructure, especially at \( \sigma_{\text{B}} < 5\% \). The specimens were afterward brazed in a high vacuum furnace at a temperature of \( T = 1200 \, ^\circ\text{C} \) with a dwell time of \( t = 10 \, \text{min} \) under high vacuum of \( p < 5 \times 10^{-5} \, \text{mbar} \). Figure 1 shows the tensile shear strengths of the specimens determined during the study, as well as two cross sections. The gap widths of the tensile shear specimens ranged from \( 70 \, \mu\text{m} < W_{\text{gap}} < 100 \, \mu\text{m} \). The results showed a significant change in microstructure, especially at \( \sigma_{\text{B}} = 5\% \), as well as increased tensile shear strength due to the addition of Ti, with the maximum tensile shear strength determined at \( \sigma_{\text{B}} = 3\% \). As shown in the previous studies,\textsuperscript{13} the splitting and distribution of the NiSi\textsubscript{2} brittle phase band were discussed as the reasons for the modified microstructure, whereby this effect was initially observed at about \( 4\% < \sigma_{\text{B}} < 5\% \) in the entire brazed joint.

As part of subproject A05 of the Collaborative Research Center SFB 1120 at RWTH Aachen University, this inoculation effect is being investigated in more detail to increase the precision of brazing with Ni-based brazing alloys. In a first step, the effects of inoculation on the processing qualities or the properties in the brazing process are to be characterized. This study focuses on the melting and remelting behavior of inoculated brazing pastes, as well as on the "brazeability," using the example of a brazing joint consisting of the hot-work tool steel X38CrMoV5-1 and the brazing alloy Ni 620. The brazeability is determined by the materials, the brazing process, as well as the design, which is the reason for a detailed consideration of the material behavior with regard to the melting and flow behavior of the brazing alloy. The following questions are in focus.

1) Which effect does Ti inoculation of the brazing alloy have on the melting and remelting behavior of the brazing alloy? 2) How does Ti affect the flow behavior and microstructure of the filler metal?

2. Experimental Section

Combined differential scanning calorimetry (DSC) and thermogravimetric (TG) analyses were conducted to investigate the influence of the Ti content on the melting interval of the filler metal alloy, as well as to design the brazing process. Two measurements were carried out in succession. The first measurement described the melting behavior in the powder state of the filler metal and the additive. The second measurement represented the melting behavior in the alloyed state, whereby a significant difference between the first and second measurement was to be expected. For the measurements, a combined DSC/TG system of the type Setsys Evolution from the manufacturer Setaram Inc. (Caluire-et-Cuire, France) was available.

All presented measurements were carried out on powder mixtures consisting of Ni 620 filler metal powder and Ti powder. The used powder mixtures are shown in Table 1. In the following

**Table 1. Targeted chemical composition of filler metal powder mixtures.**

| Powder mixture | Proportion Ni 620 [wt%]\textsuperscript{14} | Addition [wt%] |
|----------------|---------------------------------|---------------|
| I              | 82.4 7.0 4.5 3.1 3.0 0.0      |               |
| II             | 81.6 6.9 4.5 3.1 3.0 1.0      |               |
| III            | 80.8 6.9 4.4 3.0 2.9 2.0      |               |
| IV             | 79.9 6.8 4.4 3.0 2.9 3.0      |               |
| V              | 79.1 6.7 4.3 3.0 2.9 4.0      |               |
| VI             | 78.3 6.7 4.3 2.9 2.9 5.0      |               |

**Figure 1. Results of tensile shear tests A) of X5CrNi18-10 brazed with Ni 650 and Ti inoculations between 0% < \sigma_{\text{T}} < 5% and B) light microscopic images of cross sections.**
section, only mixtures I, IV, and VI will be discussed as representative of the test series in detail.

The DSC/TG measurements were carried out after an evacuation and purging process with argon (Ar) under a flowing Ar inert gas atmosphere of $v = 20 \text{ ml min}^{-1}$ at a heating rate of $T = 10 \text{ K min}^{-1}$ in Al$_2$O$_3$ crucibles. A previous characterization of the shape and grain size distribution of the powders (Figure 2) using a Morphologi G2 particle image analysis system from Malvern Instruments Ltd. (Malvern, United Kingdom) showed a grain size of $d_{90, \text{Ni}620, 90/10} = 88 + 19 \mu m$ (A) for the Ni 620 powder. In contrast, the used Ti powder, with a purity of $m_{\text{Ti}} = 99.995 \%$, had a grain size of $d_{90, \text{Ti} 90/10} = 43 + 21 \mu m$ (B). The Ti powder, which was significantly finer grained than the filler metal powder, was used here to achieve a statistically more homogeneous distribution of Ti within the brazing paste.

