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SPRAY FORMING OF COPPER BASED MATERIALS

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ABSTRACT

The properties of spray deposited materials are critically determined by a number of process parameters, such as the superheat of the melt, the atomisation gas pressure, the ratio of the flow rate of the molten material and the atomisation gas or the flight distance of the disintegrated droplets. This presentation reports on examinations ofthe infiuences of various process parameters on the spray deposition behaviour, the resulting microstructure development and the mechanical properties of copper based materials. The investigations were at fust focused on pure copper to eliminate influences of alloying elements. The microstructure and porosity development of pure copper showed a well defined deuendence on process parameters and process technology as well as a sensible reaction on temperature distribution within the deposited products. While mostly billets had been sprayed, some results gained from the spraying of sheet material are also shown and discussed to demonstrate the special aspects of different product forms.

INTRODUCTION

Spray deposition is the inert gas atomisation of a liquid metal stream into variously sized dropiets, which are then propelled away from the region of atomisation by the fast flowing atomising gas. The droplet trajectories are interrupted by a substrate, which collects and solidifies the droplets into a coherenf near fully dense preform. By continuous movement of the subsbate relative to the atomiser as deposition proceeds, large preforms can be produced in a variety of geometries including billets, tubes and sheets (Figure 1). The combination of a rapid solidification of the droplets during atomisation with cooling rates of $10^3 - 10^5$ Ws [1] and a subsequent slower cooling ofthe bulk material after deposition is characteristic for the spray forming process. The resulting material properties are critically determined by a number of process parameters, such as the superheat of the melt, the atomisation gas pressure, the ratio of the flow- rate of the molten material and the atomisation gas or the flight distance of the disintegrated droplets. By optimisation of these parameters, the spray deposition process becomes suitable to produce homogeneous, segregation free materials with fine equiaxed grain structures, increased solubilities of alloying elements and small sized precipitates [2, 3]. A prerequisite for the optimisation and successful operation of the spray deposition process however mandates a knowledge of the effect of each process parameter and its interference with the other ones on preform shape, microstructure and mechanical properties for the relevant base materials and its alloys.

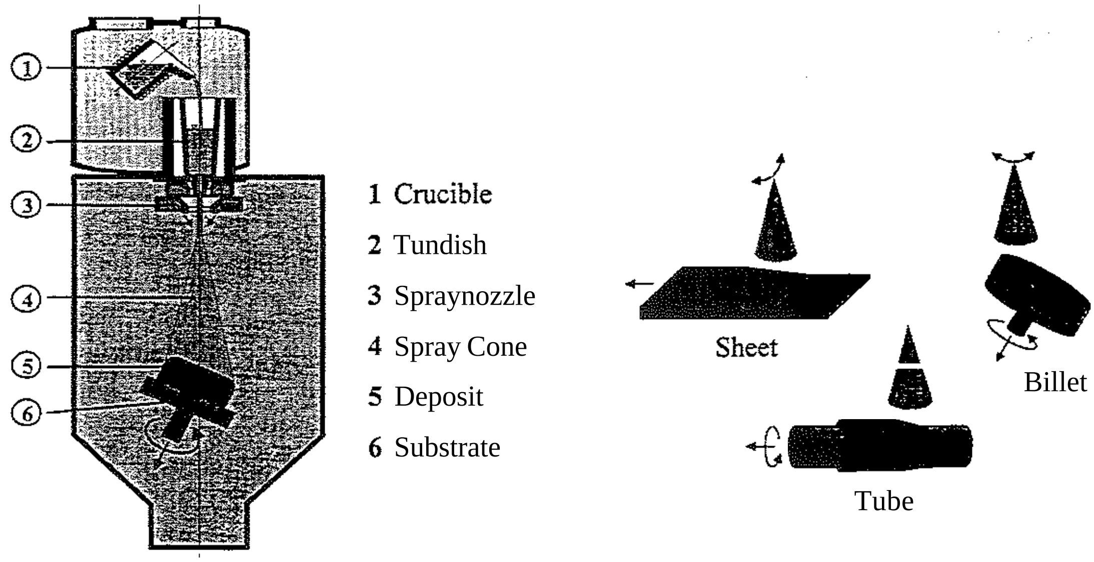


Figure 1. Schematic view of an experimental spray forming facility and of spray formed products

The compiling of the necessary understanding of the entire process is the main objective of the special research program "Spray Forming" (SFB 372) at the University of Bremen. For the achievement of this objective the SFB 372 follows a widespread, interdisciplinary approach, where steel, copper and its alloys as well as aluminium alloys (in future) both unreinforced and particle reinforced are the materials under consideration (Figure 2).

