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Phase Transformations in the Brazing Joint during Transient Liquid Phase Bonding of a γ -TiAl Alloy Studied with *In Situ* High-Energy X-Ray Diffraction

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Abstract. TiAl alloys are increasingly used as a lightweight material, for example in aero engines, which also leads to the requirement for suitable repair techniques. Transient liquid phase bonding is a promising method for the closure of cracks (in non-critical or non-highly loaded areas). The brazing solder Ti-24Ni was investigated for brazing the alloy Ti-45Al-5Nb-0.2B-0.2C (in at. %). After brazing, the joint exhibits different microstructures and phase compositions.

The transient liquid phase bonding process was investigated in the middle of the joint region *in situ* to acquire time resolved information of the phases, their development, and thus the brazing process.

These investigations were performed using high-energy X-ray diffraction at the “High-Energy Materials Science” beamline HEMS, located at the synchrotron radiation facility PETRA III at DESY in Hamburg, Germany. For this, we used an induction furnace, which is briefly described here.

During the analysis of the diffraction data with Rietveld refinement, the amount of liquid was refined with Gaussian peaks and thus could be quantified. Furthermore, while brazing four different phases occurred in the middle of the joint region over time. Additionally, the degree of ordering of the β_0 phase was determined with two ideal stoichiometric phases (completely ordered and disordered). Altogether, the phase composition changed clearly over the first six hours of the brazing process.

Introduction

TiAl alloys are recently introduced as high temperature lightweight materials [1] as for example as low-pressure turbine blades in aero engines. This leads to a demand for suitable repair techniques for the closure of cracks (in noncritical or not highly loaded areas) for these materials to extend the service life of the components. For this purpose, transient liquid phase bonding [2] is a promising method as it is already employed for Ni-base superalloys [3]. The process is performed at a constant temperature, which is chosen above the melting point of the brazing solder but below the melting point of the substrate material and does not change the microstructure of the substrate significantly [2]. The brazing solder contains a melting point depressing element, which is in our case Ni [4]. The solidification of the joint region takes place isothermally due to diffusion of the melting point depressing element into the substrate and of alloying elements from the substrate into the joint region. The homogenization process continues further on while holding the brazing temperature.

The whole brazing process was investigated *in situ* with high-energy X-ray diffraction (HEXRD). The diffraction patterns were analyzed with Rietveld refinement. This leads to knowledge about phase formations and development of phase fractions time resolved in the joint region. Additionally, information about the amount of liquid could be received. This results in a better understanding of the whole brazing process.

Experimental

A TiAl alloy with the composition Ti-45Al-5Nb-0.2B-0.2C (in at. %) was used as substrate in hot extruded condition. The substrate was eroded in form of cylinders. Furthermore, the eutectic composition Ti-24Ni was chosen as brazing solder (melting point 942 °C) [5]. It was produced by arc melting, cut, and subsequently ground down to a thickness of 300 μm [4]. The single parts were stacked on top of each other, as shown in fig. 1a with the relevant dimensions. The surfaces of the stacked parts were ground with 240 SiC paper resulting in some remaining surface roughness, thus the stacked specimens did not slip while being rotated during the *in situ* measurements.

The transient liquid phase bonding was executed at 1110 °C.

For the *in situ* HEXRD measurements, we used a furnace with an induction-heating unit produced by the company iew Induktive Erwärmungsanlagen GmbH, Gumpoldskirchen, Austria with a power of 3 kW. The furnace chamber is equipped with two Kapton windows for the synchrotron radiation. It is possible to operate under Argon atmosphere or in vacuum with a pressure of about 10^{-6} mbar. The brazing experiments were performed under Argon 6.0 atmosphere after flushing two times. We used a two-color pyrometer from the company Sensortherm GmbH, Sulzbach/Ts., Germany with the appropriate controlling software for the temperature measurement. Because this temperature measurement works contactless, it was possible to rotate the specimens continuously during the measurement, which would not be feasible with a spot welded thermocouple. In principle, a temperature measurement with thermocouples would also be possible with this furnace. Furthermore, different water-cooled induction coils are available for different sample geometries and heating rates. The specimen is mounted on a ceramic tube on the rotation axis of a rotary feedthrough. The set-up in the furnace chamber is shown in fig. 1b in the viewing direction against the direction of the incoming X-ray beam.