For the investigation of the flow behavior and the microstructure, specimens corresponding to Figure 3 were produced from two X38CrMoV5-1 sheets. The chemical composition of the base material is shown in Table 2. For specimen preparation, the sheets were separated and a central hole of $d_\phi = 5 \text{ mm}$ was drilled in one sheet per specimen. The sheets were cleaned in an ethanol ultrasonic bath. A brazing gauge with a thickness of $w_{\text{gap}} = 80 \mu m$ was placed between the sheets. Due to the supercritical level of the gap width, the formation of brittle phases within the filler metal was to be expected. Subsequently, the sheets were mechanically clamped and spot welded by tungsten inert gas (TIG) welding without filler metal.

**Figure 2.** Powder characterization with particle size distribution and SEM image of the A) used Ni 620 filler metal powder and the B) Ti additive.

**Figure 3.** Technical representation of the used specimen geometry.
Table 2. Chemical composition of the tool steel X38CrMoV5-1 according to DIN EN ISO 4957.[24]

| Element | Min. | Max. |
|---------|------|------|
| Fe      | 0.33 | 0.41 |
| C       | 0.80 | 1.20 |
| Si      | 0.25 | 0.50 |
| Mn      | 4.80 | 5.50 |
| Cr      | 1.10 | 1.50 |
| Mo      | 0.30 | 0.50 |
| V       |      |      |

After welding, the specimens were prepared for the brazing process. For this purpose, brazing pastes consisting of $m_{\text{powder}} = 90 \text{ wt\%}$ of the powder mixtures shown in Table 1 and $m_{\text{Binder}} = 10 \text{ wt\%}$ of an organic binder were prepared. Then, about $m_{\text{paste}} = 1.5 \text{ g}$ of the paste was applied in the hole and predried for about $t = 20 \text{ h}$ at room temperature. To prevent the molten filler metal from flowing over the surface of the specimen during the brazing process, Stop-Off was applied around the hole.

A furnace of the type POV MOV 553 T from the manufacturer PVA TePla AG (Wittenberg, Germany) was available for the brazing process. The process took place under high vacuum at $p > 5 \times 10^{-3} \text{ mbar}$ and consisted of several holding stages (Figure 4). To monitor the real component temperature, a thermocouple was placed on a dummy specimen without filler metal, directly at the brazing gap. The first holding stage at $T_1 = 300 \degree \text{C}$ and $T_2 = 600 \degree \text{C}$ were used to remove the binder. The second holding stage at $T_3 = 940 \degree \text{C}$ was used for homogenization of the temperature within the specimens. Based on the DSC investigations, a brazing temperature of $T_4 = 1070 \degree \text{C}$ was selected with a dwell time at brazing temperature of $t_4 = 10 \text{ min}$. Afterward, the base material was quenched or hardened by means of a rapid cooling device at $p = 800 \text{ mbar}$ argon. Following quenching, the specimens were annealed at a low tempering level of $T_5 = 300 \degree \text{C}$ for $t_5 = 2 \text{ h}$.

Two specimens were prepared for each filler metal mixture (Table 1). After the brazing process, one specimen was examined by means of acoustic microscopy (c-scan) to determine the flow behavior. For this purpose, a system of the type NDT CF 300 from the manufacturer Okos Solutions Llc. (Manassas, USA) was used. In this study, a probe with a frequency of $f = 15 \text{ MHz}$ was used. The focus width was $W = 200 \mu \text{m}$, focusing on the brazing gap. With this technique, the specimens which were to be tested were placed in a water basin. Subsequently, the ultrasonic probe was scanned over the specimen from above by means of a fully automatic X and Y axis. The water was used to feed the ultrasound into the specimen. The ultrasonic probe measured a signal comparable with that of a conventional hand-held ultrasonic probe. This signal was also called A-scan. In the case of location-resolved testing in several axes, it was typically called a C-scan. Finally, a false color image could be generated from the determined data, which indicated relative amplitude within the focus in a location-resolved manner. If there was no defect, the amplitude was $x = 0$. In contrast, if there was a crack, void, or a wetting defect, the result was an error echo with a correspondingly higher amplitude.

