Mechanical Properties of New Ni-Mn-Based Braze Alloys for the Fast Epitaxial Braze Repair of Single-Crystalline Ni-Base Superalloys

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Abstract. Diffusion brazing is a widely-used technology for the repair of cracks in hot section turbine components, mostly fabricated from single-crystalline Ni-based superalloys. Typically, braze alloys with a composition similar to the base material, enhanced by fast diffusing melting point depressants like B are used. If single-crystalline (SX) components are repaired, an epitaxial healing can be achieved, however, the filling of wide cracks in the range of 100-300 μm is difficult, since the process is completely diffusion controlled which means that wide cracks require very long hold times. If the temperature is lowered before a complete isothermal solidification has been awaited, the poor solubility of B in Ni leads to the precipitation of borides, serving as nucleation sites for stray grains. Thus, especially for the repair of wide cracks, new Ni-Mn-based braze alloys were developed which allow a very fast epitaxial healing. As B is replaced by Mn, the repair process can be significantly shortened since the epitaxial solidification is no longer diffusion controlled but can be enforced by cooling. This is due to the fact that Ni and Mn are almost completely miscible which means that the precipitation of secondary phases during solidification is eliminated. The Ni-Mn-based braze alloys were enhanced by Al, Cr and Ti to provide a sufficient high temperature strength and an appropriate oxidation behavior. Furthermore, heat treatment cycles have been developed producing a γ / γ'-microstructure very similar to the base material. In this work, results from mechanical testing of wide-gap samples which were filled with the new braze alloys are presented and discussed.

Introduction

During the last years the use of nickel-base superalloys in aero-engines as well as in stationary gas turbines has increased as these materials allow for higher operating temperatures and, therefore, for an improved efficiency. Within the thermally and mechanically extreme stressed areas SX-components are used due to their excellent creep resistance. However, the fabrication of these components is very expensive. Thus, the repair of damaged parts is of special economical interest. Damages which usually occur during operation are plastic deformation, damages of the coating systems, oxidation and corrosion, erosion and crack formation as well as intrinsic damages such as degradation of microstructure [1-3]. For the repair of cracks diffusion bonding is a very well established technology. Mostly, B-containing braze alloys are applied as the diffusion of B as melting point depressant (MPD) within Ni is very fast. During the brazing process B diffuses into the surrounding base material which leads to an isothermal solidification and in case of SX-materials also to an epitaxial healing of the cracks [4]. However, as the whole solidification runs diffusion controlled, the epitaxial repair of wide cracks in the range of several hundred microns requires very long hold times. If the temperature is lowered before the epitaxial solidification is completed, the poor solubility of B within Ni leads to the formation of brittle secondary phases serving as nucleation sites for stray grains and therefore deteriorating mechanical properties [4, 5].

Thus, a completely different approach for the development of high-temperature braze alloys has been chosen: B as MPD has been replaced by Mn since the Ni-Mn-system provides almost a complete miscibility. This means that epitaxial solidification can be achieved by cooling and the process is no longer diffusion controlled. In earlier publications dealing with Ni-Mn-base braze alloys, gaps in the range of 300 μm could be repaired epitaxially within hold times being as short as 10 min. It was found that small amounts of Si can be added to the Ni-Mn-systems to decrease the amount of Mn [6, 7]. Furthermore, the influence of Al, Ti and Cr within the binary system has been investigated. Results from brazing experiments conducted in earlier publications, showed that a composition of Ni as base element, 20-25 wt.-percent Mn, 3-4 wt.-percent Al, 4-6 wt.-percent Ti and 5-8 wt.-percent Cr leads to optimal brazing results [8]. By the addition of a typical heat treatment consisting of 6 h solution annealing at 1140°C and 4 h precipitation hardening at 1020°C a γ / γ'-microstructure very similar to the base material could be produced within the braze gaps (Fig. 1) [9, 10].
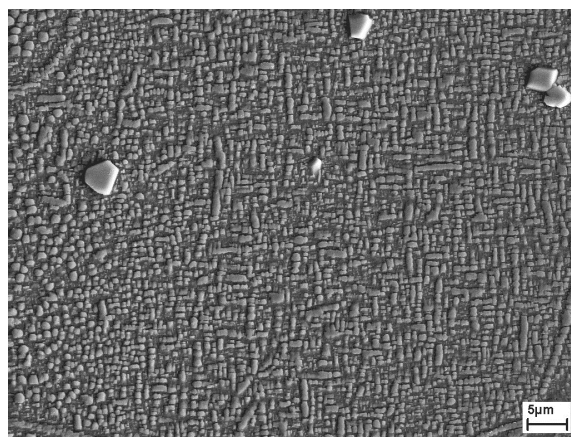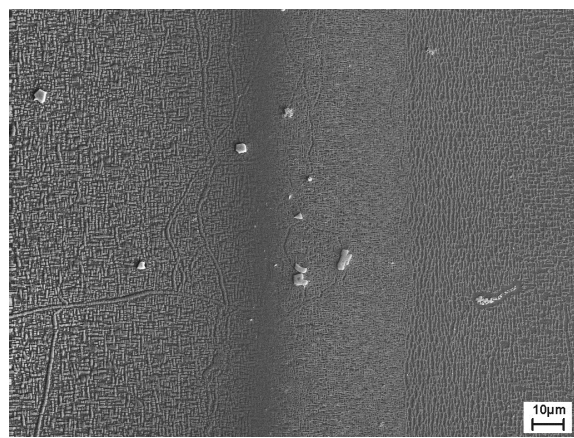