The HEXRD measurements were conducted at the “High-Energy Materials Science Beamline” HEMS P07, located at the synchrotron radiation facility PETRA III at DESY, Hamburg, Germany and operated by HZG [6]. We used an energy of 100 keV, which corresponds to a wavelength of 0.124 Å. The set-up at the beamline is shown in fig. 1c. The induction furnace was mounted on a hexapod, which moved the whole furnace and made it possible to scan over the joint region. While brazing, we scanned in several steps over the joint region with a beam, which was 400 μm in width and only 25 μm in height for a better resolution of the different layers of the joint region. For the sake of brevity, only results from one position in the middle of the joint region over time are discussed. Furthermore, we continuously rotated the specimen for a better grain statistic with a rotation speed of about 5 s per rotation. For the data recording, we used a Perkin Elmer XRD 1621 flat panel detector, and summed 12 pictures for reduction of the background, each with an exposure time of 0.2 s. This results in about 2.5 s integral measurement time per diffraction pattern, which corresponds to half a rotation of the specimen. Thus, almost all grains came in diffracting condition for one diffraction pattern. Afterwards, the diffraction patterns were analyzed with the program fit2d [7] and the Rietveld refinement program MAUD [8]. For this purpose, we used the ideal stoichiometric composition of the phases, see tab. 1.

For the refinement, we started with the diffractogram after 0:50 h as the diffuse background is rather high (and thus easy to fit) and three phases are detectable (β , α , and α_2). The results of this refinement were used as starting parameters for the evaluation of the next diffractogram forward in time. The subsequent diffractograms were automatically processed always using the parameters from the diffractogram before until no liquid phase could be detected anymore. For the period with no liquid, we started with the last diffractogram. There, we proceeded stepwise as before but now backwards in time. Also the evaluation of the period between measurement of the first diffractogram and the one at 0:50 h was done by starting with the evaluation of the diffractogram after 0:50 h and then going backwards in time. Thus, the refinement was stabilized better as the diffuse background and the fractions of the phases with small amounts decreased or stayed constant over the automatic refinement of the single diffractograms. During this procedure, we refined the background parameters, the phase fractions, the cell parameters, and the crystallite sizes of the phases.

The amount of liquid in the beginning of the brazing process in the middle of the joint region was fitted with normalized Gaussian peaks in the Rietveld refinement. For the first main diffuse reflex, we used two Gaussian peaks due to the asymmetry. The summed integrated intensity of both Gaussian peaks was used to calculate the amount of liquid with a linear correlation. Therefore, we assumed the amount of liquid to be 98 vol. % in the beginning of the brazing process and that it is finally solidified after 2:40 h.