The second specimen was used to prepare cross sections (Figure 3) and for subsequent scanning electrode microscopic examination. For this purpose, a Phenom XL scanning electron microscope (SEM), which also has energy-dispersive X-ray spectroscopy, by Thermo Fisher Scientific Inc. (Walhama, USA), was used.

In the brazing tests, a significant influence on the flow behavior as well as on the microstructure of the brazing material was expected due to the addition of Ti. In general, reactions of Ti with the carbon of the base material and possibly with B and Si of the brazing alloy were expected.

3. Results and Discussion

3.1. DSC/TG Analyses

The first DSC/TG analyses of different powder mixtures are shown in Figure 5. Here, in the context of this work, a (melting) interval is defined as the temperature interval between the start temperature and the maximum heat flow of the reaction. All three measurements show three exothermic peaks in the temperature interval between $449 \degree \text{C} < T < 595 \degree \text{C}$, which can be attributed to the recrystallization of the probably previously amorphous filler metal powder Ni 620. In the initial state (A) without the addition of Ti, a melting interval of $961 \degree \text{C} < T < 1031 \degree \text{C}$ can be seen. The melting interval is wider than that specified in DIN EN ISO 17672,[14] although a deviation is to be expected due to the wide tolerance in the standard with regard to the chemical composition. The melting interval is also composed of three different endothermic peaks, and therefore the melting of three different phases can be assumed here. Comparable results were shown by J. Ruiz-Vargsa et al. on amorphous filler metal foils of comparable alloys.[15]

With an addition of a mass fraction of $s_{\text{Ti}} = 3 \% \text{ Ti}$ (B), a significant change in the melting behavior compared with the initial state (A) can be seen. While the beginning of the melting interval was determined congruent to the initial state at $T = 963 \degree \text{C}$, the end of the melting is at $T = 1065 \degree \text{C}$ and thus $\Delta T = 34 \degree \text{K}$ is higher than that in the initial state. This melting interval also consists of several peaks, whereby a superimposition of the endothermic melting reaction with an exothermic reaction can be seen. It can be assumed that this is a reaction of the dissolved Ti with

![Figure 4](https://www.advancedsciencenews.com/content/2100497/fig/4)

Figure 4. Schematic representation of the furnace program with set temperature and measured real temperature.
Further elements. As the TG analysis did not show any irreversible increase in mass at the same time, a reaction of Ti with further elements from the molten filler metal is assumed. Exothermic reactions may be caused by the formation of Ti-B phases \((G = 77.48 \text{ kcal mol}^{-1})\) or Ti-Si phases \((G = 36.33 \text{ kcal mol}^{-1})\).\(^{16}\) However, the occurrence of a reaction with the Al\(_2\)O\(_3\) crucible cannot be excluded either.

The measurement of the powder with a mass addition of \(\sigma_{Ti} = 5\%\) Ti (C) shows an even stronger reaction compared with the powder with an addition of \(\sigma_{Ti} = 3\%\) Ti (B), which is attributed to the higher Ti content. The melting interval is also wider and between \(963 ^\circ\text{C} < T < 1089 ^\circ\text{C}\). Compared to the initial state (A), the end of the melting interval is thus higher by \(\Delta T = 58\) K. Based on the measurements, a brazing temperature of \(T = 1070 ^\circ\text{C}\) was selected for the brazing processes, which is thus slightly higher than the recommended brazing temperature of \(T = 1050 ^\circ\text{C}\).\(^{17}\) This partly compensates the increased melting interval due to the Ti addition.

