The role of decompression and micro-jetting in shock wave synthesis experiments

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Abstract. In a set of shock experiments under comparable porosities at pressures of about 35 GPa the melting behavior of porous copper was investigated. All experiments were performed with the impedance corrected sample recovery system and different degrees of decompression were used. It was possible to reduce the degree of molten metal in parts of the sample after sample recovery down to zero. The avoiding of melting was possible only by avoiding larger degrees of adiabatic decompression. This behavior implies a complete dependence of the melting on the release path for porous copper under the given conditions. The zones, where the melting processes are avoided, include also areas with intense micro jetting. Because also in these zones melting does not occur, it is possible that the melting curve of copper along the Hugoniot is not yet solved. The experiments have verified, that it is possible to use equation-of-state calculations for the solid state only, concerning the pressure area of currently commercial interest for the production of nitrides and diamond with copper-powder as pressure medium. Furthermore in this work the role of different parts of the sample recovery capsule is described to improve the comparability of shock wave synthesis experiments. On the other hand, the experimentally results given in this work show significant differences to data, obtained by a number of simulations.

1. Introduction

The employment of metal powders, particularly copper, as impedance medium and coolant in the shock wave synthesis of diamond powders from their respective low pressure forms is a well established method since the 1960ies [1]. In more recent times, this method was extensively used for the dynamic synthesis of refractory materials like cubic silicon nitride [2], cubic boron nitride [3] and aluminum nitride with rocksalt structure [4, 5].

Often, the metal powder is used in large excess, such as 90 or 95 wt % and the shock conditions are assumed as those of the pure porous metal alone, as the bulk shock behavior of these metals is well investigated. These investigations included also effects like micro jetting [6, 7], melting processes at particle surfaces [8], the temperature gradients in the grains [9, 10] and also the friction energy [11]. Furthermore the investigations of porous metal powders concerns also the jetting phenomena on the macro-scale [12–14].
Figure 1. Standard shock synthesis equipment used at the TU Bergakademie Freiberg with plane wave apparatus and the combination of different steels for the sample recovery capsule which avoids shock wave reflections from the top of the sample holder piston along the release path. Standardized dimensions of the sample holder unit are: container diameter 55 mm, height of the container 50 mm, outer diameter of the sample holder and of the sample piston 30 mm, inner height of the sample holder 5 mm.

However, despite the fact that the metal “additive” method was often patented in various constellations and may be an object of commercial interest, the interplay between the metal powder and the intermixed starting materials for the HP-synthesis, in particular the influence of these starting materials which partially fill the voids between the metal powder particles on the microscopic shock parameters is only poorly documented in literature so far. In many cases the compacted metal powder recovered from the shock synthesis is dissolved in nitric acid or other aggressive media without any detailed investigations [2] in order to retain the purified high pressure phase.

Doing so, important information on the melting behavior on the release path [15], degassing processes of the sample materials [16], the cooling behavior of the HP-phases [17] and the influence of microjetting on the synthesis success may be lost. Furthermore it is not well known if it will be required to take melting processes into account for the temperature calculation of the metal powder. For the calculation of the cooling rates of the sample powder (e.g. after the “thin skin-model” for the example for silicon carbide, as given by Kondo [18] and references therein), the determination of the thickness of the melted rim of the consolidated (metal) particles recovered from shock treatment is required.
In the present work, we therefore investigate the microstructures of shock-consolidated copper powders with and without added sample material (i.e. a silicon nitride precursor) from a series of experiments with external shock conditions identical to those for the successful synthesis of high pressure spinel-type silicon nitride ($\gamma$-Si$_3$N$_4$) with high phase purity [19], i.e. at calculated bulk shock pressures of 35 GPa, upwelling of the container top and observation of an upstream jetting phenomenon [14]. Opposite to these successful synthesis experiments [19] the additional tests, described in this work, were performed after the development of the impedance corrected container [20].

### Table 1. Pressure and temperature conditions of the four performed experiments. Asterisks denote temperature calculations based on copper alone, assuming a constant heat capacity of 0.383 J/(g K) at 295.15 K without melting [22] and with calculation of the Grueneisen parameter as a function of the specific volume alone [23] with a value of $\gamma_0 = 1.96$ [24].

| No. | Comments                                                                 | $U_p$, km/s | $P$, GPa | $T$, K (bulk) | Porosity |
|-----|---------------------------------------------------------------------------|------------|---------|---------------|----------|
| SN50 | Original SN50 [19], sample: Cu-powder with Si$_2$N$_2$NH (< 10 wt %), without impedance corrected container, with upwelling of the container top (uncontrolled adiabatic decompression), with upstream jetting. | 1.32       | 35      | 6200*         | 2.00     |
| SN69 | Like SN50, impedance corrected container, without jetting, adiabatic decompression strictly restricted to the sample holder itself, with Cu-foil on top, sample: Cu-powder with Si$_2$N$_2$NH (< 10 wt %). | 1.33       | 35      | 6200*         | 2.00     |
| Cu2  | Like SN69, but without sample ($k = 2.0$), without Cu-foil, impedance corrected container, sample: only Cu-powder, adiabatic decompression strictly restricted to the sample holder itself. | 1.36       | 33      | 6200          | 2.00     |
| Cu3  | Like Cu2, but with porosity like sum porosity SN50 & SN69 ($k = 1.72$), without Cu-foil, impedance corrected container, sample: only Cu-powder, adiabatic decompression strictly restricted to the sample holder itself. | 1.22       | 35      | 4100          | 1.72     |

2. Experimental methods

For all experiments Cu-powder, manufactured by atomization, with an average grain size of approximately 40 $\mu$m was used [21] (figure 2a). All experiments were performed with the flyer plate method as given in figure 1. The investigations, given in this paper, were only possible because two disturbing effects were excluded: the upstream jetting [12–14] and the shock wave reflections from bottom of the sample holder or the top of the sample piston, respectively. Superposition of these shock interactions would seriously affect the microstructure of the retained sample material and would make a reconstruction of the processes occurring during the loading and unloading path impossible.