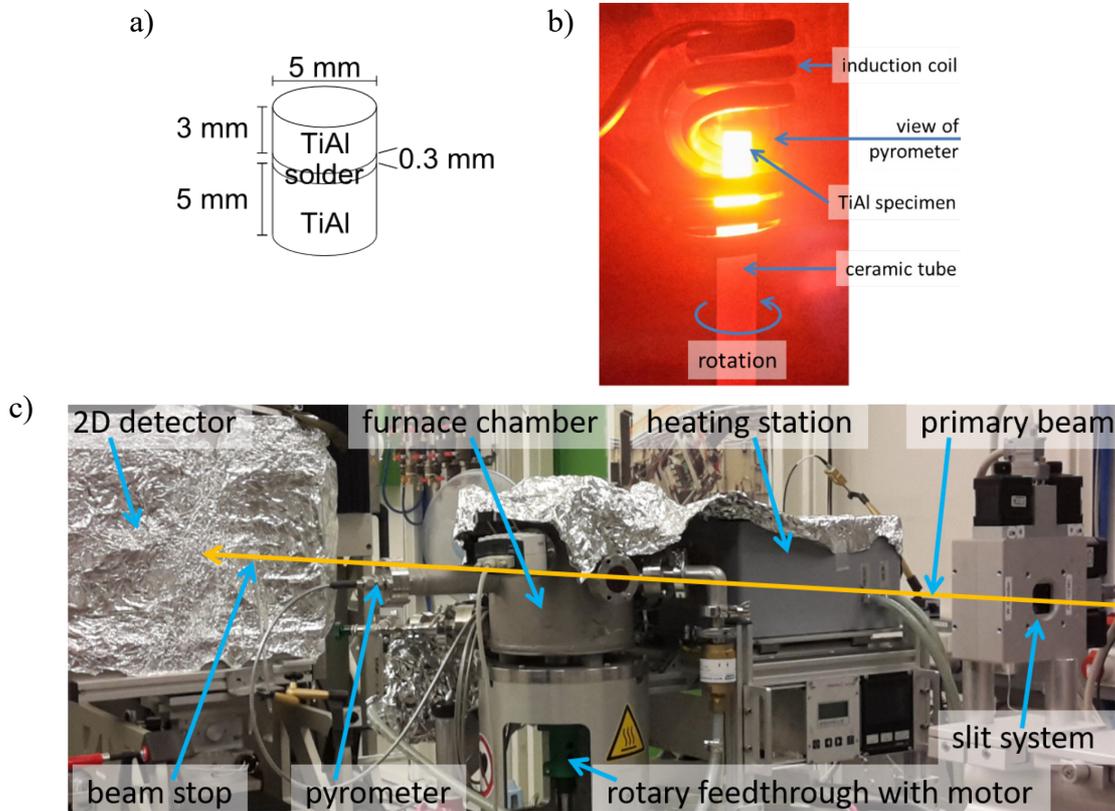


Fig. 1: The experimental set up: a) scheme of the stacked specimen with its dimensions, b) set-up in the furnace chamber with the heated specimen in the viewing direction against the direction of the incoming X-ray beam, c) set-up at the beamline.

Tab. 1: Crystallographic data of the phases.

Phase	Space Group, No.	Pearson Symbol	<i>Strukturbericht</i> Designation	reference
γ -TiAl	P4/mmm, #123	tP4	L1 ₀	[1]
α_2 -Ti ₃ Al	P6 ₃ /mmc, #194	hP8	DO ₁₉	[1]
TiB	Pnma, #62	oP8	B27	[1]
Ti ₂ Ni	Fd-3m, #227	cF96	---	[5]
α -Ti	P6 ₃ /mmc, #194	hP2	A3	[5]
τ_3 -Al ₃ NiTi ₂	P6 ₃ /mmc, #194	hP12	C14	[9]

Results and Discussion

The substrate material consists of about 80 vol. % γ -TiAl, about 20 vol. % α_2 -Ti₃Al, and less than 1 vol. % TiB phase at room temperature. Furthermore, the initial phase composition of the brazing solder was determined to be about 70 vol. % Ti₂Ni and 30 vol. % α -Ti at room temperature. Fig. 2 shows X-ray diffractograms out of the middle of the joint region after 0:50 h, 2:50 h, and 6:40 h at brazing temperature. In addition, the difference curves between the fit and the measurement are shown below the single diffractograms. They show that the Rietveld refinements fit well, even with the diffuse scattering signal of the liquid and the stoichiometric composition of the phases.

