Impacts of layout, surface condition and alloying elements on diffusion welding of micro process devices

Einfluss von Layout, Oberflächenzustand und Legierungselementen auf das Diffusionsschweißen mikroverfahrenstechnischer Apparate

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The formation of a monolithic part during diffusion bonding is accompanied by the diffusion of atoms across the bonding planes. At sufficient low roughness, it mainly depends on the temperature and dwell time. At the same time, the diffusion process competes against grain growth. By adjusting an appropriate level of bearing pressure, it is possible to control deformation taking into account additional parameters resulting from mechanical microstructures and the design and aspect ratio of the part. Furthermore, material properties, such as the content of alloying elements, the degree of cold work hardening and the grain size, have an impact on diffusion and deformation behavior. Also the surface condition of mating surfaces is important to diffusion kinetics and the quality of the joint. Especially passivation layers of corrosion-resistant alloys, such as stainless steels and nickel-based alloys, impair diffusion. In contrast to this, cold work hardening at low depth below the surface, e.g. by means of a blasting processes, may facilitate formation of a good bond and help to limit grain size. For oxide dispersion-strengthened materials, additional impacts on diffusion bonding behavior applies.

Keywords: Surface condition / passivation layer / diffusion bonding / diffusion welding / corrosion-resistant materials

Die Bildung monolithischer Teile während des Diffusionsschweißens wird durch Diffusion von Atomen über die Fügeebenen erreicht. Bei hinreichend geringer Rauheit sind die Hauptparameter Fügetemperatur und Fügedauer. Zugleich konkurriert der Diffusionsprozess bei hohen Temperaturen mit Kornwachstum. Durch Optimierung der Flächenpressung ist es möglich, die Verformung beim Diffusionsschweißen zu kontrollieren. Hierzu müssen aber weitere Faktoren wie mechanische Mikrostrukturen sowie Design und Aspektverhältnis der Bauteile berücksichtigt werden. Zudem haben Werkstoffeigenschaften wie der Gehalt an Legierungselementen, der Grad der Kaltverfestigung und die Korngröße Einfluss auf Diffusion und Verformungsverhalten. Auch der Oberflächenzustand der zu fügenden Oberflächen beeinflusst die Diffusionskinetik und Qualität der Verbindung.

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Besonders Passivschichten korrosionsbeständiger Werkstoffe wie bei rostfreien Stählen und Nickelbasislegierungen beeinträchtigten die Diffusion. Im Gegensatz dazu begünstigt eine Kaltverfestigung oberflächennaher Bereiche, z. B. durch eine Strahlbehandlung, die Bildung einer guten Verbindung und hilft, das Kornwachstum zu begrenzen. Für Oxid-dispersionsverfestigte-Werkstoffe kommen weitere Einflussfaktoren hinzu.

Schlüsselwörter: Oberflächenzustand / Passivschichten / Diffusionsschweißen / korrosionsbeständige Legierungen

1 Introduction

Diffusion bonding is a special welding technique for full cross-sectional joining, also of internal surfaces. It is expensive, as a high vacuum is needed and an external force has to be applied to the parts to be joined. Diffusion bonding results in the forming of monolithic parts with mechanical properties similar to those of semi-finished products subjected to comparable heat treatment. In contrast to soldering techniques, mechanical properties are better and no different phases exist, which promote e. g. intergranular corrosion.

Diffusion bonding is mainly used for special applications. For small parts, fixed costs can be reduced by processing multiple parts at once. For diffusion bonding of multiple parts, it is distinguished between welding of multiple parts in one layer, welding in a stacked arrangement, or a combination of both. The goal always is to reduce the high fixed costs to a reasonable value per part. However, the tolerances of each single part or of each layer must be considered when evaluating feasibility. The equipment, setup, size, and arrangement of parts have an impact on thermal expansion and tolerances. Multiple anti-adhesion layers made by manual spraying of boron nitride or alumina powders are used to prevent sticking of separation layers. The uniformity of the separation layers determine the achievable planarity.

Process temperatures range from 70 % to 90 % of the starting temperature of melting of the materials to be diffusion-bonded, calculated in Kelvin. Finally, there is no heat-affected zone, since the complete part is subjected to high temperatures for a long time. Any cold work hardening effects disappear. By diffusion of atoms across the fusion zone, monolithic parts are obtained. Due to the high temperatures the parts are subjected to, grain growth takes place. This is a problem especially in materials exhibiting no polymorphic transformation with temperature. This is an issue for stabilized ferritic or austenitic stainless steels or nickel-based alloys, whereas martensitic stainless steels with ferritic-austenitic transformation can be diffusion-bonded easily and exhibit a fine-grained microstructure.

The same holds for titanium alloys: Ideally, original sheets cannot be recognized after diffusion bonding. Contrary to stabilized steels and nickel-based alloys, however, the passivation layer of titanium is soluble in the matrix material and does not impair diffusion of atoms across the bonding plane.

For the diffusion bonding process, it has to be kept in mind that the cooling rate is rather low. It depends on the size and thermal mass of the equipment and parts to be welded. Quenching using inert gas circulation in a cooling cycle may increase the cooling rate. Due to its high heat conductivity, use of helium is preferred to argon. For some materials tending to sensitization, i. e. the formation of grain boundary precipitations, such as nickel-based alloys, intercrystalline corrosion may be relevant to diffusion-bonded parts.

For most applications of diffusion bonding, e. g. manufacturing of mold tools, control of the degree of deformation is not critical, since finishing is performed afterwards.

For micro process devices containing mechanical microstructures in the range of the materials microstructure, however, it is very difficult to control the deformation during the diffusion bonding process. Strong deformation may affect functionality. Deformation significantly depends on geometric conditions. Grain boundary sliding may occur depending on the width of bars. Parameters, such as the bonding temperature, bonding time, and bearing pressure cannot be transferred easily to other parts of the same material. The aspect ratio of micro process devices as well as friction occurring between ridged dies and the part will affect deformation, too. Special design rules have to be met.

For multilayered stacks, the varying surface roughnesses must be leveled. Hence, a value of deformation necessary to achieve vacuum tightness cannot be specified.

2 Aim of the paper

The main process parameters for diffusion bonding, such as bonding temperature, bonding time, and bearing pressure, are widely known in the community of diffusion welders. For special applications, however, there are many other impacts on the result of diffusion bonding. In the paper, materials science concerns applying to special sorts of materials, e. g. different classes of stainless steels, nickel-based alloy, titanium, and oxide dispersion-strengthened (ODS) materials will be described, discussed, and evaluated. Also the delivery state in terms of passivation layer thickness and degree of cold work hardening has a strong impact on the diffusion bonding process and the resulting material's microstructure. Surface layers may behave differently for different alloys. Alloying elements influence the diffusion coefficient and may alter the temperature of lattice transition or even suppress the transition completely, causing severe differences in diffusion behavior and impacts on the material's microstructure.