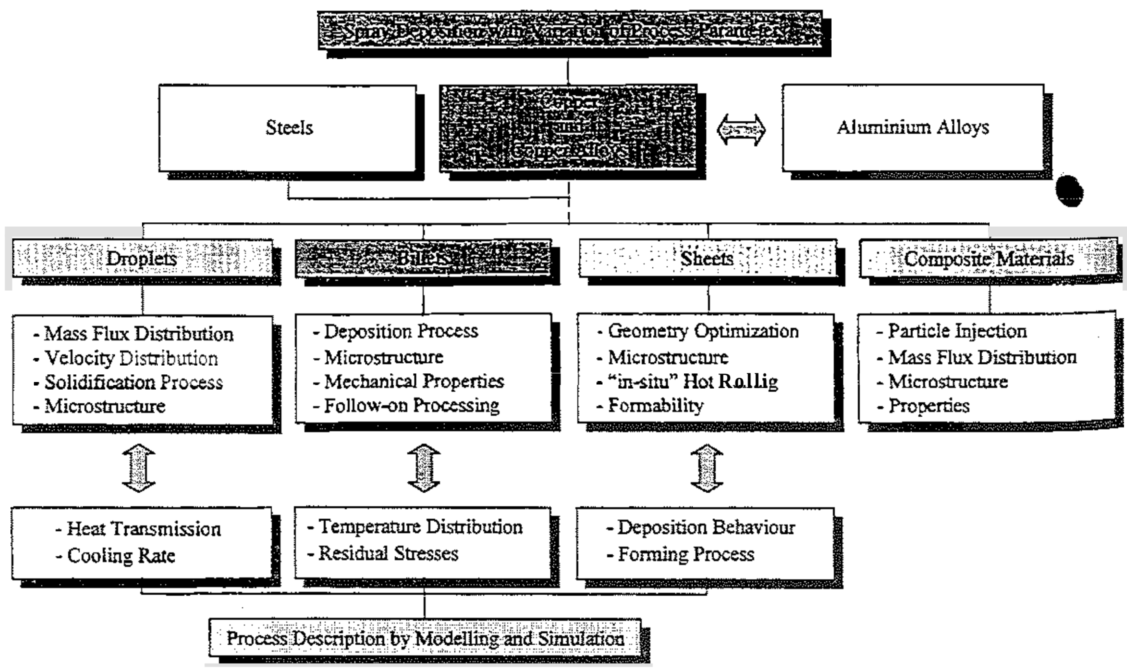


Figure 2. Overview of the interdisciplinary research activities in the field of spray deposition at the University of Bremen

The experimental parts of the research activities comprise the performance of spray deposition experiments with variation of process parameters subdivided into the deposition of billets and sheets as well as of droplets for the examination of more fundamental aspects. The evaluation of these expenments considers aspects as the development of the microstructure, the resulting geometry, mechanical properties and follow-on processing in dependence on the product form. The evaluations are rounded off by an intensive feedback with the analytical parts of the program, the modelling and simulation of the process. The present article descrihes mainly the experiments and results for pure copper billets supplemented by results for pure copper sheets, which cover the influence of different product forms.

EXPERIMENTAL ASPECTS

All described spray deposition experiments had been performed in the spray forming pilot plant at the University of Bremen. Its main technical data is given in Table I The spray forming unit is equipped with a single "free fall atomiser" unit with a scanning system. It can be used for the spray fonning of billets. sheets and tubes. Especiallv for the generation of flat products a linear substrate motion has to be combined with an atomiser oscillation with high scanning angles. With its spray chamber dimension of 1.2x2 m, a melting power of 50 kW and a melting capacity of 5 litre copper billets of up to 160 mm diameter and 200 mm height and sheet material with a typical size of 600x158x20 mm can be sprayed.

Table I. Technical data of the spray forming plant at the University of Bremen

Melting Unit	Melting Power [kW]	Melting Capacity [l]	Metal-Flow-Rate [kg/s]	Atomizer Unit	Atomizer Gas	Max. Gas-Flow-Rate [kg/s]	Chamber-Dimension [m]	Deposit-Shapes
inductive	50	5	0.1-0.5	"free fall atomizer" with scanning system	N_2, (Ar)	0.5	1.2x2	Billets, Sheets, Tubes

The material used for the present study was disintegrated by N_2 gas. As described later, the essential process Parameters investigated had heen the superheat of the melt AT, the gas (over-)pressure p or rather the gas/metal-ratio GMR and the atomiser-deposit distance z, which had been varied in the range of ΔT=200-350 K, p=1.5-4.0 bar and z=500-600 mm respectively. The melt flow rate was kept constant at 0.217 kg/s so that the range of the gas pressure corresponded to a GMR of 0.69 to 1.35. In the following the GMR will be added within brackets behind the values for the gas pressure.

For microstructure analyses of the sprayed billets discs of 10 mm thickness were sawed out of the middle of the deposit and halved. One half of each disc was macro etched, the other was used for density measurements. Mechanical properties of the sprayed billets were evaluated by Vickers hardness testing (HV 0.3/25). To avoid faulty measurements regions with extremely high porosity were not considered.

