Influence of nitrogen in brazing atmospheres on the hardness of the microstructural constituents of brazed stainless steel joints

Influence of nitrogen in brazing atmospheres on the hardness of the microstructural constituents of brazed stainless steel joints

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Abstract. Stainless steel components, such as heat exchangers for energy and air-conditioning technologies are commonly manufactured using nickel-based brazing fillers in continuous furnaces or vacuum furnaces. In the continuous furnace, the brazing process is often supported by a protective gas. As protective gas is commonly used nitrogen or mixtures of nitrogen and hydrogen. In the vacuum furnace, nitrogen is often used as cooling gas. The arising nitrogen enrichment of the braze metal and the base material influences the mechanical properties of the microstructural constituents of the brazed joints, especially the hardness. In this work, the influence of the nitrogen enrichment on the hardness of the microstructural constituents of the joints was investigated with regard to the process conditions. The amount of nitrogen in the braze metal as well as in the base material was determined using a carrier gas hot extraction technique. The hardness of the microstructural constituents of the brazed joints was determined using nanoindentation due to their small size (few microns). The results of samples, brazed with and without the influence of nitrogen, were compared.

1. Introduction

Brazing of stainless steel components is commonly carried out in continuous furnaces or vacuum furnaces. A significant part of these components is brazed with nickel-based fillers, which provide the highest corrosion and oxidation resistance of the resulting joints. Nickel-based brazing fillers offer a great potential for joining of stainless steels [1-3]. By alloying with the elements silicon and phosphorus, the melting temperature of the nickel or the nickel-chromium alloy is reduced and thus brazing temperatures between 1000°C and 1200°C are possible. The processing, structure and properties of the resulting brazed joints have been extensively reported [4-6]. The alloying elements provide excellent flowing and wetting properties, because they are able to eliminate the oxide film on the surfaces of the base materials. However, the alloying elements adversely affect the microstructure and the mechanical properties of the joints when the gap size exceeds 50 µm [7]. In case of continuous furnace brazing, the process is often supported by a process gas. Nitrogen (N_2) or mixtures of nitrogen and hydrogen (N_2+H_2) are commonly used as process gases. In previous work, the influence of the process parameters holding time and N_2 content in process gas on the N_2 contents of the base material and the braze metal of the joints, brazed using different brazing fillers, was investigated [8]. The brazing process in the continuous furnace was carried out using different holding times of 5 min and 10 min and different process gases, 100% N_2 and 50% N_2/50% H_2. As reference, a brazing process in the vacuum furnace was carried out using a holding time of 10 min and a free cooling. During continuous furnace brazing, a nitrogen enrichment takes place in the braze metal and in the near-surface area of the base material. It was found out that the process parameters holding time and N_2

content in process gas do not have a significant influence on the N_2 contents of base material and braze metal. The results of corrosion tests show that the arising nitrogen enrichment of the braze metal and the base material have a significant influence on the corrosion behavior of the brazed joints [8]. Due to the nitrogen enrichment, the mechanical properties of the microstructural constituents in the brazed joints may also be affected. These local properties, especially the hardness, influence the mechanical properties of the joints globally. The knowledge about the properties of the microstructural constituents allows the determination of potential points of crack initiation inside the joints. In this work, the influence of the nitrogen enrichment on the hardness of the microstructural constituents in brazed joints is investigated with regard to the process conditions. The nitrogen content in the braze metal as well as in the base material is determined using the carrier gas hot extraction technique (CGHE). The hardness of the microstructural constituents in the brazed joints is determined using nanoindentation. The results of samples, brazed with and without the influence of nitrogen, are compared.