For special applications, such as for micro process devices possessing mechanical microstructures in the range of the material's microstructure, the deformation behavior during diffusion bonding varies considerably. Compared to macroscopic parts, different deformation mechanisms, such as grain boundary sliding, may appear.

Parts used for micro process engineering often consist of multiple microstructured thin-sheet materials. Here, it is not possible to consider design rules applicable to large parts consisting of a few layers only to control the degree of deformation. Microstructured diffusion bonded parts usually cannot be machined to final dimensions afterwards, but the deformation must be limited without affecting internal mechanical microstructures, e. g. in terms of pressure loss.

The manufacturing tolerance of thickness for thin sheet material ranges between 20 μm to 50 μm, depending on thickness and rolling width of the semi-finished products. For stacks consisting of a few dozens or even hundreds of layer, tolerances may be added up or balanced without reasonable possibility for restriction. Multiple surface roughnesses must be levelled to bring the cross section into atomic contact for enabling diffusion. Doing so, it becomes clear that the percentages of deformation will be larger than for parts consisting of two or three layers only. Particular experience is required to control the deformation during diffusion bonding such that vacuum tightness is achieved, and it is not possible to specify a general percentage deformation applicable to all different designs for that.

3 Factors affecting deformation during diffusion bonding

For demanding injection molding applications, the injection molding tool has to be heated such that the polymer can fill tiny details completely. Before ejecting the polymer part, the whole molding tool has to be cooled down far below glass transition temperature of the polymer. Hence, one common application of diffusion bonding is the realization of cooling channels near the mold cavity, which cannot be accomplished by conventional drilling and milling techniques, to obtain short injection cycle times. However, this application involves bonding of large cross sections that are not prone to excessive deformation. According to fundamental design rules for e. g. a platform for enlarging the mating cross section after reaching a certain level of deformation, the deformation of macroscopic parts can be controlled very easily and precisely. Often, large parts are cut into smaller pieces by wire-cut electrical discharge machining (EDM) and finish-machining is performed afterwards. Hence, there are no tight tolerances in terms of deformation and the only challenge is to ensure a good bonding quality during diffusion bonding.

Furthermore, deformation depends on the aspect ratio and the size of the cross section of the part, due to friction between the part and dies, and varies for identical parameters of

- bonding temperature,

- dwell time, and
- bearing pressure.

For micro process devices, determination of these three main parameters to achieve a certain deformation requires vast expertise. Nevertheless, it is afflicted with uncertainty.

It must be stated that the diffusion coefficient exhibits a strongly nonlinear behavior in the temperature range used for diffusion welding. A temperature increase of 20 K only causes the coefficient of diffusion approximately to double. A measurement uncertainty of ± 2–3 K results from the thermocouples and aging. For this reason, calibration of thermocouples should be performed periodically.

The resulting deformation also depends strongly on the bearing pressure and the material's microstructure, e. g. grain size: The deformation mechanism may switch between lattice diffusion (Nabarro-Herring creep) and grain boundary diffusion (Coble creep) [1]. Oxide dispersion-strengthened alloys, however, take advantage of low impact of grain boundaries due to prevention of dislocation movement and gliding due to submicron precipitations dispersed inside the grains. Here, dislocation density is not reduced significantly at high temperature. Therefore, quite different values of bearing pressure may be appropriate during diffusion bonding.

4 Distinctive features of diffusion bonding of micro process devices

Contrary to molding tools, micro process devices are mostly made of thin sheet material that is stacked to form multilayered assemblies.

Diffusion bonding of these stacks results in additional influences on deformation:

- Structural designs for limiting deformation are mostly not applicable.
- Mechanical microstructures are often in the range of some tenths of a millimeter, which initiates additional deformation mechanisms, such as grain boundary sliding.
- Often, the grain size is a function of the thickness of semi-finished products. Metal sheets of several millimeters in thickness used for adapting micro process devices to the macroscopic world, exhibit grain sizes that exceed those of thin metal sheets by a factor of up to ten. The reasons are repeated rolling and recrystallization operations that are necessary to obtain thin sheet material. After cold work hardening, recrystallization, accompanied by grain refinement, has to be performed before subsequent rolling steps to reduce forming forces. In case of thicker sheets, only a limited depth is subjected to cold work hardening, and the grain size remains comparably coarse.
- The cross section to be joined commonly ranges from 15 %–85 % in the area of stacked layer of thin sheet material. However, the deformation behavior of coarse-grained cover plates differs from that of fine-grained material. For thick plates without mechanical microstructures the full cross section is subjected to the joining force, leading to decreased bearing pressure. Consequently, the deformation is concentrated on the microstructured height of the part and cover plates exhibit only minor deformation. This is another reason why a percentage deformation for the diffusion bonding process is not helpful in all cases, since the ratio of microstructured height and thickness of cover plates is arbitrary for different parts.
- Leveling of multiple surface roughnesses for multilayered stacks of thin sheet materials increases the deformation compared to parts consisting of two or three layers only.
- For parts consisting of multiple layers, manufacturing tolerances may add up. The final accuracy cannot be better than the input.

For these reasons, it is impossible to give a certain percentage of deformation necessary for obtaining vacuum tightness. Depending on the particular design as regards the number of microstructured thin layers, thickness of cover plates, and aspect ratio, the bonding temperature, dwell time, and bearing pressure must be adjusted based on experience, if the part cannot be machined to final dimensions after diffusion bonding.

In addition, tight tolerances must be guaranteed for micro channels to reach a reproducible level of pressure loss and to be able to specify values in technical information.

Apart from the temperature, dwell time, and bearing pressure, the following parameters are relevant to diffusion bonding of micro process devices:

- The impact of grain boundary sliding as percentage of the cross section. The lower it is, the more pronounced may this effect be.
- The absolute cross section due to the friction between the sample and the dies, together with the aspect ratio of the parts, *Figure 1, Table 1* [2].
- The homogeneity of the bonding area distribution over the cross section. Compact areas tend to deform less. Areas with internal microstructures tend to evade the load [1]. This effect is limited due to the stiffness of compression dies. However, it cannot be neglected and depends on bonding temperature and bearing pressure, *Figure 2*.

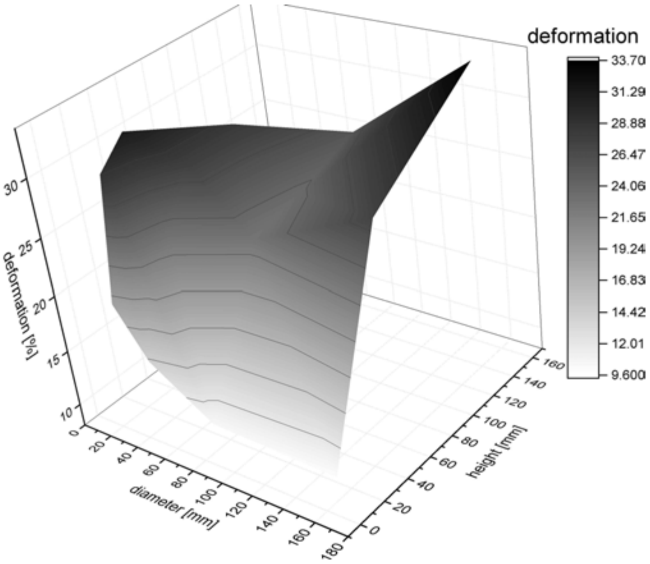

Figure 1. Dependence of deformation on the aspect ratio as well as on the cross sectional area. Parts made of two halves. Austenitic stainless steel 1.4301, $T = 1075\ ^{\circ}\mathrm{C}$, $t = 4$ h, $p = 25$ MPa.