For all experiments except SN50 [19] the impedance-corrected sample recovery capsule [20] was used in order to avoid undesirable shock reflections from the surface of the sample piston. The upstream jetting phenomenon, as given by Gu et al [14] and Milyavskii et al [12, 25] was
Figure 2. SEM-microphotographs of the starting material: a—overview over grain size and grain shape, grains partially with inner large pores (SE-microphotograph, length of the scale bar 10 \(\mu\)m); b—one single grain with its four phases: single crystallites, large pores, porous matrix and thin surrounding skin (BSE-picture, length of the scale bar 10 \(\mu\)m); c—detail of one single grain with different structural orientation of skin and matrix and with well rounded single crystallites (BSE-image, length of the scale bar 2 \(\mu\)m).

avoided by a stepwise compaction of the sample with three steps for a sample height of 5 mm (also except sample SN50). Using this procedure, strong density gradients often observed during the compaction in a single step [26] can be avoided, thus leading to a more homogeneous porosity distribution.

Furthermore only samples without uncontrolled volume change of the metal powder along the release path will be usable for these investigations, the gap between sample holder piston and container should be free of molten copper in every case (figure 3a) and also an upwelling of the top of the container should be avoided (the volume of the sample after recovery should be strictly restricted to the sample holder alone, see figure 3c).

The average bulk pressures in the porous samples were calculated with the material data for porous matter after Milyavskii [24]. As basic parameter for these calculations the flyer plate velocity was used (incoming particle velocity) for the open sandwich configuration [27], using the Gurney-parameter for the employed plastinated military high-explosives (RDX), provided by the Federal Institute of Material Testing (BAM Berlin). The temperature (also over average bulk) was calculated after the scheme given by Sharp & DeCarli [28] using the heat capacity data after Chekhovskoi [22] (0.383 J/(gK)) and with the calculation of the Grueneisen parameter as a function of the specific volume alone [23] with a value of \(\gamma_0 = 1.96\) [24]. It was also assumed that all copper was in the solid state along the loading path. For all calculations the Matlab software package R 2009b was used.
For the sample SN50 and for the sample SN69 the porosity was calculated for the Cu-powder alone, the contribution of the precursor Si$_2$N$_2$NH with its unknown Hugoniot was in this case neglected. For this reason a metal powder-precursor ratio of $> 9 : 1$ was used. For the sample Cu2 the same porosity of 2.0 was used but in this case without any precursor. For the sample Cu3 (also pure metal powder) the porosity was identical to the sum porosity of the samples SN50 and SN51 using the scheme by Resnyanski [29] taking the precursor density (approximately 2.4 g/cm$^3$) into account. This density was measured with an He-Pyknometer AccuPyc 1330 (by micrometrics) at the Institute for Ceramics, Glass- and Construction Material Technology (TU Bergakademie Freiberg). The measurements were performed at approximately 25 $^\circ$C at a chamber volume of 12.25 cm$^3$ with 10 scavenging cycles. Sample masses vary between 0.584 and 0.81 g.

The additional Cu-foil between sample and container, as shown in figure 1, was only used for the sample SN69.

The recovered sample containers were manually sectioned and inspected, sliced, embedded in epoxy and finally prepared for the SEM-and EBSD-investigation.

3. Results

3.1. Starting material

The copper powder consists on spherical particles with an average size of 40 $\mu$m. The complex internal structure is build up by four different components. The main volume (and hence cross sectional area) is formed by single crystals with a diameter of 1 to 20 $\mu$m (figure 2b). Each crystallite is surrounded by a porous matrix. The pores therein show often an elongated, “needle like” shape (figure 2c, upper part of the lower grain). This matrix contains small Cu-crystallites with a diameter down to the sub-microscale (figure 2c, upper grain). Additionally the whole grains are surrounded by a thin, also porous skin with a thickness of approximately 2 $\mu$m, clearly separated from the internal porous matrix (figure 3c, lower grain). Another kind of pores occurs as fourth structural part in the 40-$\mu$m-grains itself with a diameter similar to the crystallites (figure 2a, b).

3.2. Investigation of recovered samples and sample containers

The state of the recovered sample capsules is given in figure 3 and the state of the samples itself in figure 4.

The sample, given in figure 3a show neither indications of melting, the surface of the container show a concave form, the sample holder is free of traces of copper (the volume of the sample is strictly limited to the sample holder volume).