Fig. 2a, after 0:50 h of brazing, shows a high diffuse scattering peak in the region of $2\theta=3.1^\circ$ belonging to the high amount of liquid. As described before, we used two normalized Gaussian peaks below the first diffuse peak and one below the second, which are also shown in fig. 2a. Additionally, small peaks of the phases β , α , and α_2 were detected. α and α_2 are both present but exhibit different lattice parameters visible from the different positions of the fundamental reflections. After 2:50 h of brazing, the diffuse scattering peak has clearly decreased, fig. 2b, but the same phases are still visible as after 0:50 h of brazing. Subsequently, after 6:40 h, additional phases occurred, fig. 2c. An ordering reflex of the β phase occurred at $2\theta=2.2^\circ$. The ordering takes place only partly as the ordering reflex is too small for the whole amount of β phase. We used simultaneously two ideal β/β_0 structures with the same lattice parameter, one completely disordered (β -bcc) and the other with an ideally ordered B2 crystal structure (β_0 -B2). Hence, we can determine the degree of ordering of the β_0 phase with the weighted amounts of the two ideal phases. This leads us to the degree of ordering of the β_0 phase of 15 % in fig. 2c. In addition, the ternary τ_3 -Al₃NiTi₂ [9] phase was identified, and marked in fig. 2c. Beside that, an oxide peak is visible, but could be neglected for the Rietveld refinement.