Additionally, deformation exhibits a strongly nonlinear behavior. The ability of atoms to change their positions within the lattice depends on the density of vacancies. The vacancy density and the coefficient of diffusion depend exponentially on temperature. In the temperature range applied for diffusion bonding, the coefficient of diffusion doubles for a temperature raise of about 20 K only. Therefore, aging of thermocouples cannot be neglected and they should be calibrated after several runs.

According to the level of bearing pressure, the flow behavior of the material changes drastically [1]. Especially for small mechanical micro-

Table 1. Deformation as a function of sample geometry. Stainless steel (1.4301, $T = 1075\ ^{\circ}\mathrm{C}$, $t = 4$ h, $p = 25$ MPa). Flatness tolerances were calculated based on five values for the edges and in the center. Measuring was performed using a micrometer gauge with a nonius of 0.001 mm.

Sample (Ø and height)	Aspect ratio	Tolerance of flatness before diffusion bonding [µm]		Tolerance of flatness after diffusion bonding [µm]	Deformation [%]	Tolerance of flatness related to percentage deformation [%]
		part 1	part 2			
20 mm; 10 mm	0.5	5	8	8	18.54	0.44
20 mm; 20 mm	1	13	20	19	28.91	0.33
20 mm; 40 mm	2	1	2	51	31.07	0.41
40 mm; 10 mm	0.25	10	49	34	14.19	2.38
40 mm; 20 mm	0.5	13	11	22	20.44	0.53
40 mm; 40 mm	1	4	1	11	22.78	0.12
40 mm; 60 mm	1.5	61	29	11	27.84	0.07
40 mm; 100 mm	2.5	9	5	50	28.37	0.18
80 mm; 10 mm	0.125	23	39	84	9.64	8.55
80 mm; 10 mm repeated	0.125	28	35	103	11.23	9.02
80 mm; 60 mm	0.75	49	40	71	23.01	0.51
80 mm; 60 mm repeated	0.75	29	40	139	22.25	1.04
80 mm; 100 mm	1.25	38	31	98	23.62	0.41
80 mm; 150 mm	1.875	55	20	323	25.59	0.84
160 mm; 10 mm	0.0625	23	17	114	10.02	11.06
160 mm; 60 mm	0.375	24	26	297	27.35	1.81
160 mm; 150 mm	0.9375	18	10	460	33.66	0.91

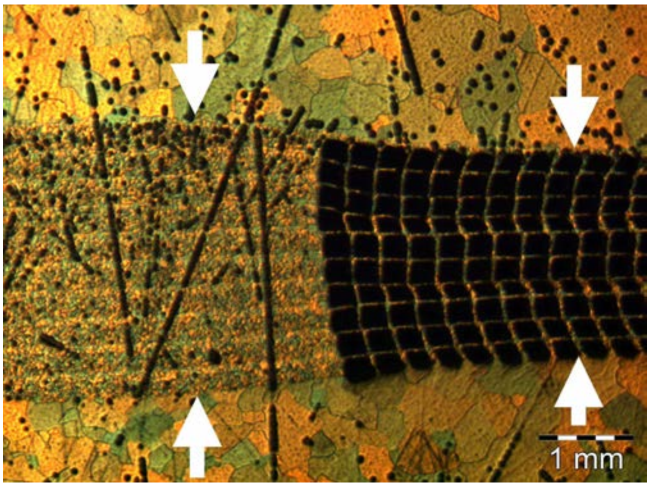

Figure 2. Irregular deformation of microstructured and ridged areas, although the compression die made of TZM is considered inflexible.

structures, the deformation mechanism may change to grain boundary sliding [3]. Diffusion bonding parameters that are appropriate for macroscopic parts may not be applicable to micro process devices due to excessive deformation.

For thin walls, glide steps can be found and can be formed, even despite they were not subjected to direct shear stress, *Figure 3*a. The effect is more pronounced for narrow trenches between micro channels with grain boundaries of about 45° related to compression forces, Figure 3b.

4.1 Diffusion bonding of multiple parts

To obtain reasonable costs per part, it is essential to distribute fixed costs of the diffusion bonding process to multiple parts. Generally, different setups can be distinguished: Arrangement of multiple small parts in one layer or a stacked setup of multiple layers or a combination of both, depending on the size of parts to be bonded. Up to a certain level, the size of the part determines the costs per part and, hence, the incremental costs of the whole process for industrial applications.

If a setup in one layer is chosen, the tolerances of height must be within a certain range. Even the lowest part must achieve a deformation sufficient to reach vacuum tightness, and to prevent 100 % testing. Finally, a deformation in the range of 4.5 % to 6 % is appropriate for parts consisting of 30–50 layers and an overall height of 30 mm, *Figure 4*.

Whereas the variation of the height over the cross section is not relevant to small parts of about 20 mm–30 mm in diameter only, a variation of height after diffusion bonding in the range of 0.3 mm relative to a distance of about 400 mm must be accepted for parts with larger cross sections. This will be discussed in detail in section 4.2. To assess the eligibility for diffusion bonding, the internal design of parts must be evaluated.

Parts possessing a large cross section may be stacked on top of each other, *Figure 5*. Additional plates of high-temperature-resistant material are used to separate parts and to prevent sticking to each other. Titanium-zirconium-molybdenum (TZM), an ODS-molybdenum alloy or carbon material may be used for this purpose. Due to the ma-

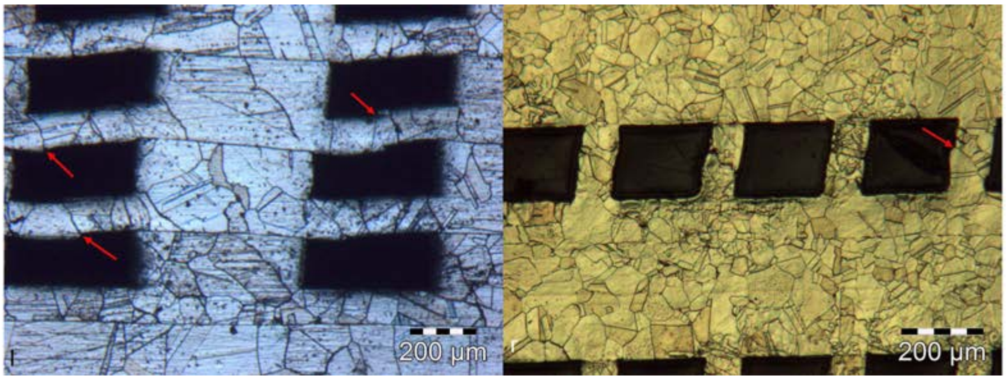

Figure 3. Grain boundary sliding at elevated temperatures. Left: For thin walls without external shear stress. Right: On a coarse-grained thin wall with a sustained grain boundary around 45°.