The sample in figure 3b shows traces of molten and solidified copper outside the inner sample holder, indicative for a leaking and rapid expansion during unloading, despite the lower pressures under similar initial porosity, compared with sample 3a. Therefore, the sample was not further investigated, as its microstructure would have been significantly changed, not allowing for any conclusions on the loading history any more. The sample recovery capsule of sample SN46 [19] was not usable for the following investigations too, because it showed a convex form of the sample holder surface.

The sample SN50 shows the metal jet in its solidified state (figure 4a). Because the possibility to obtain a sample in this state is very limited this jet was the key sample for the explanations of the state of copper powder in this work. The high-pressure-phase was located besides the jet and was determined as $\gamma$-Si$_3$N$_4$, completely free of other crystalline impurities [19] and was separated mechanically from the jet. The container top was bulged out upwards 5 mm above the original level.

The sample SN69 was recovered as a compact disc without any fractures and visible jetting (figure 4b). The high pressure phase in this special case was not analyzed separately, but
Figure 3. Examples of three recovered sample containers, diameter of all containers 50 mm: a—successful experiment, usable for this work (the complete sample is still in the sample holder, the container surfaces show a concave form; pressure (whole bulk) 48 GPa, initial porosity (only Cu) 1.8, shock temperature (whole bulk) 7000 K, 15 wt % precursor $\beta$-SiAlON); b—unsuccessful experiment, the volume of recovered copper was changed by decompression and molten copper does also occur between sample piston, container and screw bottom (pressure (whole bulk) 31 GPa, initial porosity (only Cu) 1.8, shock temperature (whole bulk) 2970 K); c—container with convex form of its top (not usable for this work), sample SN46 [19], $P$–$T$-conditions like SN51 (table 1); d—recovered sample holder from c with complete molten metal and with separation of the high-pressure phase from the metal.

Comparable experiments using the new impedance corrected sample recovery system [30] show a decrease of the amount of HP-phase from 100 wt % to a value between 80–90 wt % in all cases with minor amounts of $\alpha$- and $\beta$-$\text{Si}_3\text{N}_4$.

The samples Cu2 and Cu3 were both welded with the top of the sample container and a separation of the samples was impossible (figure 4c, e). To avoid a mechanical destruction as in the case of sample Cu2 as seen in figure 4d, the sample Cu3 was prepared for the SEM-investigations together with a part of the container top (figure 4f). The thickness of both samples was reduced compared with its initial state. In all four experiments the sample piston was free of any traces of molten copper.

The reduced sample thickness, compared with its initial state and the theoretical thickness, assuming a full compaction and the difference between the measured thickness and its theoretical value will be given in table 2.

3.3. SEM-investigations

In the case of experiment SN50 columnar grain structures can be recognized in the copper material close to the sample holder, consisting of elongated crystallites, oriented perpendicular to the sample holder surface. This structure is comparable with the texture of ridging in steel where the heat sink is located in its lower part (in the case of SN50 the sample holder). This structure is commonly divided into the chill zone on its base (with smaller crystallites with
Figure 4. Graphical documentation of all samples after recovery and subsequent sectioning: 
a—sample SN50 with solidified upstream jet; b—sectioned sample assembly of experiment SN69 
(from left to right bottom: compacted sample inside copper holder, sectioned recovery container, 
sample piston); c—view of the copper sample holder inside the sectioned recovery container 
of experiment Cu2; d—top view into copper sample holder with shocked and compacted Cu 
powder; e—sliced sample container with welded sample at the container top; f—sample before 
preparation for SEM-analysis together with the container top.

Table 2. Comparison of the sample thicknesses $\Delta$ after recovery with its theoretical values. 
Asterisk denotes calculated theoretical thickness together with 10 wt % $\gamma$-Si$_3$N$_4$.

| No.  | $\Delta_{\text{initial}}, \text{mm}$ | $\Delta_{\text{recovery}}, \text{mm}$ | $\Delta_{\text{theor (after full compaction)}}, \text{mm}$ | Missmatch, % |
|------|-----------------------------------|--------------------------------------|-------------------------------------------------|--------------|
| SN69 | 5.1                               | 3.9                                  | 3.03*                                          | 28.7         |
| Cu2  | 4.9                               | 3.1                                  | 2.45                                           | 27.7         |
| Cu3  | 5.0                               | 3.1                                  | 2.87                                           | 12.5         |

different orientations) and into a zone, consisting on columnar crystallites, as given for example 
in the work by Shin et al [31] (figure 5c). The jetting direction was opposite to the incident
Figure 5. SEM-images of sample SN50: arrow—direction of incident shock; enlargement at scale; inlay—positions of the investigated area in the sample (cut section), contact copy; dotted rectangle—position of EBSD-measurements (length of the sample—25 mm). Area b is a part of area a: a—overview of the upstream jet with spherolitically orientated vacuoles, SE-image; b—detail with elongated vacuoles, SE-image; c—cast structures (upper part) perpendicular to the sample holder (lower part), BSE-image.

shock wave and the mushroom-like jet contains elongated vacuoles (figure 5a) in its upper part. The columnar structured copper is completely separated from the sample holder and the high pressure phase was completely separated from the former molten metal as no traces of Si-bearing material could be observed over the whole area of the sample.

The main area of the sample SN69 consists of orientated deformed grains, so called “parachute structures” [32].