Figure 6 shows the second DSC measurements, which directly followed the first measurements (Figure 5). As expected, no exothermic peaks can be observed in the temperature interval between \(449 ^\circ\text{C} < T < 595 ^\circ\text{C}\). The starting temperatures of the melting reactions of all three measurements are shifted to higher temperatures between \(10 \text{ K} < \Delta T < 30 \text{ K}\) compared with the first measurements, which may be attributed to the closer equilibrium cooling in the experiments compared with powder atomization. In contrast, the final temperatures of the melting reactions are slightly lower than the first measurements. The detailed evaluation also shows that for the specimen with a mass fraction of \(\sigma_{Ti} = 3\%\) Ti (B), a small endothermic peak occurs at a temperature of \(T = 976 ^\circ\text{C}\), possibly representing the melting of an additional phase (peak 0). In contrast, this peak is not observed in the measurement with a mass fraction of \(\sigma_{Ti} = 5\%\) Ti. Overall, the endothermic peaks are very comparable for all three measurements except for peak 0 (B). However, the melting reactions are shifted toward higher temperatures with increasing Ti content, possibly indicating a binding of the melting-point-lowering elements B and Si by Ti to Ti\(_3\)B\(_2\) and Ti\(_3\)Si\(_2\) phases, respectively. In line with previous work investigating phase formation in the Ni 620 or BNi-2 filler metal, the superimposed peaks can be attributed to the dissolution of Ni\(_3\)B, Ni\(_3\)Si, and CrB.\(^{18-20}\) Considering published calculations using ThermoCalc,\(^{18,21}\) the dissolution of (NiCrFe)\(_3\)B seems likely as “peak 1,” of the Ni solid solution as “peak 2,” and of CrB as “peak 3.”

3.2. Flow Behavior

To characterize the influence of the Ti additive on the flow behavior of the molten filler metal, the brazed specimens were examined by acoustic microscopy (C-scan). Figure 7 shows the specimens after the brazing process. Optical differences can already be seen in the specimens. The molten filler metal of the specimen without the addition of Ti (A) flowed completely into the hole and generated an optically flawless brazed joint. In contrast, the specimen, in which a mass fraction of \(\sigma_{Ti} = 3\%\) Ti was added (B), exhibits a complete filling of the hole. In the specimen with a mass fraction of \(\sigma_{Ti} = 5\%\) Ti (C), in contrast, a larger proportion of the filler metal solidified above the component surface. This behavior already indicates a deterioration of the brazing gap filling with increasing Ti content in the brazing alloy.

Figure 8 shows the results of the ultrasonic examinations from the same perspective as in Figure 7. The reference specimen without Ti addition (A) shows only minor defects. It can therefore be concluded that the flow behavior is very good, which confirms optical investigations. In contrast, the specimen with a mass
fraction of \( \varpi_{Ti} = 3\% \) (B) already shows significant defects, which are distributed over the specimen. The defects also exhibit a preferred direction. The reason for this phenomenon can be assumed to be the grinding direction or the orientation of the grinding marks. The specimen, with a mass fraction of \( \varpi_{Ti} = 5\% \) (C), shows only wetting in the closer vicinity of the borehole, compared with specimens A and B. The results could also be verified from transverse cross sections, but their presentation is omitted here. Overall, the results of the ultrasonic investigations support the assumption that an increasing Ti content causes a deterioration in the flow behavior of the molten filler metal.

### 3.3. Influence of Titanium on the Microstructure

Figure 9 shows the results of SEM and EDX analyses of a specimen, which was brazed without the addition of Ti and thus represents the initial state. It should be noted that due to the nonquantifiability of B and C, the evaluation of these elements by EDX is omitted.

The base material shows a martensitic microstructure, as shown in Figure 9. It has a hardness of \( H = 185.1 \pm 11.5 \) HV10 in the initial state and a hardness of \( H = 635.7 \pm 65.6 \) HV10 in the brazed, quenched, and tempered state. Cr-rich phases...
(4, B) can be seen directly at the interface to the filler metal. It can be assumed that these are also mainly chromium borides (CrB) phases. Due to the significantly higher diffusion coefficient of B compared with Cr, the B in the austenitic microstructure diffuses preferentially along the grain boundaries during the brazing process. Here, B forms the CrB phases with Cr contained in the base material, causing local Cr depletion of the adjacent material and the formation of a Cr gradient. In Figure 9B, a corresponding Cr gradient was indicated by EDX measurements. After martensitic transformation, these phases are found on the previous austenite grain boundaries. Due to the pronounced diffusion of B into the base material, pore formation (Kirkendall voids) also occurs at the interface to the base material.