Figure 4. Multi-diffusion bonding of 50 small parts consisting of several dozens of layers in one plane.

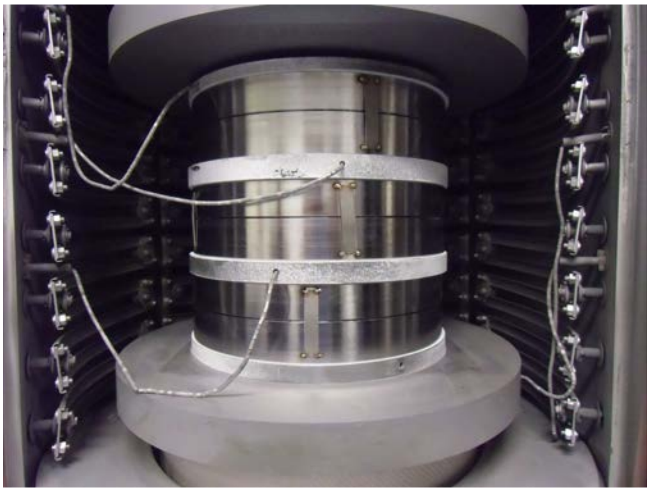

Figure 5. Multi-diffusion bonding of stacked large-sized parts. The die diameter is 500 mm.

chining process of these plates, additional tolerances are introduced, adding up in height for each layer. Additional anti-sticking coatings like boron nitride spray or alumina are applied. For these porous layers of flaky boron nitride, for instance, no exact thickness can be specified, and additionally tolerances are introduced, *Figure 6*.

The thinner large parts are, the greater is the impact of the absolute variation of the lateral dimension of height in terms of a calculated percentage deformation. For a part with a thickness of 5 mm and a diameter of 300 mm the variation of thickness after the diffusion bonding process may be as big as 150 µm. This spread is in the range of the difference of the averaged heights of the part before and after the bonding process, and in the range of the percentage deformation itself. Especially thin, large-sized parts show a strong decrease in deformation to one third compared to larger aspect ratios, Table 1. Consequently, it is not helpful to specify a percentaged deformation for very thin parts with large cross section at all. Technically speaking, the local deviation of the deformation for thin parts varies considerably. If the part contains multiple necking in line, pressure loss will vary extremely for different parts.

These considerations lead to section 4.2 covering the evaluation of tolerances to assess whether diffusion bonding is a suitable joining technique or not.

4.2 Consideration of tolerances

Taking into account the complex setup of a diffusion bonding furnace and tolerance chain, the following constraints result for micro process devices:

- The alignment and parallelism of compression dies can be assessed at room temperature only. Depending on the size of the dies, tolerances common in mechanical engineering of several tenths of a millimeter has to be acceptable [4].
- Thermal expansion and distortion of the complex setup depend on the height of the parts to be bonded and the length of the compression dies subjected to high temperatures as well as on temperature gradient in the furnace.
- Each layer of material possesses a certain tolerance in thickness due to the manufacturing process. For sheet material of 1 mm in thickness, thickness tolerance ranges from 30 µm–70 µm depending on rolling width. For tighter tolerances, 25 µm–50 µm apply [5]. Additional plates made of titanium-zirconium-molybdenum to sep-

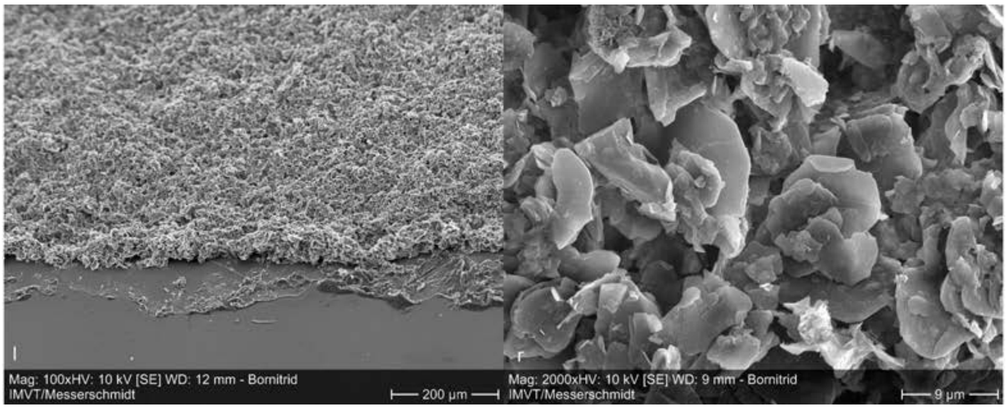

Figure 6. Structure of sprayed boron nitride layer.

arate several parts stacked up, and anti-sticking coatings increase the tolerances.

- The final part after diffusion bonding cannot exhibit tighter tolerances than the semi-finished products used for it. Tolerance chains must be considered. Tolerance depends directly on the cross-sectional area. Whereas it is not critical for small parts, several tenths of a millimeter are common for cross sections of more than 100 mm × 100 mm, Table 1.

For diffusion bonding of multiple small parts in one layer, also the lowermost part must be deformed sufficiently. Assuming a deviation of height after diffusion bonding of about 0.3 mm for all parts within one level, a deviation in deformation of about 1 % applies to a height of 30 mm. For several layers containing multiple parts, the deviation of deformation may vary from layer to layer in terms of the absolute value as well as the distribution over the area, e. g. due to thermal gradients.

Generally, experienced staff is required to predict and to control deformation of microstructured parts.

5 Impact of surface conditions on diffusion bonding

5.1 Surface preparation: contaminations, burrs and impact of alloying elements

5.1.1 Contamination and formation of burrs

It is well known that all surfaces must be cleaned thoroughly before they are subjected to diffusion bonding. Oil and grease residues from mechanical machining must be removed completely. Also inorganic impurities, e. g. from grinding or sand blasting, must be removed, since they impair formation of a monolithic compound and may contaminate the furnace. When temperatures are increased for subsequent furnace runs, cross-contaminations may result.

For cleaning, sonicating in surfactant solutions and rinsing with acetone or isopropanol are employed [6].

If many parts must be cleaned, electrolytic degreasing by commercial providers should be preferred. The process can be automated and ready-to-use parts are supplied at reasonable costs. For external providers, however, reproducibility and traceability of the cleaning conditions may be a problem.

Mechanical microstructures must be free of burrs that prevent locally intimate contact of surfaces and high vacuum tightness and may cause wedge error, if multilayered parts are stacked up. Brushing or sandblasting may be used to remove burrs. It should be considered that brushing may not remove burrs, but smudge surface layers, leaving irreproducible surface conditions.