2. Experimental procedures

Austenitic stainless steel (AISI 304) was used as base material. The components to be brazed (circular and semi-circular blanks with a diameter of 30 mm) were made of finely rolled sheets by laser cutting, which leads to burr-free and distortion-free samples. The thickness of the produced brazed joint was adjusted at 50 µm by means of inserted spacer foils. The quantity of applied filler was the same for all samples and was dimensioned, such that a joint thickness of at least 50 µm was ensured on average. The brazing filler Ni60CrPSi was applied on the base material as powder. The use of binder was avoided to eliminate carbon residues and their consequences, for example, the formation of chromium carbide in the braze metal. The brazed single lap samples, used for the analysis of the nitrogen enrichment were produced at the temperature of 1125°C in a conveyor belt furnace applying a process gas. The brazing temperature was recorded as sample temperature by a trailing thermocouple attached just below the sample surface. A content of 100% N_2 and a holding time of 10 min were used, which should lead to noticeable effects according to [8]. As reference, a brazing process in the vacuum furnace was carried out using a holding time of 10 min and a free cooling. The brazing temperature was measured by a thermocouple, attached in the base material below the brazed surface. The heating rate and cooling rate was adjusted at 50 K/min in both furnaces. The quantitative determination of the nitrogen enrichment in the braze metal as well as in the base material is possible by means of CGHE. For this purpose, sample masses of about 100 mg are required. The process principle is described by Bagel [9]. Specific areas of the overlap samples are extracted by milling using a cutter with an associated cemented carbide indexable insert. The sample preparation for the analysis of the nitrogen enrichment is schematically presented in figure 1. The surface of the base material is cut off on the upper part of the sample in a depth of 100 µm. The braze metal is cut out of the braze fillet and the wetted surface without contact to the base material. The emerging material chips are used for CGHE.

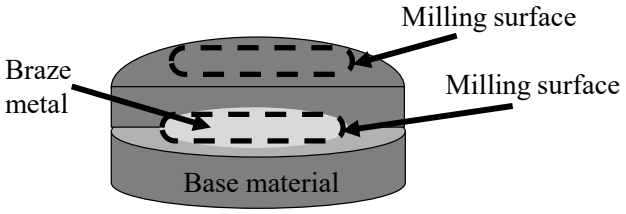


Figure 1. Scheme of sample preparation for the analysis of nitrogen enrichment

The nanoindentation experiments were carried out using a fully calibrated nanoindentator UNAT of the company Asmec GmbH equipped with a standard Berkovich indenter. The process principle is described in DIN EN ISO 14577-1 [10]. The indentation test consisted typically of three steps: loading

(10 s), holding at a maximum force of 5 mN (5 s) and unloading (4 s). The calibration for the maximum force took place on sapphire and quartz. The evaluation of the measurement results was performed using a Poisson's ratio of $\nu = 0.31$ according to the Oliver and Pharr method [11].

3. Results and discussion

3.1. Microstructure of the brazed joint

In figure 2, the microstructure of the vacuum brazed joint inside the gap is presented. The microstructure of joints, brazed in process gas, is similar. Due to the diffusion of Fe into the braze metal, Fe-enriched Ni-Cr-Si solid solutions (1) are formed at the interface to the stainless steel and inside the braze metal. Additionally, the resulting braze metal consists of Cr-enriched Ni-P intermetallics (2) and chromium phosphides (3).