The microstructure of the filler metal shows several phases. According to numerical calculations from other research work,[18,21] it is assumed that CrB is formed first during solidification of the molten filler metal, which has also already been discussed in the context of DSC results. Consequently, in point 5, CrB is to be assumed. Upon further cooling of the residual melt, the Ni solid solution is formed in the interface between the filler metal and the base metal (1). In addition, a Fe-rich phase (4) can be identified, although the presence of B cannot be ruled out here. Finally, isolated, probably B-containing phases (2) as well as the eutectic Si- and B-rich residual melt (3, C) solidify from the residual melt. During solidification, a Ni-rich phase (6) is formed first, and the residual melt is further enriched with Si and possibly B (7). Finally, this also solidifies, together with the Ni-rich phase, and the residual melt forms a lamellar structure.

Overall, the results on the brazed joint without Ti addition can be considered as a good reference and representation of the current state of the art for this filler metal/base material combination. Comparable microstructures have already been investigated in previous research work.[15,22,23] Also, the formation of Cr-rich phases in the adjacent base metal and of pores in the filler metal have already been investigated by Tillman et al. using the same base and filler metal.[24]

Figure 10 shows the results for a specimen with Ti addition with a mass fraction of $\sigma_{Ti} = 3\%$. The microstructure looks similar to the specimen without Ti in Figure 9. The phase formation in the base material is also comparable, as is the formation of larger Cr-rich phases (4), which are probably CrB. In this case, larger Si-rich Ni phases can also be observed (2), which were not observed in this form in the initial state without the addition of Ti. Furthermore, finely distributed darker phases can be found in the microstructure at the interface to the base material. In points 5 and 7, the EDX results show a significantly high Ti content. Because of the phases, which are formed preferentially in the immediate vicinity of the base metal, the formation of titanium carbide (TiC) out of Ti from the molten filler metal and C from the base metal can be assumed. According to the DIN EN ISO 4957 standard,[25] the base material contains a relatively large amount of C with a mass fraction of 0.33% $< \sigma_C < 0.41\%$, which, due to the concentration gradient and the high diffusion coefficient of C, can diffuse quickly into the filler metal. However, binder residues can also act as another source of C. In addition, the formation of Ti$_2$B$_7$ phases cannot be ruled out. Only a fraction of available Ti is required for these phases, thus leaving additional Ti available for the formation of other precipitates. The deterioration of the flow properties (Figure 8) can also be explained by the observed precipitates or reaction products at the interface between filler metal and base metal. In addition to the interface, an increased Ti content can also be measured in point 3. However, the composition of the precipitates cannot be determined with sufficient accuracy by EDX due to their small size. Nevertheless, finely distributed precipitates surrounded by two different matrix phases can be seen (B).

Ti inoculation of the Ni 620 filler metal with a mass fraction of $\sigma_{Ti} = 5\%$ significantly deteriorates the flow behavior of the molten filler metal (Figure 8). In view of alternative application methods, such as amorphous braze foils, the microstructure will nevertheless be described here. Figure 11 shows the microstructure and the EDX results for a specimen with Ti addition of a
mass fraction of $\varpi_{Ti} = 5\%$. Compared with the initial state (Figure 9), the specimen shows a completely changed microstructure. Overall, the higher Ti content leads to increased formation of Ti-containing precipitates in the interface between the brazing material and the base material (7), as well as in the center of the filler metal. In between is a Ni-rich region (1), in which relatively few precipitates are found. It is probably a Ni solid solution, comparable with the initial state without Ti addition. In the center of the filler metal, two different matrix phases can be found in addition to the Cr- and Ti-rich precipitates (B). While the lighter phase (3) is a Ti-containing Ni-rich phase, a significantly higher Cr and Si content characterizes the darker phase (5, 6, C). It is also noticeable that the Cr-rich precipitates are more numerous but also significantly smaller than in the initial state. As already seen in the specimen with a mass fraction of $\varpi_{Ti} = 3\%$ Ti (Figure 10), more Si-rich Ni phases can be seen. However, a lamellar or eutectic structure, as shown in Figure 9, cannot be identified.