5.1.2 Impact of alloying elements and thermal constraints during diffusion bonding

Diffusion bonding may not be used, if the materials contain metals like zinc or lead, due to their low vapor pressure. Examples are brass and German silver. In brass, lead as a soft chip breaker precipitates at grain boundaries. Due to its low melting point, a liquid phase forms at diffusion bonding temperatures. For brass as well as German silver, zinc exhibits a partial pressure of several hundred millibars, *Figure 7*. Under vacuum, it evaporates as soon as it diffuses to the surface. In this case, the vacuum gauge of the furnace can be destroyed.

When using copper, an excess of phosphorus as deoxidizer or remaining oxygen may impair the formation of a monolithic compound. The result is very sensitive to minor changes of the composition of these elements. Below, diffusion bonding results for 850 °C, 900 °C, and 1000 °C are shown, *Figure 8*. Whereas at 850 °C there is no grain growth across the bonding plane, excessive grain growth across all layers starts at 900 °C.

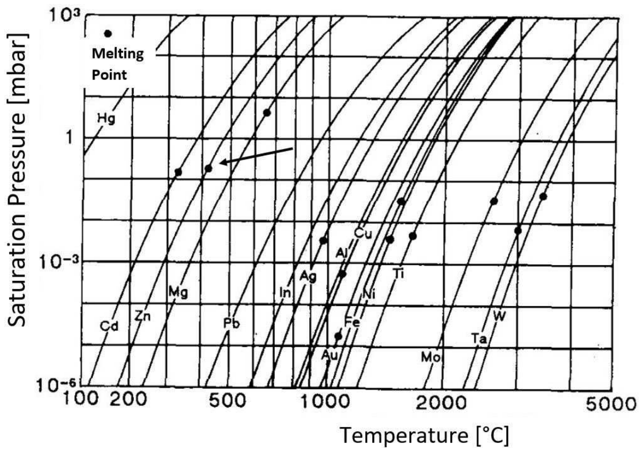

Figure 7. Vapor pressure of several metals depending on temperature. According to [7].

The behavior of ODS-copper alloys largely differs from that of pure copper. By means of ceramic particles that are insoluble even at very high temperatures, motion of dislocations is suppressed very effectively. ODS-copper alloys are made by either internal oxidation of a certain aluminum content or adding of precipitation-forming elements, such as titanium, boron, and carbon, and subsequent high-energy reactive milling. Compaction to dense semi-finished products is performed by means of extrusion. For this, powder is filled into claddings of pure copper. A high degree of cold working is applied, leading to a high dislocation density. In ODS-copper, no real grain boundaries are visible, *Figure 9*. Due to the high density of dispersoids, even high temperatures just below the melting point, e. g. 1000 °C applied for 1 h reduce hardness by 15 % only. Hence, these materials are widely used for spot welding electrodes.

Due to lacking grain boundaries that are responsible for diffusion rates higher by several orders of magnitude, only volume diffusion takes place. Hence, longer bonding durations, higher temperatures, and higher loads are required. Due to the composition and the size of dispersoids and the high oxygen content of the copper matrix, it is hard to form a strong bond [8]. The strength achieved by diffusion bonding is far below that of the matrix material, since there are no dispersoids in the interlayer, *Figure 10*. It was found, that coating of any different metal, exploiting concentration gradients, or forming an eutectic with low melting temperature as a temporary liquid phase, led to formation of pores. According Kirkendall effect, insoluble

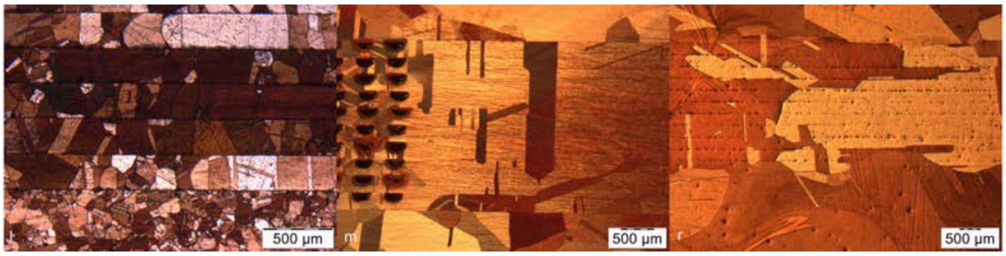

Figure 8. Diffusion bonding of oxygen-free copper, $t = 4$ h: Left: $T = 850$ °C. Middle: $T = 900$ °C. Right: $T = 1000$ °C.

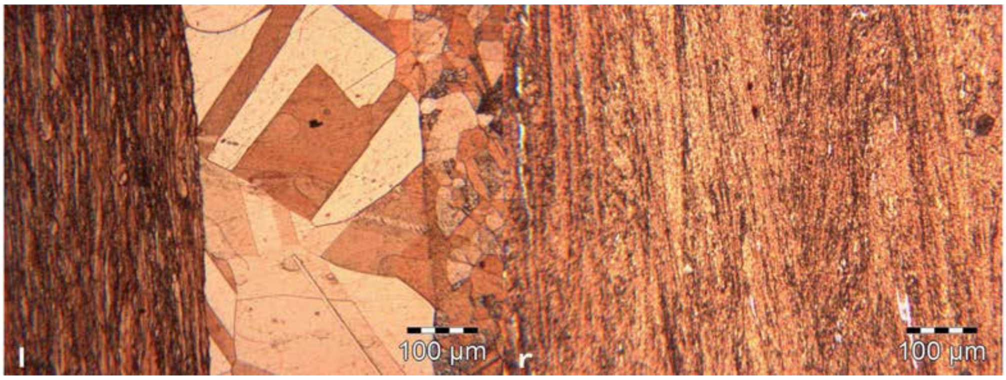

Figure 9. Semi-finished products of different ODS-copper alloys. Left picture: Glidecop Al-60, right and middle part of this picture: Cladding material with coarse-grained microstructure. Right picture: Microstructure of Discup C3/80.