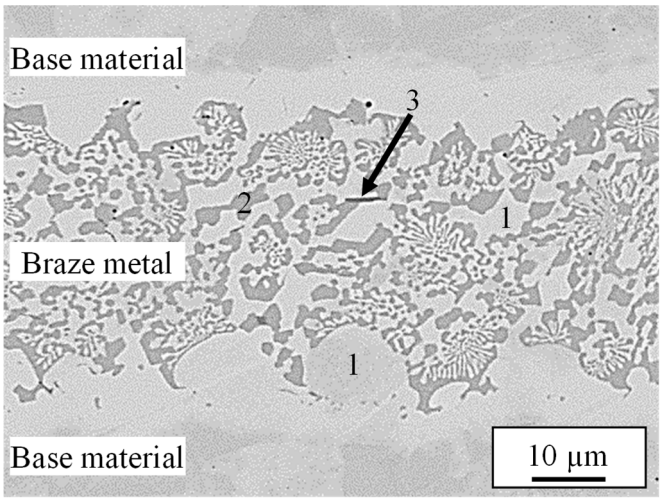


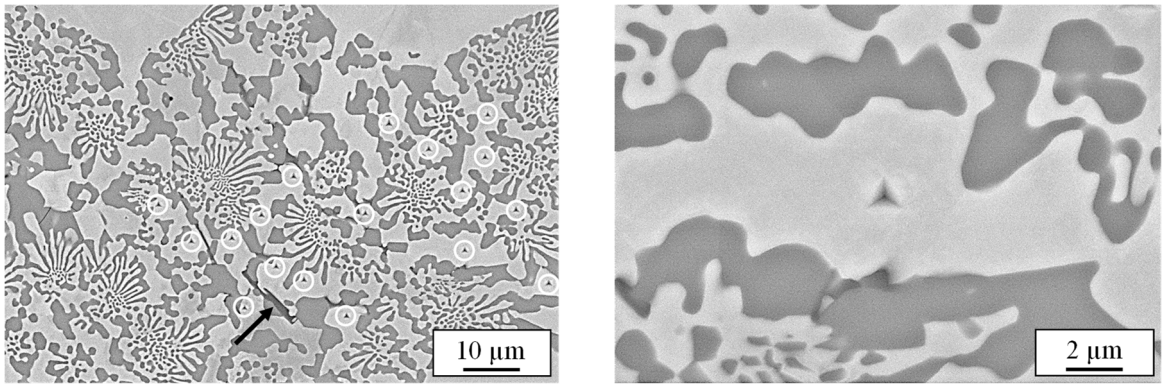
Figure 2. Microstructure of the vacuum brazed joint:
1 – Fe-enriched Ni-Cr-Si solid solution,
2 – Cr-enriched Ni-P intermetallic,
3 – chromium phosphide

3.2. Analysis of the nitrogen enrichment

In the as-delivered condition, the nitrogen contents are 0.04 wt.% in the brazing filler Ni60CrPSi and 0.07 wt.% in the base material AISI 304. As expected, these values are relatively low. The vacuum brazing process does not influence the N_2 contents of the base material and the braze metal in comparison to the as-delivered condition. After vacuum brazing, N_2 contents of 0.04 wt.% in the braze metal and 0.07 wt.% in the base material are determined. In contrast to that, samples, brazed in the continuous furnace, are strongly affected by the process gas. The N_2 content in the braze metal increases to 1.14 wt.% while the base material is enriched by N_2 to a value of 0.4 wt.%. In comparison to the as-delivered condition, the N_2 contents of the base material and the braze metal increase significantly. The enhanced diffusion of nitrogen atoms into the braze metal and the base material is caused by the high brazing temperature as it is known from nitriding processes of steels [12]. Additionally, it can be seen that the braze metal is more intensively enriched with N_2 in comparison to the base material. The difference can be explained by the fact that liquid metals can absorb a higher amount of N_2 in comparison to solid metals, which is dissolved in the braze metal after solidification.

3.3. Hardness of the microstructural constituents in the brazed joints

To investigate the influence of the arising nitrogen enrichment on the mechanical properties of the microstructural constituents in the brazed joints, nanoindentation experiments were carried out on the braze metal and the base material. In order to determine a potential influence of the measuring position within the joints, measurements were carried out on the braze gap in the center of the overlap as well as on the braze fillet. At the adjusted maximum force of 5 mN, indents of about 2 µm in size arise. Due to the small size of the chromium phosphides (less than 2 µm), the determination of their hardness is not possible with this measuring technique. For other microstructural constituents less than 5 µm in size, edge effects of the surrounding phases can occur during the nanoindentation experiments. To avoid these effects, all indents were investigated using a scanning electron microscopy (REM). Various indents in the Fe-enriched Ni-Cr-Si solid solution at different positions are shown in figure 3a. In figure 3b, an indent in the Fe-enriched Ni-Cr-Si solid solution, used for the evaluation of the measured results, is presented. Indents with a distance of less than 2 µm to the surrounding phases were ignored. This procedure was also carried out for the Cr-enriched Ni-P intermetallics. After that, at least 10 values per phase could be used for the evaluation of the measured results.



a) b)

Figure 3. REM images: a) various indents in the Fe-enriched Ni-Cr-Si solid solution; b) example of an indent, used for the evaluation of the measured results

In figure 4, the results of the nanoindentation experiments are summarized. The nitrogen enrichment does not influence the hardness of the base material significantly. It can be seen that the base materials of vacuum brazed as well as process gas brazed joints show similar hardness values of 3000 MPa on average. The hardness of the Fe-enriched Ni-Cr-Si solid solutions does not differ with regard to the measuring position in the braze gap and in the braze fillet. There is also no significant influence of the brazing process on the hardness of the Ni-Cr-Si solid solutions. The values of 4000 MPa on average are almost the same for joints brazed in vacuum and in process gas. Consequently, the nitrogen enrichment does not have an influence on the hardness of the Fe-enriched Ni-Cr-Si solid solutions. In the braze gap, the hardness values of the Cr-enriched Ni-P intermetallics are not affected by the brazing process. In all cases 14000 MPa are measured at this position. In contrast to that, the hardness of the Cr-enriched Ni-P intermetallics, measured in the braze fillet, strongly depends on the brazing process. In vacuum brazed joints an average value of 13000 MPa was determined. Their hardness in joints, brazed in process gas, increases to 18000 MPa, which corresponds to an increase of 22%. Consequently, the difference in hardness of the Cr-enriched Ni-P intermetallics, formed in the braze fillet, is caused by the nitrogen enrichment. The small differences in the hardness values of the microstructural constituents of the brazed joints can be explained by the scatter, shown as standard deviation in the diagram. Additionally, the hardness of the Cr-enriched Ni-P intermetallics is significantly higher than that of the base material and the Fe-enriched Ni-Cr-Si solid solutions.