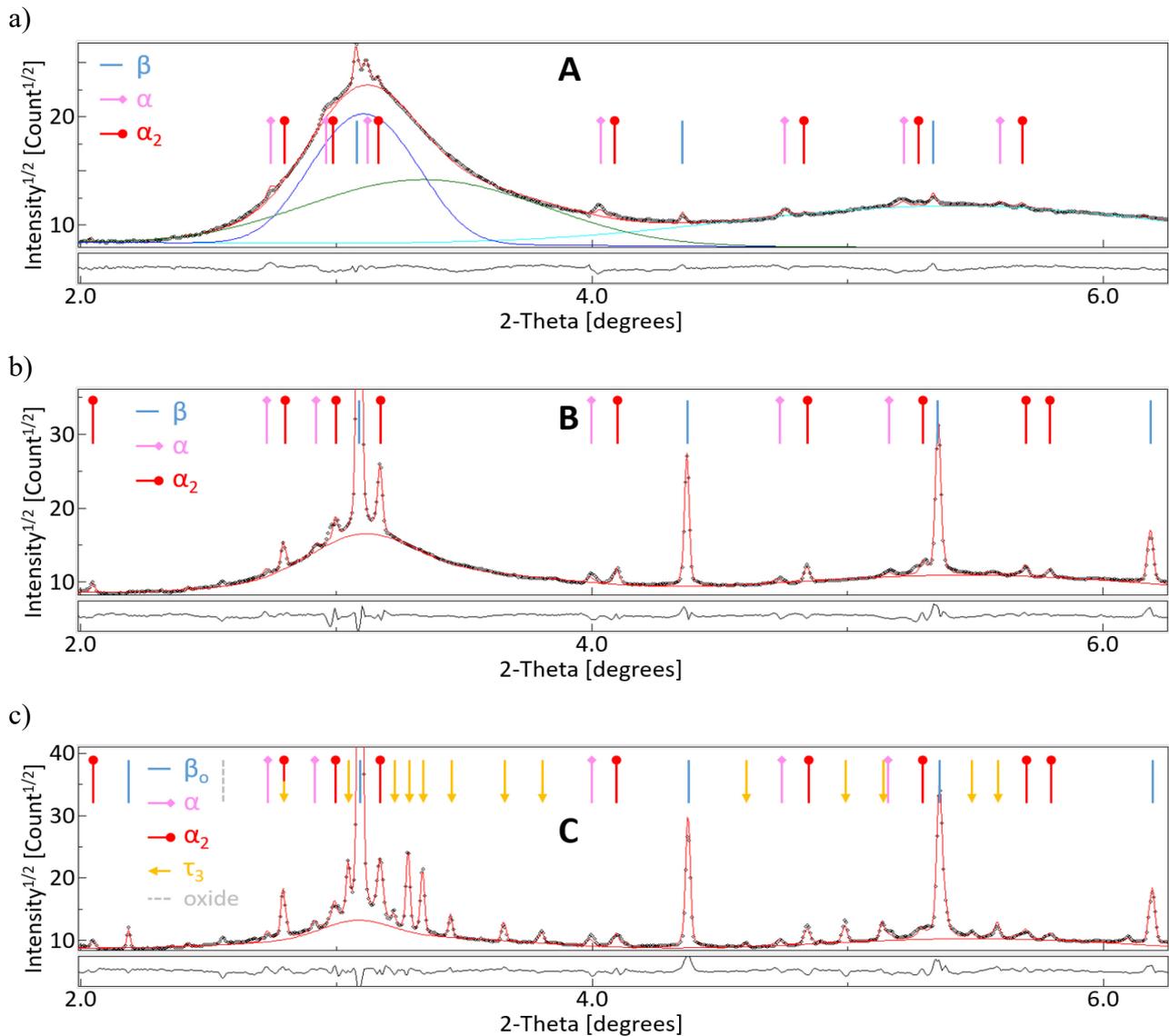


Fig. 2: X-ray diffractograms out of the middle of the joint region, a) after 0:50 h, b) after 2:50 h, and c) after 6:40 h at brazing temperature. The black dots show the measurements and the red lines show the fits with additional background. Fig. 2a additionally shows the Gaussian peaks for the diffuse peaks of the liquid. The time of the single diffractograms during the brazing process is marked in fig. 3.

Fig. 3 shows the development of the volume fraction of the liquid and the crystalline phases over time at one fixed position in the middle of the joint region. The results of the Rietveld refinement (fig. 3a) are plotted next to the stacked diffractograms (fig. 3b). The Rietveld refinement revealed that small amounts of β and α phase exist from the beginning next to the high amount of liquid. The amount of α stays constant at 5 at. % after 0:30 h at brazing temperature for the whole remaining brazing time. After about 0:45 h at the brazing temperature, the α_2 phase occurred. The split of the α peak into peaks of α and α_2 phase with different lattice parameters is visible in fig. 3b at $2\theta=4.1^\circ$. Furthermore, the amount of liquid clearly decreases after about 1 h at brazing temperature and, at the same time, the amount of β clearly increased. Finally, all liquid seemed to be solidified after 2:40 h, but there is still a small diffuse background visible. This could either be attributed to an increased amount of lattice defects during the intensive formation and transformation of new phases or (unlikely from our point of view) to a small amount of remaining melt. Subsequently, the amount of β decreased and the amount of α_2 increased slowly to 78 vol. % and 17 vol. %, respectively. After about 3:45 h at brazing temperature, an ordering peak of the β phase is visible. The degree of ordering increased for about 45 min to 15 %. In the meantime, the amount of β/β_0 phase remains constant. Furthermore, after about 4:30 h, the τ_3 phase occurred and the low diffuse background finally decreased. In the meantime, the amounts of β_0 and α_2 phase decreased. After the initial six hours of brazing where significant changes in the phase composition took place, it remains almost constant for the next 10 h at 67 vol. % β_0 (with a degree of ordering of 15 %), 5 vol. % α , 10 vol. % α_2 , and 18 vol. % τ_3 . Finally, the evolution of the phases in the middle of the joint region over time is identified: $L+\beta+\alpha \Rightarrow L+\beta+\alpha+\alpha_2 \Rightarrow \beta+\alpha+\alpha_2 \Rightarrow \beta_0+\alpha+\alpha_2 \Rightarrow \beta_0+\alpha+\alpha_2+\tau_3$.

Furthermore, the Gibb's phase rule implies that four different elements are necessary for four phases in the solid state. Under the assumption that an equilibrium phase constitution was already achieved in the middle of the joint region, the Gibb's phase rule can be fulfilled due to diffusion of Nb from the substrate to the middle of the joint region acting together with the elements Al, Ni, and Ti.