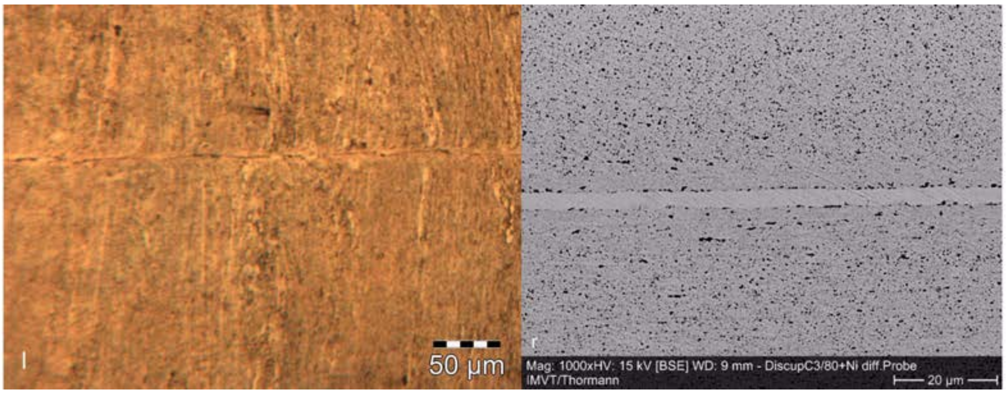

Figure 10. Diffusion welding tests of ODS-copper Discup C3/80. Left: $T = 1000$ °C, $t = 4$ h. Right: Sputtered with a nickel interlayer after $T = 1000$ °C, $t = 16$ h.

particles stick at their positions and do not participate in diffusion [9]. Using nickel as an interlayer for diffusion bonding of DISCUP C3/80, an ODS-copper alloy, it diffused out of the bonding plane. Due to the much lower melting temperature of copper, and hence its much higher diffusion coefficient at bonding temperature, the original layer was completely substituted by copper.

Additional restrictions arise from the limited cooling rate after diffusion bonding. This applies even if the furnace is cooled using inert gas and a gas circulation cooling system is used. Due to its high heat conductivity of 0.15 W/m·K, helium is preferred to argon that has a conductivity of 0.018 W/m·K only. Although helium is much more expensive, it may be the better choice for economic reasons, as the cycle time can be shortened from two to one days for big furnaces and parts with a high thermal load.

Nevertheless, cooling rates may be much lower than specified in material data sheets to guarantee certain corrosion properties or microstructure of the material, and depends on the thermal mass of the parts and inventory of the furnace.

For nickel-based alloys, sensitization is an issue. Quenching in water, as often suggested for thick parts, is not possible. Intercrystalline corrosion, accompanied by excessive grain growth due to lacking polymorphy, may occur after diffusion bonding.

For martensitic stainless steels, e.g. 1.4021, different microstructures and mechanical properties may result depending on time-temperature-transformation (TTT) diagrams, *Figure 11*. Beside an carbon content of 0.16 %–0.25 %, this sort of steel contains about 13 % of chromium. Chromium reduces the diffusivity, shifting the critical cooling rate for the formation of martensite to lower values, thus increasing the effective hardening depth. If

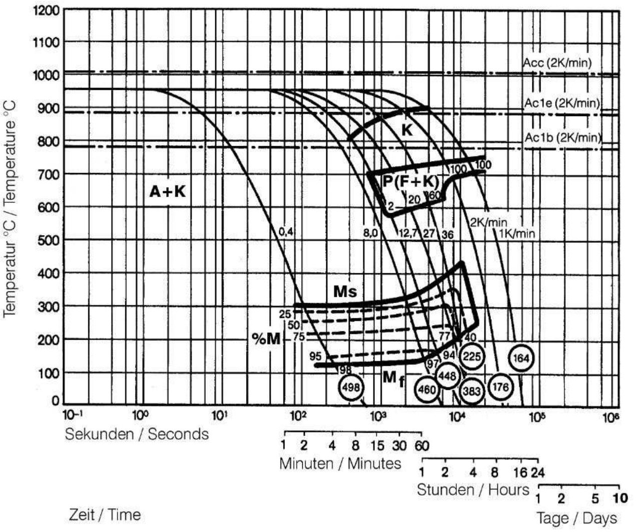

Figure 11. TTT diagram of martensitic stainless steel 1.4021 (X20Cr13) [10].

necessary, for 1.4021 a heat treatment must be performed afterwards.

Alloying elements may also affect transition temperature between different types of lattices. At a certain level, they even suppress polymorphy as applies for ferritic or austenitic stainless steels, leading to differences of some orders of magnitude of the diffusion coefficient.

Although the carbon content of 1.4021 is specified to range from 0.16 %–0.25 % depending on the batch, different microstructures with a more or less pronounced carbide network may result, *Figure 12.*

5.2 Impact of roughness on deformation

Deformation during diffusion bonding depends not only on bonding temperature, dwell time, and bearing pressure, but also on the number of surfaces that must be leveled. Surfaces to be joined must contact each other on the atomic level so as to enable diffusion of atoms across bonding planes. With time, the contact area is increased by diffusion, and pores are filled by volume diffusion. For this, the coefficient of diffusion along grain boundaries is several orders of magnitude higher than inside the metallic lattice. Hence, a long dwell time is necessary to achieve full cross-sectional joining without voids.

Leveling of surface roughness contributes to overall deformation. It is clear that deformation varies when joining two layers only or multilayered stacks. On the other hand, deformation must be controlled to ensure the structural function of the part, e. g. dimensions of microchannels, and pressure loss. Depending on the layout of micro process devices, appropriate levels of deformation may vary, and a general number of percentaged deformation to achieve vacuum tightness cannot be specified.

Roughness parameters, such as R_t, R_z or $R_{\max}$ should be below 3 µm, taking into account that the ratio of R_a:R_t is in the range of 1 : 7 to 1 : 10 for mechanical machining. For R_a, values of 0.2 µm–0.5 µm are suitable. Generally, it is harder to close a few deep scratches in a surface to ensure vacuum tightness than to level an equally distributed rough-

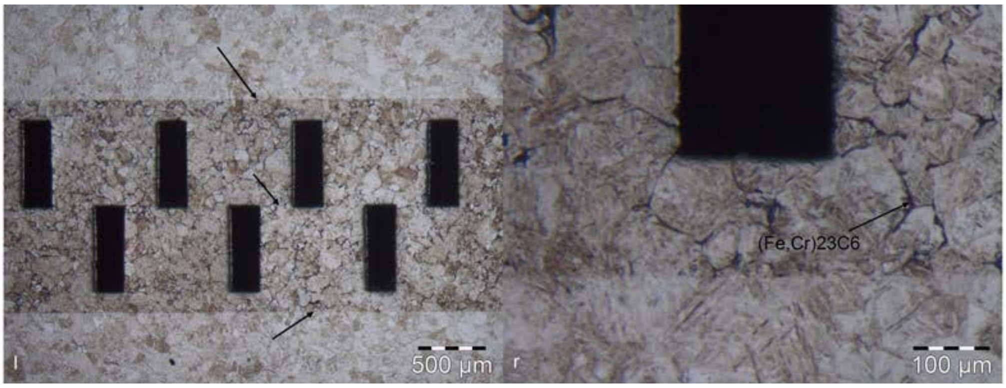

Figure 12. Diffusion bonding of martensitic 1.4021, $T = 950$ °C, $t = 1$ h, $p = 17$ MPa. Different microstructures of thin sheet material combined with thicker end plates. Obviously, the carbon content in thin sheet material is higher; the carbide network is more pronounced. Left: Arrows mark bonding planes. Right: Carbide network. Austenitization and repeated polymorphic transition compensate grain growth and facilitate bonding at a low level of deformation.

ness. Differences may appear when material is removed out of the surface or burrs form at the rim. Investigations of depths of scratches were performed in [11]. It was found that a temporary increase of bearing pressure that activates creep of material helps to close scratches.