The Si-bearing phases are located between the copper grains (figure 6a) and show no intrusion in the metal grains itself. The complex internal structure of the metal grains is completely preserved (figure 6c) and only slightly deformed without indications of micro-jetting (figure 6b), this concerns also the porous matrix between the crystallites in the grains itself down to the nanoscale (figure 6d). The sample holder and the sample are often separated by a thin gap (figure 6a). The crystallites in the copper grains show internal twinning as a consequence of the high rate of deformation (figure 6c). Molten areas only occur near free spaces in the sample (figure 6d). These zones show a columnar structure similar to the structures in figure 5c, surrounding these free spaces. Jetting in this area was only locally observed, concerning the sample and the sample holder too by an oblique incident shock by a wave deflection. In this jet itself the copper grains are unmolten (figure 6d) and strongly elongated in the jetting direction. This direction does not coincide with the direction of the incident shock, the copper metal of
Figure 6. SEM microphotographs sample SN69: grey arrows—direction of the incident shock; inlay—positions of the investigated areas; dotted rectangle—position of EBSD-measurements; c and d are parts of b, f is part of e; white line—boundary between sample and sample holder (length of the sample—22 mm; contact copy); a—copper grains with parachute structures and Si-bearing sample between the grains (grey), SE-image; b—slightly deformed copper grains in the lower part of the sample with a thin gap between sample holder and sample (BSE-image); c—internal structure of one slightly deformed grain with preservation of its complex primary internal structure, its thin skin and deformation twins in the crystallites (BSE-image); d—single crystallite in the grain from c with deformation twins and preserved porous matrix, white dots from preparation (BSE-image); e—large vacuoles, surrounded by columnar structures of copper, strongly deformed by jetting (right); unmolten zones (center right) are tilted to the direction of incident shock (SE-image).

The sample holder and of the sample shows comparable jetting. The metal powder-sample on the left side of this area is also strongly deformed and its structure is tilted from the incident shock direction, but without jetting.
The sample Cu2 shows in its cross section a large area of molten and solidified copper (figure 7a, b) with columnar structures, comparable with sample SN50. Many small vacuoles are present in the molten structures and the orientation of the columnar structures follow the orientation of the crystallites in the sample holder (figure 7c). One thin unmolten structure
Figure 8. SEM microphotographs of the molten band in sample Cu3: arrows below letters—direction of incident shock; inlay—positions of the investigated areas; white line—boundary molten and not molten areas (areas with adiabatic decompression); length of the sample—16.5 mm (measured on the base of Cu-sample holder); contact copy; a—overview over the whole sample with container top (upper left corner) and sample holder (lower right corner) and with cast structures in the center (BSE-picture); b—lower part of the molten and solidified area with unmolten grains (lower part) and cast structures (BSE-picture); c—detail of lower right part of b with bubbles in the cast structures (BSE-image); d—detail of the boundary between molten areas and grains without any melting, no transition zone with partially molten Cu-grains can be found (SE-picture).

do only occur near the sample holder in form of a linear band, now separated from the sample holder bottom, similar to the “cold boundary layer” after Nesterenko [32] (figure 7d). Only in this area with a thickness of approximately 100 µm indications of very intense micro jetting are
visible with a jetting direction parallel to the incident shock (figure 7e). This jetting concerns the central part of the grains, opposite the gap between the grains and the boundary between two neighbored grains. Between and in these jets melting was not observed. The boundary between complete molten and solidified areas and areas with intense jetting is very sharp, a transition zone e.g. with only partially molten Cu-grains was not observed.

In the sample Cu3 the area of molten and solidified copper is strongly reduced compared with sample Cu2. To obtain detailed information about the jetting behavior of the Cu-grains, the investigated area in this sample with columnar structures and unmolten Cu-grains, including micro jetting, was limited to an area in the center of the sample (white lines in inlay figure 8). This positioning concerns the horizontal and vertical position in the sample (figure 8a and inlay) and the former molten zone forms a band perpendicular to the incident shock with a thickness of approximately 400 µm. The left and the right corners of the metal powder sample were also completely molten (figure 8 inlay). The cast structures indicate a starting point of the cooling process in the lower part of the band (figure 8b, c). The boundary between molten and solidified areas is very sharp, any transition zone is not visible (figure 8d).

At the top of sample Cu3 a thin zone (thickness approximately 200 µm) can be identified which shows melting processes (figure 9) containing different structures compared with the band, especially by the influence of microjetting, comparable the experiments by Kozin & Simonov [33] or Mali [34]. An overview over this structure is given in figure 9a. The copper powder itself
shows molten porous structures (figure 9b), surrounded by a denser rim and strongly deformed metal grains without any indications of melting processes (figure 9c). The boundary between both very different zones is sharp again without any transition zones e.g. with partially melting.

The lower central part of sample Cu3 consists of copper grains without any indications on molten areas, but with micro jetting parallel to the direction of the incident shock (figure 10a). This complete absence of melting includes also the top of the microjets.