(a) Gap center   (b) bonding zone (base material on right hand side)

Fig. 1: SEM images of gaps filled with Ni-25Mn-5Cr-3Al-3Ti (in wt.-percent) after brazing at 1200 °C, 6 h solution annealing at 1140°C and 4 h precipitation hardening at 1020°C [9].
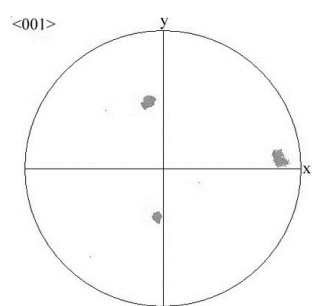
The analysis of the crystallographic orientation within the gaps by means of EBSD (*electron backscatter diffraction*) confirmed that also by use of the enhanced braze alloys very small misorientations relative to the base material are produced (Fig. 2).
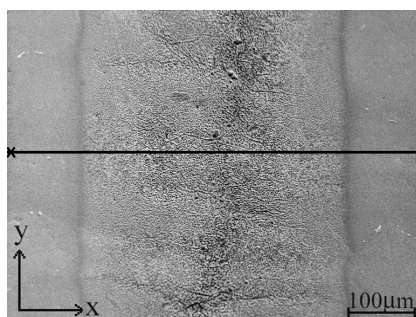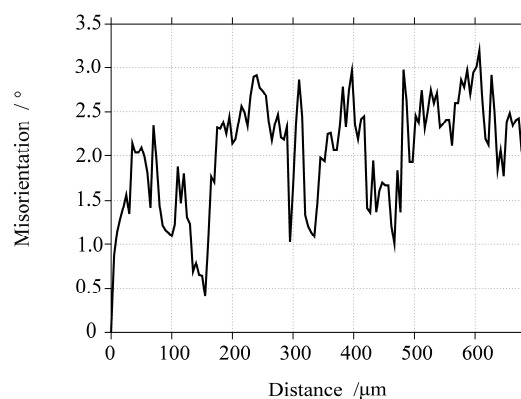
(a) SEM image   (b) Misorientation profile   (c) ⟨001⟩ pole figure

Fig. 2: Results from EBSD-analysis conducted on a gap filled with Ni-20Mn-5Cr-3Al-4Ti [9].

However, it was also found that higher amounts of Al, Ti and Cr cannot be realized as all of these elements stabilize an intermetallic phase which disturbs the epitaxial solidification. This phase could be identified as the *NiAl*-phase which is a β-phase of the B2-type [9]. Thermodynamic simulations conducted with the software *Thermo-Calc* (Fig. 3), confirmed that Al has a strongly stabilizing effect on this phase which leads to the formation of the intermetallic phase out of the liquid region in case of more than 6 wt.-% Al. The influence of Ti and Cr on the formation of the *NiAl*-phase is less pronounced, however, in combination with Al their amount also has to be restricted [9].
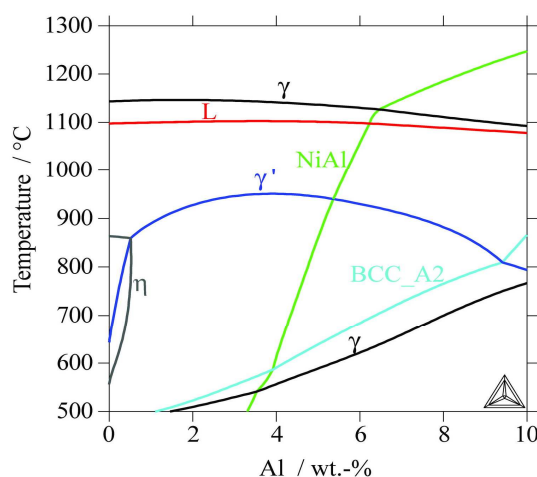