5.3 Passive layers, impact of alloying elements

Except for noble metals, whose corrosion resistance results from a positive electrochemical potential, corrosion resistance of other metals and alloys is achieved by the formation of a dense and stable passivation layer. This layer consists of a thin oxide layer, mostly of several nanometers only, which is formed by the metals of the matrix material. Corrosion resistance in aqueous media or at high temperatures under varying atmospheres may vary depending on the type and content of alloying elements. Most passive layers are formed at temperatures below 500 °C. The increase in thickness follows a logarithmic law of growth [12]. Since the coefficient of diffusion is very low for oxygen, passive layers prevent further influx of oxygen into the matrix material, thus limiting the thickness of the passivation layer. Contrary to a conventional oxide layer, passive layers are transparent due to their low thickness. As a consequence, internal stresses due to increase of volume during oxidation remain below a critical value, and flaking does not occur. Depending on thermal history, however, thickness may vary and, hence, influence the material's suitability for diffusion bonding.

Rolling and recrystallization steps required to manufacture thin sheets of austenitic materials that tend to cold work hardening, will alter and reinforce passivation layers. Auger electron spectroscopy (AES) investigations on 2.4633 showed a large differences of passivation layer thicknesses depending on surface pretreatment, *Figure 13*. It was performed with a “Physical Electronics PHI 710e / 680 Hybrid” field emission scanning Auger microscope. Acceleration voltage of the exciting electron beam was fixed at 10 keV and the sample current was aligned to 15 nA. The Auger Electron spectroscopy depth profiles were obtained using a 2 keV argon ion beam. The sputtering rate was $9.5\ \text{nm}\cdot\text{min}^{-1}$ for a SiO_2 standard. However, the real erosion rate depends strongly on the sputtered material. The depth profiles were recorded in areas with dimensions of approximately 1 μm^2.

As mentioned above, passivation layers usually impede diffusion and formation of a monolithic compound during diffusion bonding depending on thickness and composition, *Figure 14*.

For titanium, however, surface oxide films can be dissolved in the matrix material. In case of micro process devices, however, the relation between surface layers and bulk material volume has to be kept in mind: since titanium grades 1 to 4 differ only in their contents of nitrogen, oxygen, and iron, dissolution of passivation layers may considerably change mechanical properties.

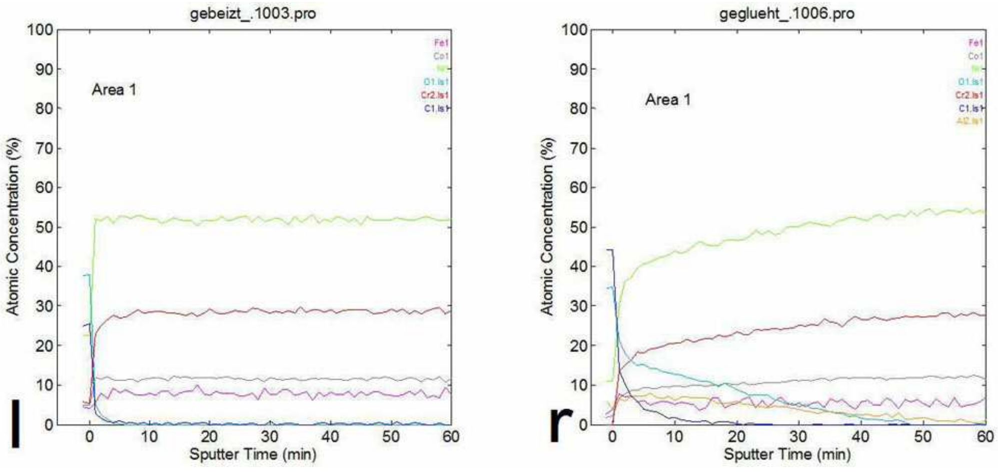

Figure 13. AES depth profiles of alloy 602CA (2.4633). Left: delivery state, surface pickled using a hydrofluoric acid-containing agent, passivation layer thickness less than 10 nm. Right: annealed, passivation layer thickness approximately 300 nm (based on the sputter rate of silica).

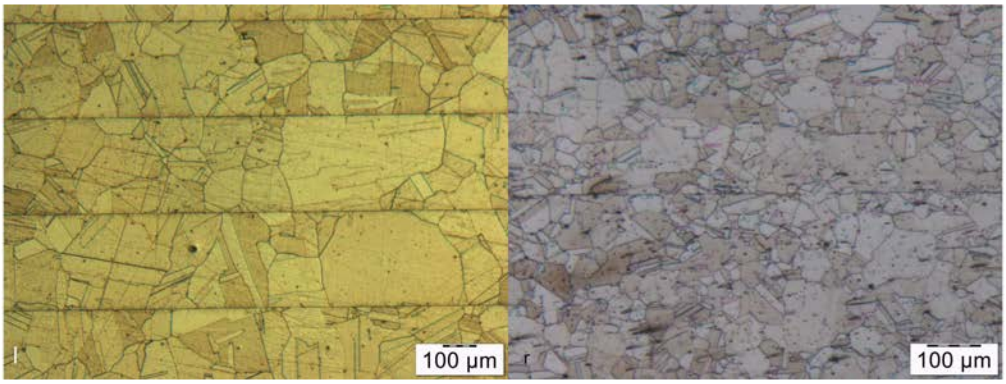

Figure 14. Impact of passivation layer thickness on the result of diffusion bonding. $T = 1200$ °C, $t = 4$ h. Left: 1.4876, passivation layer thickness approx. 90 nm, no grain growth across bonding plane. Right: 2.4633, pickled with hydrofluoric acid-containing solution, passivation layer thickness less than 10 nm, good grain growth despite higher chromium and nickel contents.

5.4 Choice of semi-finished products for micro process devices, removal of passivation layers

For chemical applications, usually well-established materials are used, even if better solutions are available, thus anticipating market penetration of newly developed alloys. Regardless, a certain level of corrosion is accepted and considered when dimensioning the wall thickness. For micro process devices, however, corrosion resistance is essential due to the wall thickness of a few tenths of a millimeter only to achieve high thermal transfer. Hence, micro process devices are often made of special alloys that are produced in minor quantities only. Mostly, semi-finished products of low thickness are required, which are not commonly used in industries. This restricts the number of potential suppliers. Additionally, several aspects have to be considered when ordering semi-finished products:

- The variation of thickness of semi-finished products should be small and considered when manufacturing thin sheet material and multilayered devices [13]. Addition of tolerances may require a high deformation during diffusion bonding to achieve vacuum tightness for sure. This may affect functionality of mechanical microstructures.
- Surface quality in terms of roughness values, especially for deep single scratches, must be specified. Personal experience and know-how are required to assess quality.
- The surface state in terms of passivation layer thickness must not be neglected.