Characteristic feature of these jetting is the positioning of the root of the jet in the center of a single grain and a jetting direction into the free space between two other grains and not a jetting with its root between two neighboring grains. In many cases the gap between these grains is still preserved after shock in a deformed state without annealing effects, this concerns also the three components of the complex internal structure as given in figure 3. These components strongly deformed on the base area of the jet under preservation of the porous matrix with intense shear bands and twinning inside the grains (figure 10b). The cauliflower-like top of the jet concerns of very small metal grains with intense twinning (lower part of figure 10c), but also without melting indications. The porosity between these grains is a residual of the porous matrix as shown in figure 3. The internal structure of the grain in which the jet has impacted is marked by intense deformation bands and partially elongated copper grains (figure 10d, lower part) and also with completely absence of melting.

3.4. EBSD-investigations

The EBSD-results of all samples are given in figure 11. Opposite to the complete melting with columnar structures in the sample with upwelling and solidified upstream jet (sample SN50, figure 11a), the sample with a Cu-powder-porosity of 2.0 and with precursor (sample SN69, figure 11b) shows in areas without vacuoles no indications of melting. The crystallites of the primary copper grains are strongly fragmented into smaller units only on its rims; the orientation of the resulting small grains is random without any relation to the parental crystallites. Intense microjetting was not observed, the beginning of jetting was stopped in the spaces between the former copper particles, filled with Si-bearing high-pressure phases. Furthermore the crystallites in the central areas of the grains are often twinned. In the case of sample SN50 the base of the columnar structures (so called “chill zone” [31]) is separated from the sample holder.

The copper crystallites of sample Cu3 in the core of the cauliflower-like impacted jet shows a grain size much smaller then the crystallites in the starting material (figure 11c), but without any plastic deformation, with polyhedral shape and random orientation. The distortion and the twinning of the crystallites, embedding the jet, is also clearly visible and the elongation of the crystallites at the base of the jet too. Only in very small areas columnar structures as indicator of melting processes do occur. The microjet has its root in the central part of its parental grain opposite the former vacuole, but at the boundary between two grains indications of a second type of jetting are already visible (upper part of figure 11c).

The most intense jetting is visible in figure 11d (sample Cu2). Here the central parts of the source grain and also the boundary between two neighbored grains shows very intense jetting. The primary crystallites on the rims of the jetted materials show intense fragmentation, but were never molten. The fragmentation of the impacted grain is very intensely with resulting crystallites down to the nanoscale and with random orientation, but without any plastic deformation and angled shape of the small crystallites. The jets lose their cauliflower like structure.

4. Discussion

The behavior of copper powder in the bulk pressure range from 33 to 35 GPa (1.22 < $U_p$ < 1.36 km/s) with comparable initial porosities varies from samples with complete melting (sample 50) to the coexistence of molten and solid areas in one sample in different ratios. Simultaneously,
Figure 10. SEM-images of the central part of sample Cu3: inlay—position of the investigation area; dotted rectangle—position of EBSD-measurements; arrows below letters—direction of incident shock; a—overview of the sample structure with slightly deformed grains with preserved internal structure, gaps without any annealing effects between the grains and microjetting parallel the incident shock into the neighboring grains (BSE-image); b—detail of the base of a microjet with elongated crystallites and preserved porous matrix of the starting material (BSE-image); c—detail of the cauliflower-like top of the impacting jet with angled small copper crystallites and preserved porous matrix. Intense twinning of the crystallites is found in the lower part of the image (BSE-image); d—overview of the impact zone of the neighboring grain with partially elongated and twinned grains in the disturbed grain (BSE-image); e—detailed image of a microjet, used for the EBSD-measurements (SE-image).

remnants of very intense microjetting are visible. Because the shock loading conditions of all four samples were very similar, it is possible to localize the reason of this different behavior only
Figure 11. EBSD-pictures of copper powder after shock experiments: arrow—incident shock; a—sample SN50 with chill zone, columnar structures and beginning equiaxial zone on the top (please note that this picture is rotated 180° clockwise compared with figure 5; length of the scale bar 200 µm); b—sample SN69 without melting and with stopped micro jets (lower part) and fractionation of the Cu-grains at their rims (black areas—Si-bearing phases, length of the scale bar—50 µm); c—microjet from sample Cu3 with its root in the center of the source-grain, very small columnar structures in the lower part and fractured angled Cu-crystallites in the center (black—free spaces; all other areas do not show indication of melting, only elongation and twinning; black—free spaces; length of the scale bar 20 µm); d—microjet from sample Cu2 with roots in the center and the rim of the source grain, intense fractionation of the rim of the source grain in all areas, including the jets, intense fractionation of all impacted grains without any plastic deformation and intense twinned internal areas of the source grain (black—free spaces; length of the scale bar 20 µm).
Figure 12. Relations between shock Hugoniot, melting and evaporation curve and release curves, based on the explanation of Antoun [15] under assumption of $T = T_{\text{shock}}$: point 1—peak pressure along the Hugoniot, finishing of the loading path; point 2—intersection of the release curve with the melting curve, melting processes in the sample do occur after this point is crossed; point 3—intersection of the release curve with the two-phase region liquid–gas, partial evaporation; point 4—end of the release process without any melting at the final volume $V_{4\text{end}}$; point 5—end of the release process under conditions of partial and/or complete melting at the final volume $V_{5\text{end}}$ with $V_{5\text{end}} > V_{4\text{end}}$.

on the release path and to explain the melting behavior as observed in all experiments with the $P = f(V_0 - V)$-function using the graphical explanation of Antoun [15] (figure 12) with the assumption of a constant temperature equal the shock temperature $T_{\text{shock}}$.