Fig. 3: Quasi-binary phase diagram of the braze alloy system Ni-25Mn-5Cr-3Ti (in wt.-percent) with varying amount of Al; calculated with *Thermo-Calc* (Version *TCS*, database *TTNi7*) [9]. Differing from conventional phase diagrams, the plotted phase boundaries mark the appearance and disappearance of thermodynamically stable phases which form as a function of temperature and Al-content. For example: The liquidus line is labeled by the precipitation of the γ-phase and the *NiAl*-phase, respectively. The solidus line is marked by the disappearance of the liquid phase (*L*).

In order to investigate the mechanical properties of the new braze alloys, tensile tests as well as LCF (*low cycle fatigue*) tests were conducted. In this work the results from tensile tests at room temperature and at 900°C are presented.

Experimental

Sample Preparation. For the mechanical testing one braze alloy with the composition Ni-25Mn-5Cr-3Al-3Ti (in wt.-percent) was selected. A small billet of this alloy was produced in a vacuum arc furnace; afterwards it was cut into thin bars which were placed on the braze gaps. Previously, the corresponding solidus and liquidus temperatures were measured by means of DSC (*differential scanning calorimetry*), applying a heating rate of 10 Kmin^{-1}.

In line with earlier experiments tensile samples were fabricated from the SX first generation Ni-base superalloy PWA 1483 (Ni-12.2Cr-9Co-1.9Mo-3.8W-3.6Al-4.1Ti-5Ta-0.07C) [9, 10]. All tensile specimens were prepared in the same way: Plates, as indicated by the dashed line in Fig. 4, were cut in with the help of a 300 μm wide cutting disc. Afterwards, the braze alloy bars were applied to the gaps and the brazing cycle was conducted under vacuum ($p < 8 \cdot 10^{-5}$ mbar). After brazing the excess braze alloy material on the top and bottom side was ground off and the heat treatment cycle was then applied. Finally, the geometry of the tensile samples was produced by wire eroding. This relatively complex sample preparation was chosen to provide an optimal filling of the central area of the plates and thus the cross-section of the tensile samples. The whole brazing cycle as well as the subsequent heat treatment are depicted and described in [9, 10].
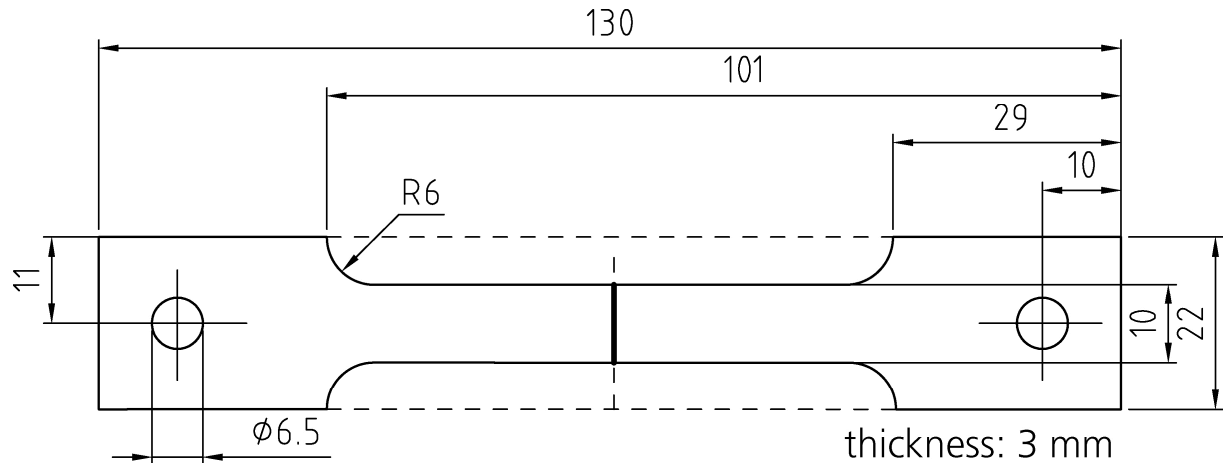
Fig. 4: Geometry of brazed tensile sample fabricated from PWA 1483; dashed lines indicate the geometry of the original plates, the thick line marks the gap of the finished sample (depth of cuts: 20 mm, gap width: 300 μm) [9].