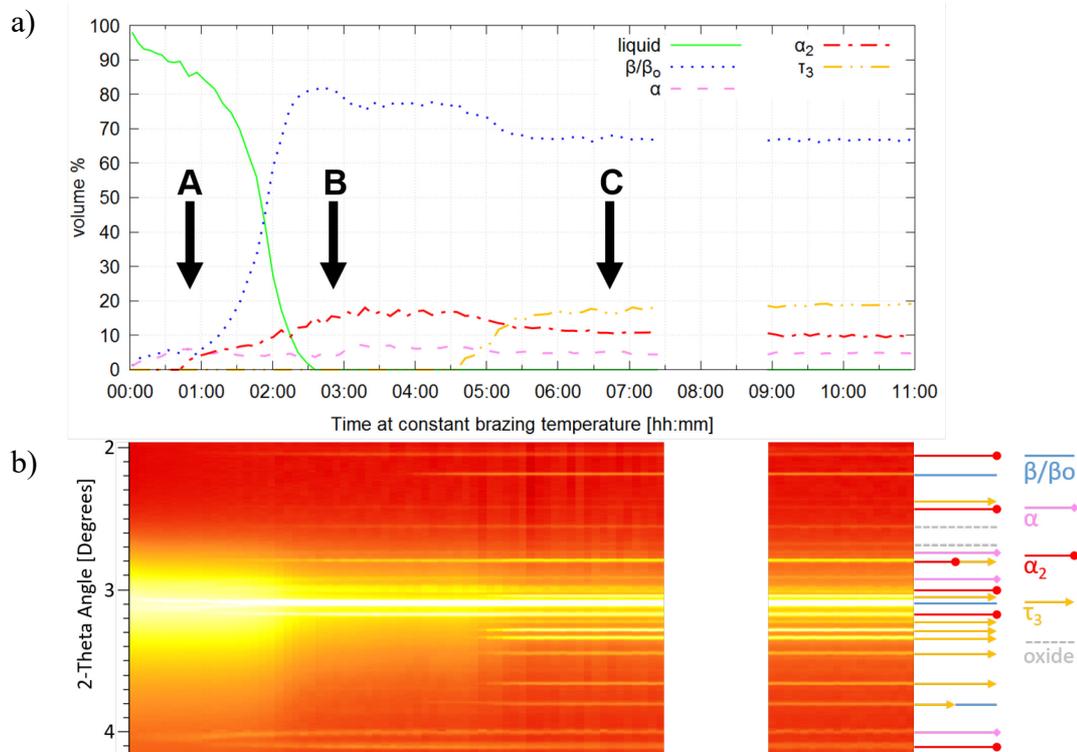


Fig. 3: Development of the single phases over time in one position in the middle of the joint region. In a) the amounts of the phases are shown and the times of the three diffractograms from fig. 2 are marked. In b) the single diffractograms are stacked next to each other and show the development of the diffuse background and the peaks belonging to the solid phases (The color scale for the intensity is a logarithmic scale.). The gap between 7:30 h and 9:00 h was caused by a beam loss.

Summary

We studied the transient liquid phase bonding process of a γ -TiAl alloy with a Ni-containing brazing solder with *in situ* high-energy X-ray diffraction. The diffraction data were analyzed with Rietveld refinement resulting in time resolved information about the phase formation in the middle of the joint region. The amount of liquid was successfully analyzed with normalized Gaussian peaks. Furthermore, the degree of ordering of the β_0 phase was determined with two phases with ideal stoichiometry (one disordered and one ideally ordered) with the same lattice parameters.

Already from the beginning of the brazing process, not only liquid, but also small amounts of β and α exist in the joint region. Furthermore, the liquid phase is fully solidified after 2:40 h at brazing temperature. The β phase started to order after 3:45 h resulting in a degree of ordering of 15 %. A small remaining diffuse background attributed to an increased amount of lattice defects was detected up to the point when the τ_3 phase formed after about 4:30 h. Altogether, the phase composition changed clearly until 6 h at brazing temperature and then remained relatively constant. This means, the process time has definitely to be longer than 6 h.

Acknowledgments

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