In the sample SN50 and SN69 areas with formerly molten and now columnar recrystallized grains are in every case surrounded by free spaces. In the case of sample SN50 this concerns the whole sample because the top of the container was upwelled by a reflected shock wave from the sample piston (figure 13a), because the impedance corrected system lacks in this case, which results in an additional free space, surrounding the sample (figure 13b).

In this case the cooling behavior of the sample follows the line between point 1 and point 3 along the release path in figure 12 to a molten state and a solidification of the sample under ambient pressure to point 5. This additional free space associated with complete melting by upwelling concerns all six samples for the successful synthesis of 100 wt % $\gamma$-Si$_3$N$_4$ [19]. The important role of this additional free space is also given in figure 3a with an unmolten sample at 48 GPa bulk pressure (without additional space) and a completely molten sample (with additional free space) at 31 GPa (figure 3b). The initial porosities in both cases were comparable (approximately 1.8). In the case of melting the high-pressure phase is completely separated from the metal.

Furthermore the separation of the complete columnar structures together with the chill zone [31] from the sample holder (figures 5c and 11a) indicates a separation after solidification of the molten metal. In this case the forming at least of the chill zone was completed before finishing of the shock wave reflections from the sample piston (this experiment was performed before the
Figure 13. Appropriation of additional free space for the melting processes in the sample powder by upwelling of the container top: a—container of experiment SN50 before cutting with upwelling; b—schematic explanation of this process with the additionally free space, the solidified Mach stem (figure 4a) and the line of theoretical position of the container top without upwelling.

The development of the impedance corrected container [20]). The heat sink for the recrystallization of the molten metal was the sample holder (position of the chill zone).

The sample SN69 shows molten zones only as rim around vacuoles in the right part of the sample (figure 6e, f). The heat sinks in this case were the unmolten grains (base of the columnar zone).

In the case on the samples Cu2 and Cu3 the explanation is more difficult because the samples show melting processes without a clear association with visible free spaces. If the copper-foil between container top and sample lacks welding processes between container and metal powder are possible (figure 9). Also microjetting effects will take place in this region in an early stage of shock, indicated by the strongly deformed copper grains at the rims of this jetting structures (figures 9b and 9c). This behavior is comparable with the experiments by Mali [34] and Kozin & Simonov [33]. Reason for this jetting are the unevenness in the container top by the turning process.

During the time of decompression the container top moves few millimeters upward (but much less as in the case of upwelling by reflected shock waves) and because the sample is in the hot and compressed state, it is now composed with the moving steel top and the complete sample will expand too. Assuming the same upward movement in the samples Cu2 and Cu3 the relatively volume increase in the sample with the higher porosity (Cu2) will be also result in a higher degree of melting (table 2). For this reason the sample Cu2 shows complete melting except a thin layer near the sample holder. This “cold boundary layer” after Nesterenko [32] is the result of a very low degree of increasing additional free space in the lower part of the sample and not the result of any difference of temperature. The role of adiabatic decompression was underestimated in his work. The additional copper foil is able to avoid the welding by jetting processes in the upper part of the sample completely.
The sample SN69 shows the highest mismatch between height after decompression and theoretical height without additional volume (table 2). The additional volume in this work is defined by the mismatch between the theoretical final volume (copper powder and high-pressure phase are in the solid state) and the real measured volume after sample recovery. But in this special case degassing processes of the precursor Si$_2$N$_2$NH plays a very important role. The synthesis of the HP-phase $\gamma$-Si$_3$N$_4$ follows the chemical decomposition reaction [35]:

$$3\text{Si}_2\text{N}_2\text{NH} \rightarrow [\text{HP}]2\gamma - \text{Si}_3\text{N}_4 + \text{NH}_3.$$ 

The formed ammonia fills the vacuoles and expands the sample; it forms vacuoles, often surrounded by molten rims, and is the main reason for these higher differences.

In sample Cu2 the heat sink was the thin unmolten layer and in sample Cu3 it is located at the lower part of molten band, which is located in the upper third of the sample. The reason for this positioning is visible in the inlay of figure 7 with beginning spall fracture in the upper third of the container top (comparable to the relative position of the molten band in sample Cu3) by expansion processes at the intersection points of different reflected shock waves [15]. A graphical explanation of this behavior gives figure 14, based on Antoun [15] and figure 15. Because the hot metal powder expands in upward direction, following the container top (figure 15c), the first crystallization will take place in the lower parts of this band, visible in the sample as asymmetric column structures from the bottom to the top. The region of shock wave intersections defines the localization of the weakest zone in the sample in its upper part. In the case of samples with copper foil between sample surface and container top a gap between container top and sample does occur (figure 15d), the decompression of the sample is limited and smaller as the movement of the container top. The melting will be strongly reduced or complete avoided.
Figure 15. Schematic representation of different states of the container unit in a shock wave experiment: a—container before the experiment; b—container in time of peak pressure, all parts are compressed maximally; c—decompression without copper foil, the sample moves upward together with the container top, resulting in partially melting; d—decompression with copper foil, sample and container top are separated, without melting of the metal powder; e—partially melting of Cu-powder at its rims of the sample holder by expansion into the gap between container and sample piston.