Particular attention must be paid to the surface condition. If possible and depending on the size and amount of parts and available techniques, a suited pretreatment is required to guarantee a reproducible surface condition. Passivation layers can be removed by appropriate chemical pickling. Still, undesired constituents, such as hydrofluoric acid, should be avoided. For materials of different compositions, different agents are required. Blasting with abrasive particles like glass beads may be favorable. The process is more flexible when using materials that differ in composition and erosion can be tailored by adjusting pressure and dwell time. If appropriate parameters are chosen, a certain degree of cold work hardening can be obtained near the surface without causing distortion of thin sheet material. Cold work hardening supports recrystallization and helps to reduce grain size. For materials exhibiting no polymorphy, recrystallization facilitates diffusion bonding, *Figure 15*.

This is an additional benefit of blasting compared to chemical pickling.

6 Diffusion bonding of stainless steels and nickel-based alloys

For diffusion bonding of stainless steels, different groups of materials with completely different behaviors have to be distinguished: austenitic, ferritic, and martensitic stainless steels as well as duplex alloy containing co-existing ferritic and austenitic grains.

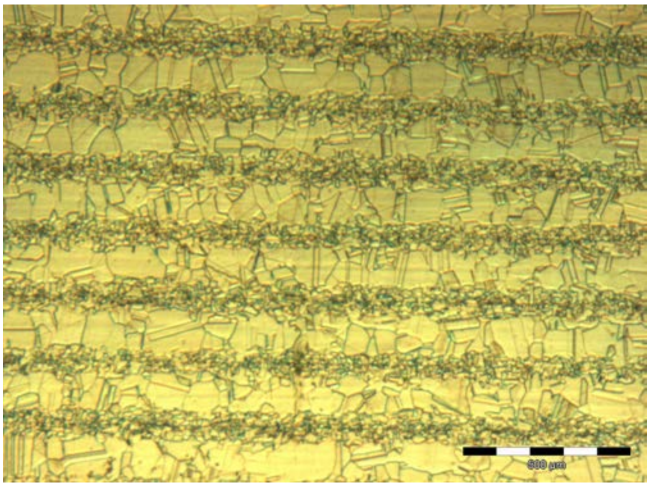

Figure 15. Diffusion-bonded stack consisting of thin layers of austenitic stainless steel 1.4571. Fine-grained microstructure in the joining region due to cold work hardening. Coarse grains inside the matrix material.

The types and contents of alloying elements and the carbon content define the crystallographic structure formed according to the Schaeffler diagram [14]. Whereas chromium stabilizes the ferritic bcc lattice, nickel does for the austenic fcc lattice. Both lattices show quite different coefficients of diffusion and dissolving powers for alloying elements with temperature, especially for carbon. Whereas austenitic and ferritic stainless steels exhibit no polymorphy, martensitic stainless steels do, *Figure 16.*

Alloying elements and contents also influence the composition, stability, and thickness of the passivation layer. This results in quite different suitability and parameter ranges for diffusion bonding. Parameters cannot transferred easily to other alloys.

7 Summary and conclusions

Generally, diffusion welding is a non-standard welding technique. The expenses for equipment and costs per batch are high and it is popular for some special applications only. For most corrosion-resistant materials, the result of the diffusion bonding process obviously depends on the surface condition, namely, on composition, thermal stability, and thickness of the passivation layer. For materials possessing a thermally stable passivation layer, it is hard to achieve a good bonding quality with grain growth across the bonding planes.

More attention must be paid to appropriate pretreatment processes to ensure a thin passivation layer with reproducible bonding properties. Sonicating and rinsing in acetone or isopropanol are not sufficient. If pickling is used for removing the passive layer, the condition and enrichment of impurities of the solution as well as subsequent rinsing must be monitored.

More appropriate to remove passivation layers, and independent on the chemical composition of an alloy, is blasting. The parameters, however, must be adapted in that way that no excessive cold work hardening occurs, causing macroscopic distortions of thin sheet material due to internal stress. Cold work hardening may facilitate the formation of a fine grained microstructure and grain growth across bonding layers by recrystallization. This is espe-

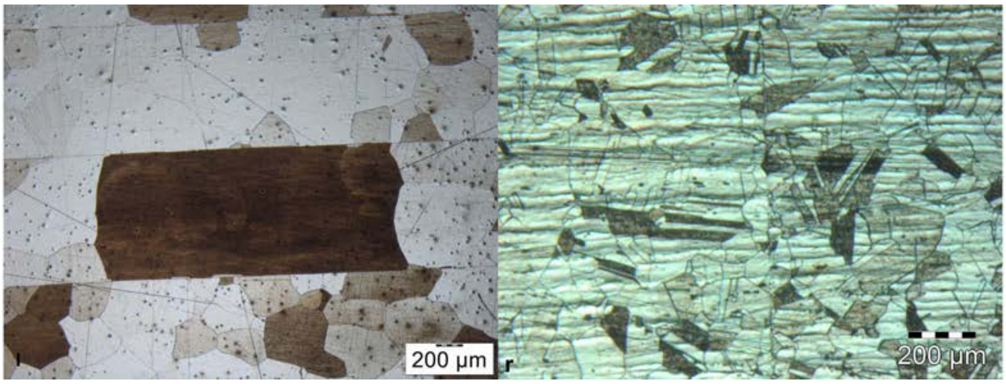

Figure 16. Diffusion bonding of stainless steels: $T = 1075$ °C, $t = 4$ h. Left: ferritic 1.4760, very stable passivation layer, bonding plane clearly visible, excessive grain growth due to high coefficient of diffusion. Right: austenitic 1.4301. Good grain growth across bonding plane. Compare both to martensitic 1.4021 in Figure 12.

cially advantageous for materials, exhibiting no polymorphy, and hence suffering from excessive grain growth at high temperatures and long bonding times. However, foreign particles must be removed thoroughly. Parts should be stacked and welded immediately after this pretreatment.

For oxide dispersion-strengthened materials, volume diffusion dominated the diffusion bonding process and it is much harder to achieve a good bond. Insoluble particles in the sub-micrometer range may concentrate at the bonding plane when pickling is applied to remove passivation layers. Any coatings of different metals forming an eutectic, promoting diffusion due concentration gradients and forming a temporary liquid phase, may cause Kirkendall effect and formation of pores, since insoluble particles are sticked on their positions and do not participate in diffusion. Further investigations should be performed for oxide dispersion-strengthened materials.

When manufacturing micro process devices, deformation mechanism may change to grain boundary sliding due to the dimension of mechanical microstructures, making it difficult to control the degree of deformation. A short raise of the bearing pressure to a level, where creep occurs, facilitates the increase of the bonding area at microscopic scale. The level of bearing pressure, however, depends on the specific materials composition, internal microstructures and bonding temperature. A short duration of increased bearing pressure prevents excessive deformation. Here, specially trained staff is required. Depending on the design and aspect ratio, additional impact factors on deformation apply. Hence, problems may occur for prototypes and small-scale series in particular. If possible, tests should be performed in advance.

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