Tensile tests at room temperature. For the tensile tests conducted at room temperature an electro-mechanic testing machine from *Zwick GmbH & Co. KG* was used. During the test the strain was recorded by an extensometer with a gauge length of 15 mm.

Tab. 1: Results from tensile tests conducted with 5 brazed samples at room temperature compared to SX base material: Tensile strength R_m, yield strength $R_{p0.2}$, young's modulus E and elongation at fracture A. For the young's modulus the data for SX Ni-base alloys in [001]-direction is listed; the elongation at fracture is given for PWA 1480 (Ni-10Cr-5Co-4W-12Ta-5Al-1,5Ti) [11].

	R_m [MPa]	$R_{p0.2}$ [MPa]	E [GPa]	A [%]
Brazed samples	849 ± 125	700	137.5 ± 2.1	1.95 ± 2.1
Base material	1100 (PWA 1483)	1000 (PWA 1483)	128.0 (SX [001])	4.0

Tensile tests at 900°C. The high-temperature tensile tests were conducted with a servo-hydraulic testing machine from *Schenck* which is equipped with a radiation furnace. During the test the samples were extended with a rate of 0.93 mm/min while the strain, the temperature, the force and the displacement were recorded. For the strain measurement a high-temperature extensometer (*Maytec GmbH*) with 15 mm gauge length was used.

Tab. 2: Results from tensile tests conducted with 3 brazed samples at 900°C compared to SX base material: Tensile strength R_m, yield strength $R_{p0.2}$, young's modulus E and elongation at fracture A. For the young's modulus the data for SX Ni-base alloys in [001]-direction at 870°C is listed; the elongation at fracture is given for PWA 1480 (Ni-10Cr-5Co-4W-12Ta-5Al-1,5Ti) at 870°C [11].

	R_m [MPa]	$R_{p0.2}$ [MPa]	E [GPa]	A [%]
Brazed samples	510 ± 10	422 ± 67	68.7 ± 8.5	0.9 ± 0.02
Base material	800 (PWA 1483)	500 (PWA 1483)	93.0 (SX [001])	12.0 (PWA 1480)

Discussion

The comparison of the mechanical data of the brazed samples compared with the base material shows that a relatively low strength in combination with a large data scattering is at hand. While at room temperature the tensile strength of the brazed samples reached 77 % of the base material's strength; at 900°C only 64 % were measured. Thus, the fracture surface of all samples was analyzed by means of SEM. It was found that within some samples a very high amount of freely solidified surface is at hand which correlates with the strength as the effective cross-section is reduced. These porous areas are caused by shrinkage holes which form during solidification (Fig. 5). Another problem occurring during the preparation was a bending of the samples which was observed after the brazing process. Even the use of weights on each side of the tensile samples could not prevent a bending of several degrees. Obviously, the CTEs (*coefficient of thermal expansion*) of the base material and the braze alloy are very different. At the same time the braze alloys provide a very good surface wetting. As for the first testing the samples were used in the bended condition, a bending stress superposed to the tensile stress could not be prevented.
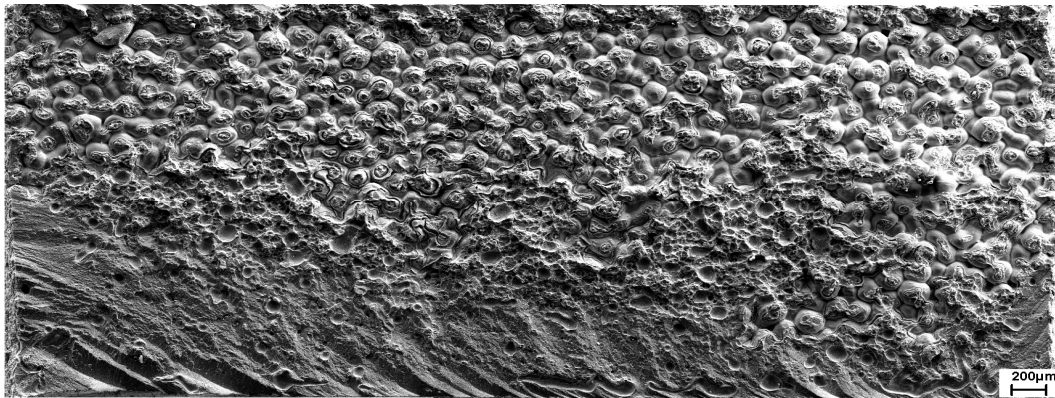