Furthermore the copper foil is able to reduce melting effects by decompression at the rim of the samples (figure 15e). This decompression and melting in the outer parts of the samples are visible in the inlay of figure 8 (not usable areas) and in the inlay of figure 7 too, here indicated by an increasing number of bubbles in the lower left corner. The reason for this onset of melting is a beginning sample flow outside the sample holder at this corner, resulting in an increase of the volume in this area. For this reasons this thin foil is able to reduce the melting rates significantly and it is required to get comparable results for different shock wave experiments, because it seals the sample also on the rims.

In this case the differences between experiments are limited to the loading path alone and the release path with its difficult (and often random) cooling behavior will be excluded. On
Figure 16. Schematic cooling curves (temperature versus time) for the case of a complete molten and a complete solid sample at the same shock temperature in relation to the maximum temperature stability at room pressure of $\gamma$-$\text{Si}_3\text{N}_4$ [36], diamond [37] and the melting point of copper [22]. Explanations are text.

The metal in the solid state (sample SN69, central areas of sample Cu3) shows a steady cooling behavior with an unkinked curve (line between point 1 and point 4 in figure 12). In contrast, the completely molten metal (sample SN50, sample Cu2) shows a kinked curve. In a first step before complete melting at beginning of decompression the cooling curve is identical to the first case. In time of adiabatic decompression, the temperature drops rapidly by consumption of melting heat (and also by the rapid decompression itself) and the curve passes very fast the maximum temperature stability of $\gamma$-$\text{Si}_3\text{N}_4$ at room pressure. This melt cools steadily to the temperature $T_{\text{melt}}(\text{Cu})$ under preservation of the HP-phase with a stability point larger than the melting point of copper. At the point of solidification the melting heat will be removed as crystallization heat, resulting in a fast and short reheating of the sample [38], it will melt and solidified again, the cooling rate follows a zig-zag-line. If this processes are finished, the hot solid copper cools steadily again and passes the thermal stability limit of diamond. Afterwards the back transformation of diamond into graphite will be stop. For this reasons the experiments with an output of 100% crystalline phase of $\gamma$-$\text{Si}_3\text{N}_4$ [19] are restricted on experiments with complete melting of the metal powder. This effect is much more important for phases with high thermal stability because the cooling time below the stability limit of diamond is comparable in both cases.

Because the samples often show a complete solidification before finishing of all shock wave reflection, marked by separation of the solidified sample from the sample holder (figures 5c and 6a) another case will be possible. If the $T = f(t)$-curve passes the melting point of copper, it melts under consumption of melting heat again, but the temperature drop by consumption of melting heat together with the adiabatic decompression itself leads to a very fast cooling.
below the melting temperature, resulting in a very fast solidification. This behavior implies a (currently not jet known) maximum pressure for the synthesis of $\gamma$-$\text{Si}_3\text{N}_4$ with high purity, because the “overheating” of the sample should be avoided.

One great advantage of the hypothesis for melting processes only on the release path is the simplified temperature calculation. Under the pressure conditions obvious for the commercial HP-synthesis it is not required to take the changes of heat capacity and enthalpy after onset of melting after e.g. Chekhovskoi [22] into account, all calculations are possible for the solid state.

The mechanical stress of the unmolten copper grains was very high, as shown by the EBSD-measurements (figure 11). This concerns the sample with microjetting and the sample without microjetting too. In both cases the internal crystallites show an intense mechanical fractionation.

But at which $P$–$T$-conditions the synthesis of HP-phases will take place (e.g. in sample 69)? The $P$–$T$-calculation using the Hugoniot-respectively the Mie–Grueneisen equation of state gives only temperatures over the whole sample. The complete and fast melting of the metal grains in the time of adiabatic decompression and the lacking of any zones with only partially molten grains indicates a temperature of the whole grain (rim and core) much higher than the melting temperature under ambient pressure. On the other hand the existence of bubbles in the solidified copper is not a sure indicator for a temperature exceeding the boiling point because this vacuoles may also occur if the volume expansion along the release path exceeds the volume of the melt.

To estimate the conditions in the areas filled with sample powder the knowledge of the jetting velocity (which is equal to the collision velocity of the jets with the copper grains in figures 10d, 7e, 11c and 11d) is required. Because an experimental determination of this micro-scale process is not yet possible computer simulations will be a helpful tool as given by Cooper et al [6]. In his work he calculated the jet velocities for two different geometries (figure 17) in the input velocity range (equal the particle velocity in the copper powder) from 0.5 to 0.85 km/s. To obtain similar data for the samples Cu2 and Cu3 the data of Cooper et al were fitted linearly for the particle velocity of 1.22 km/s and 1.32 km/s respectively.