The specimens demonstrate the significant influence of Ti on the microstructure of the filler metal. Ti-containing precipitates

| No. | Ni     | Cr     | Si    | Fe    | Ti    |
|-----|--------|--------|-------|-------|-------|
| 1   | 74.8 ± 1.2 | 7.4 ± 0.2 | 4.4 ± 0.1 | 13.4 ± 1.4 | -     |
| 2   | 90.1 ± 0.2 | 3.4 ± 0.1 | -     | 6.5 ± 0.1 | -     |
| 3   | 80.7 ± 0.1 | 3.7 ± 0.1 | 5.8 ± 0.1 | 9.8 ± 0.1 | -     |
| 4   | 9.4 ± 0.2 | 6.8 ± 0.4 | -     | 76.1 ± 1.8 | -     |
| 5   | -      | 100    | -     | -     | -     |
| 6   | 88.8 ± 0.2 | 4.0 ± 0.2 | -     | 7.2 ± 0.2 | -     |
| 7   | 90.4 ± 0.5 | 3.8 ± 0.2 | 5.9 ± 0.3 | 9.9 ± 0.3 | -     |
| 8   | 28.7 ± 18.8 | 80.7 ± 22.6 | 2.1 ± 1.2 | 3.9 ± 1.7 | -     |
| 9   | -      | 4.0 ± 0.4 | 1.1 ± 0.1 | 95.1 ± 0.6 | -     |

Notes: Measurements were validated by at least 5 individual measurements ($n \geq 5$). Secondary measurements (*) were validated with three individual measurements ($n = 3$). The elements which cannot be quantified by EDX, especially boron and carbon, were not considered.

Figure 9. A) SEM overview and B,C) detailed images as well as EDX analysis on selected spots of a specimen made of X38CrMoV5-1 with Ni 620 without addition of Ti, brazed at $T = 1070^\circ C$ for $t = 10$ min in high vacuum.
are formed, which are finely distributed within the filler metal, but also in the interface to the base material. It is noticeable that Ti is always present in the form of precipitates or in areas with many small precipitates and is not present within the Ni solid solution and the other detected phases. Moreover, at a mass fraction of $\varpi_{\text{Ti}} = 5\%$, the results show few well-defined phases, observed in the initial state (Figure 9) and even still at $\varpi_{\text{Ti}} = 3\%$ (Figure 10). In contrast to these specimens, the specimen in Figure 11 exhibits a relatively chaotic microstructure. The brittle phases are smaller and more distributed. Thus, the effect of Ti inoculation on this brazing joint appears to be similar to the described brazing joint of X5CrNi18-10 with the Ni 650 brazing alloy.

4. Conclusion and Outlook

The basic hypothesis of this work, that the Ti inoculation of the filler metal Ni 620 has a significant influence on melting behavior, brazeability, and the microstructure of the filler metal, is

**Figure 10.** A) SEM overview and B,C) detailed images as well as EDX analysis on selected spots of a specimen made of X38CrMoV5-1 and Ni 620 containing $\varpi_{\text{Ti}} = 3\%$ Ti by mass and brazed at $T = 1070^\circ \text{C}$ for $t = 10$ min in high vacuum.

| No. | Ni   | Cr   | Si   | Fe   | Ti  |
|-----|------|------|------|------|-----|
| 1   | 76.9 ± 0.3 | 3.0 ± 0.1 | 5.9 ± 0.1 | 14.2 ± 0.2 | -   |
| 2   | 84.7 ± 0.2 | -    | 15.3 ± 0.2 | -    | -   |
| 3   | 81.4 ± 0.4 | 2.5 ± 0.1 | 3.6 ± 0.1 | 9.3 ± 0.3 | 3.2 ± 0.2 |
| 4   | 7.5 ± 3.2 | 88.4 ± 3.7 | -    | 4.1 ± 0.5 | -   |
| 5   | 65.4 ± 0.2 | 3.4 ± 0.1 | 5.0 ± 0.1 | 11.4 ± 0.2 | 14.8 ± 0.2 |
| 6   | 72.6 ± 6.0 | 4.8 ± 0.6 | 4.8 ± 0.4 | 19.8 ± 2.4 | -   |
| 7   | 47.2 ± 3.0 | 3.4 ± 0.2 | 5.9 ± 0.7 | 8.4 ± 0.3 | 35.1 ± 3.4 |
| 8   | -    | 10.2 ± 0.2 | -    | 89.8 ± 0.2 | -   |
| 9   | -    | 4.9 ± 0.1 | 1.0 ± 0.1 | 94.1 ± 0.1 | -   |

**Notes:**
Measurements were validated by at least 5 individual measurements ($n \geq 5$). Secondary measurements (*) were validated with three individual measurements ($n = 3$). The elements which cannot be quantified by EDX, especially boron and carbon, were not considered.
confirmed. In detail, the DSC investigations show a shift of the melting interval of the filler metal to higher temperatures proportional to the Ti content of the filler metal powder during the first melting process as well as during remelting. It can be explained by the bonding of the melting-point-lowering elements B and Si by Ti. However, corresponding phases could yet not be fully identified within the filler metal yet.