Fig. 5: Fracture surface of a sample tested at 900°C with large shrinkage holes on the top side [10].

In order to measure the intrinsic strength of the brazed samples an appropriate filling of the gaps is very important. A well-known technology which is used to improve the filling is the hot isostatic pressing (*HIP*, also *hipping*). The influence of *hipping* on the strength of brazed samples was investigated by Miglietti and Du Toit [12, 13]. In this work braze alloys with Hf and Zr as MPDs are applied to wide gap samples, fabricated from IN 738 with a gap width of 1.5 mm. Results from tensile tests, LCF- and creep rupture tests at different temperatures are described; the samples were tested in different conditions. Specimens which were tested directly after brazing for 4 h at 1230°C, reached 43 % of the base material's strength, however, after 12 h brazing at 1238 °C, 4 h solution annealing at 1232°C and 4 h *hipping* at 1080°C the tensile strength reached 94 % of the base material's. As the *hipping* has a significant influence on the strength and also on the ductility, it is expected that the strength of the Ni-Mn-base braze alloys can also be increased by the addition of a *hipping* cycle.

Another aspect which influences the high temperature strength at higher temperatures is the stability of the γ'-phase. SEM-analyses that were conducted on the tensile samples after testing at 900°C, showed that the amount of γ' within the braze gap is still comparable to that within the base material. However, it was also found that Mn as MPD has a γ'-destabilizing effect [9]. Thus, the strength could be increased by increasing the γ'-solvus temperature. In principle, this can be achieved by the addition of higher amounts of Al and Ti, however, as already mentioned, this leads to the formation of the *NiAl*-phase which can disturb the epitaxial solidification. Alternatively, Co could be added as it decreases the solubility of Al and Ti within the γ-matrix and, therefore, stabilizes γ'. First *Thermo-Calc*-simulations showed that the epitaxial solidification is not disturbed if 10 wt.-percent Co are added to the system Ni-25Mn-5Cr-3Al-3Ti [9].

Another important aspect which has to be investigated is the stability of the γ/ γ'-morphology in the Ni-Mn-based systems. It was found that Mn is predominantly dissolved within the γ-phase and increases the γ-lattice parameter [9, 14]. To minimize the γ/ γ'-misfit this effect has to be compensated by higher amounts of elements increasing the lattice parameter of the γ'-lattice.

Conclusions

New Ni-Mn-based braze alloys have been developed for the epitaxial repair of wide cracks in SX Ni-base superalloys. Experiments presented in earlier publications, show that these alloys allow for a very fast epitaxial healing. Furthermore, the epitaxial solidification is not disturbed by elements such as Al, Cr and Ti. By the addition of a heat treatment as it is typically conducted on Ni-base superalloys, a microstructure very similar to the base material could be produced. The results from first mechanical testing show that shrinkage holes within the braze gaps occurring during solidification, form a seriously mechanical problem. Moreover, the bending of the samples during the brazing process has to be avoided by use of smaller specimens. It is expected that the mechanical data can be significantly improved if *hipped* samples are used. Further aspects which have to be considered in order to improve the high-temperature strength of the new braze alloys, are the stability of the γ'-phase as well as the γ/ γ'-morphology. Generally, it is expected that the strength of the new braze alloys is comparable to Ni-base superalloys. Thus, after a validation by further mechanical testing such as LCF and creep-rupture, the Ni-Mn-based braze alloys could offer new possibilities for the epitaxial repair of wide cracks in SX-components.

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