To calculate the (theoretical) maximum peak pressure in the time of crystal nuclei growth in the free spaces it is required to calculate the pressure in the copper grain (e.g. in figure 11b). Because all phases are in the solid state it is possible to calculate these pressures with a common

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**Figure 17.** Schematic representation of two different cases after Cooper et al [6] with apex-case (a) and base-case (b).
Table 3. Jet velocities $U_j$ and resulting theoretical maximum collision pressures $P_m$ with data after Cooper et al [6] for the impact of the jet into a neighbored copper-grain. Asterisks denote calculated values with KEOS5 [40] using of the particle velocity of experiment Cu2 and Cu3.

| Sample | Input velocity, km/s | $U_j$ (apex), km/s | $P_m$, GPa | $U_j$ (base), km/s | $P_m$, GPa |
|--------|----------------------|--------------------|------------|--------------------|------------|
| 0.500  | 4.206                | 134                | 6.317      | 246                |
| 0.620  | 4.691                | 157                | 6.514      | 257                |
| 0.800  | 5.774                | 214                | 8.358      | 380                |
| Cu3    | 1.22*                | 7.431*             | 316*       | 10.512*            | 548*       |
| Cu2    | 1.36*                | 8.060*             | 358*       | 11.370*            | 622*       |

solid-solid collision for equal materials on both sides. For this calculation, the shock wave database [39] containing the caloric equation of state KEOS5 [40] were used. The results are given in table 3.

Because the copper grains show jetting after the base- and also after the apex-case, it is required to calculate the pressures for both cases. Despite the fact that the jetting conditions for the sample Cu2 were significantly higher than in sample Cu3, the head of the cauliflower like jet in the sample with the lower initial porosity shows small columnar structures, indicating melting processes. One explanation for this behavior may be the internal structure of the used Cu-grains with internal large vacuoles (figure reffig2a). In this case, a locally adiabatic decompression in the microscale, followed by melting, in the head of the jet itself is possible.

5. Problems and uncertainties

At first, because the used jetting-model is very sensitive against changes in the width of the shock front [6], the pressures in table 3 are approximated values. After Nesterenko [32] the shock front width in porous media is similar to the diameter of the grains in the porous media. But for the copper powder used in this work two possible diameters do exist: the diameter of the single grain, separated by vacuoles, sometimes filled with precursors (figure 2a, b) and the diameter of the internal crystallites, separated by a porous matrix (figure 2c). For this reasons the shock front width and the correct pressure at the collision point of the jet, given in table 3, are currently first assumptions.

Another question is the melting point of copper on the Hugoniot. Dai [41] gives for this parameter a value of 196 to 210 GPa. On the other hand in the work by Milyavskii [24] it was possible to calculate the equation of state for porous copper up to 480 GPa without any melting and also Errandonea [42] and Japel et al [43] give for copper a high slope of the melting curve. Despite the uncertainties in the calculations given in this work the complete lack of melting also in the top area of the jets implies a melting point of copper along the Hugoniot far above a pressure of 2 Mbar, which does not coincide with the description by Dai [41]. Also in the work by Mamalis et al [7, 44] and Schwarz et al [8] the melting point of copper powder along the Hugoniot is, compared with this work, underestimated.

The third problem consists in the conditions at the beginning of the high pressure synthesis. The bulk pressure, given in table 1, describes the conditions under stable pressure but not in the time of pressure build up. The given jet pressures are calculated for the conditions of a completely free space between the samples, but not for vacuoles filled with precursors for the high pressure synthesis. In the second case the micro jetting is strongly reduced. But where is the kinetic energy? Will it be completely stored in the sample powder and the shock wave synthesis starts in the higher Mbar range or should a calculation with lower pressures be possible because the high jet velocities will never be reached? Also the time span between room pressure and
stable bulk pressure (and for this reason also the time for crystal nucleation) depends strongly on the grain size and is also not yet solved.

6. Conclusion
Under a given reference pressure of about 35 GPa four experiments with similar porosities were performed. This pressure is comparable with the commercially used synthesis conditions for refractory materials (diamond, cubic boron nitride, $\gamma$-Si$_3$N$_4$, rs-AlN).

The behavior of the samples varies from complete melting over partial melting to a complete unmolten state in different parts of the samples. Because the single variable was the degree of adiabatic decompression it is possible to reduce the reason for the observed differences to the degree of adiabatic decompression alone. It was also possible to solve the “cold boundary layer”-problem after Nesterenko [32] as decompression with limited additional free volume on the base of the sample.

A very important role for the control of this decompression plays not only the sample capsule, composed of different materials simultaneously for the impedance correction, but also an additional copper foil on top of the copper-sample powder mixture is very important. This foil avoids welding processes between sample and container top. With this property it controls the degree of decompression, induced by an upward movement of the container top, alone. Furthermore it seals the sample against container and for this reason it is able to avoid decompression processes also on the sample rims.

It is possible to postulate that the characteristic feature of porous copper under the commonly used conditions for the industrial synthesis of refractory materials under shock loading up to 35 GPa is the solid state. This includes also all kinds of jetting phenomena and the grain boundaries too. For this reason it is not required to take the changed values of heat capacity and entropy for the $P$–$T$-calculations into account, all calculations are simple solid state calculations.

Furthermore the melting effects by decompression are able to change the cooling path and influence the back transformation behavior of synthesized high pressure phases. Especially for nitrides with a higher thermal stability the melting of the copper matrix may be an advantage.

Without the consideration of decompression effects a comparison of shock experiments, performed in different laboratories, is very difficult. For this reason a description of the decompression behavior (e.g. in the table of the experimental data) will be helpful. With methods here discussed it is possible to delimit the uncertainties in shock synthesis experiments to the loading path alone. Nevertheless, the experiments in this work rise few new questions, i.e. the jetting conditions, the melting point of copper along the Hugoniot and the conditions in the time of beginning of shock synthesis itself.

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