In addition, the analyses of the flow behavior using the acoustic microscope show that Ti inoculation has a negative influence on the flow behavior of the brazing material in this brazed joint. This behavior is attributed to a reaction of Ti with C from steel to form TiC and the resulting wetting problems of the base metal. Corresponding Ti-containing precipitates are clearly visible at the interface of the filler metal to the base metal, although evidence of TiC formation is still pending.

Furthermore, the microstructure shows a significant influence of Ti, especially at a mass fraction of \( \varphi_{Ti} = 5\% \) in the filler metal. Overall, the microstructure observed here is completely different from the microstructure in previous research on NiCrSi brazing alloys, where the NiSi phase band was present in a split and distributed form (Figure 1). It seems possible that the Ti-containing precipitates promote heterogeneous nucleation, leading to the observed significant influence of Ti on the microstructure. In this case, small higher-melting Ti precipitates or dispersoids such as TiC or TiB are already formed in the molten filler metal and promote solidification at many

| Mass fractions of the various elements in mass percent (%) |
| No. | Ni   | Cr  | Si  | Fe   | Ti  |
|------|------|-----|-----|------|-----|
| 1    | 72.4 | 5.4 | 4.8 | 17.4 | -   |
| 2    | -    | 100.0 | 0.0 | -    | -   |
| 3    | 83.9 | 1.6 | 0.0 | 6.8  | 7.7 |
| 4    | 82.4 | -   | 15.4 | 2.2  | 1.2 |
| 5    | 78.2 | 3.9 | 15.2 | 2.7  | 0.1 |
| 6    | 53.4 | 26.0 | 10.5 | 3.7  | 6.4 |
| 7    | 39.1 | 4.3 | 2.7 | 17.4 | 36.6 |

Notes:

Measurements were validated by at least 5 individual measurements (\( n \geq 5 \)). Secondary measurements (*) were validated with three individual measurements (\( n = 3 \)). The elements which cannot be quantified by EDX, especially boron and carbon, were not considered.
precipitates at higher temperatures. The large number of initial points results in a finer microstructure. This also results in a finer distribution of the B- and Si-rich residual melt, which also explains the observed smaller CrB phases with increasing Ti content. As the effect of these dispersoids is inversely proportional to their size, larger Ti precipitates are enclosed by the solidifying phase or enriched with the residual melt, which also allows further growth. However, a clear analytical verification of this explanation is difficult due to complex alloying as well as solidification and diffusion processes during brazing. The fact that nucleation probably has a non-negligible influence in brazing with Ni-based alloys was, however, demonstrated by Böttger et al.\cite{26,27} on the basis of phase-field studies.

Overall, this work shows the effects of Ti inoculation on the brazeability and microstructure of X38CrMoV5-1/Ni 620 brazed joints. A number of more detailed questions have arisen in this work. Further studies are planned to investigate these questions in more detail. The following questions and investigations are the main focus. 1) For further investigation of the influence of Ti inoculation on brazeability, further studies are planned on low-carbon steels using B-containing inoculated amorphous brazing foils, such as Ni 660. 2) In the context of the present work, the localization of boron and carbon could not be clearly clarified due to the applied method. For this reason, a more detailed analysis of the phase composition and diffusion phenomena using electron probe microanalysis (ESMA) is planned. In contrast to XRD analyses, this should enable spatially resolved examinations of the phase compositions. 3) Due to the reduced flow behavior of Ti-containing brazing materials, the production of inoculated amorphous brazing foils by melt spinning and subsequent characterization is envisaged. These amorphous brazing foils are typically used directly in the brazing gap and are thus less dependent on good flow behavior of the molten brazing alloy. To characterize the braze joints produced with them, the local or microscale mechanical properties are investigated by means of nanoindentation measurements and linked to macroscopic shear tensile tests.

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Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

Research data are not shared.

Keywords

brazeability, brittle phases, hot-work steels, vacuum brazing processes

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