Therefore, the crack initiation and the damage of the brazed joints during mechanical testing will preferably take place in these intermetallics.

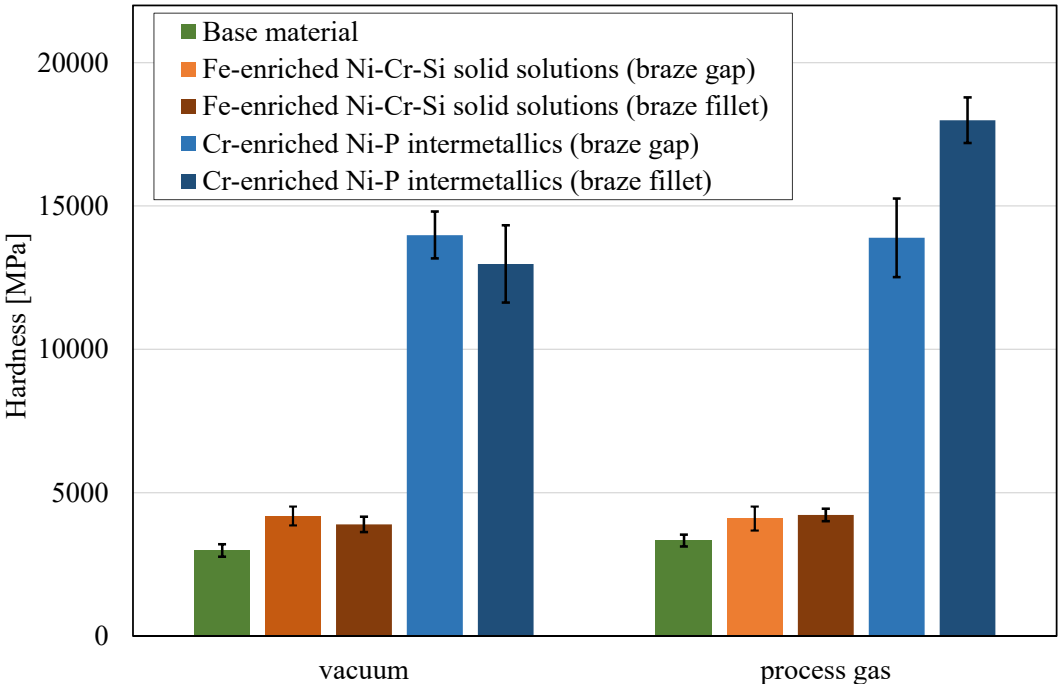


Figure 4. Hardness values of the microstructural constituents in the brazed joints

4. Conclusions

The investigated joints were produced using the brazing filler Ni60CrPSi at a temperature of 1125°C in a vacuum furnace and in a conveyor belt furnace applying nitrogen as process gas. The N_2 content in the braze metal as well as in the base material was determined by CGHE. It was determined that the braze metal is more intensively enriched with nitrogen in comparison to the base material. The influence of the nitrogen enrichment on the hardness of the microstructural constituents of the brazed joints was investigated using nanoindentation. It was found out, that the hardness of the Cr-enriched Ni-P intermetallics, measured in the braze gap as well as in the braze fillet, is significantly higher than that of all other microstructural constituents in the brazed joints. In the braze gap, the hardness of the intermetallics is 14000 MPa, while the base material and the Fe-enriched Ni-Cr-Si solid solutions show hardness values of 3000 and 4000 MPa. In the braze fillet, the hardness of the Cr-enriched Ni-P intermetallics increases to 18000 MPa, while the hardness values of the base material and the Fe-enriched Ni-Cr-Si solid solutions do not change. The high hardness of the Cr-enriched Ni-P intermetallics is caused by the nitrogen enrichment. In further investigations, these results will be correlated with the results of investigations on the fatigue behavior of the brazed joints in order to identify preferred the crack initiation areas in the brazed joints.

Acknowledgments

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