Sprayed pure copper demonstrates a well defined dependence of the microstructure and porosity development on the process Parameters, especially on the superheat of the melt and the gas pressure. Figure 3 to 5 illustrate the microstructure evolution and the measured density distribution within the billets in dependence on an increased superheat of the melt. The gas pressure was kept constant at 2.5 bar (GMR=0.95) as was the atomiser-deposit distance of 600 mm. A superheat of the melt of 200 K resulted in a fme equiaxed grain structure with an average grain size of 20 µm (Figure 3). Furthermore, the deposit showed a high porosity, especially in the upper central region and at the lower edge with measured densities of 88 % and 77 % of the theoretical density respectively. In the middle ofthe billet a density of 96 % maximum and a hardness of 42 HV were measured.

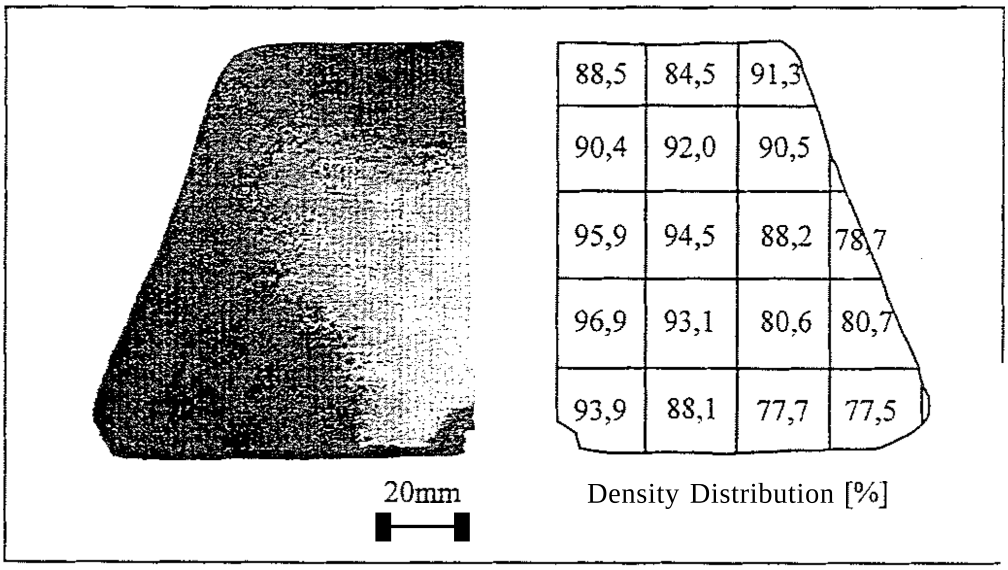


Figure 3. Cross section of a billet, sprayed with ΔT=200 K and p=2,5 bar (GMR=0.95). Macro etching for microstructure analyses (left) and density dismbution (right)

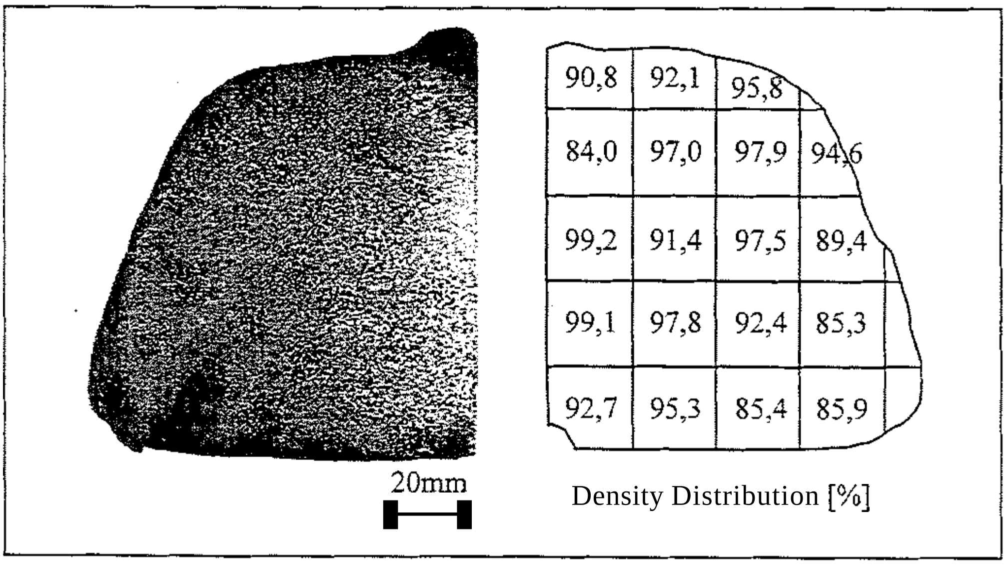
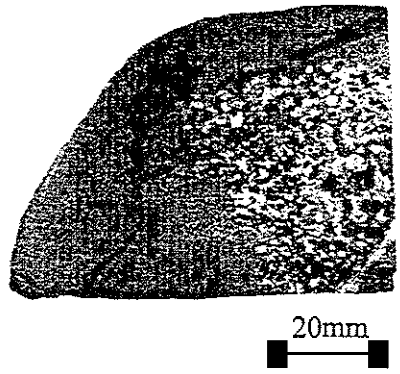


Figure 4. Microstructure development (left) and density distribution (right) of a billet, sprayed with ΔT=300 K and p=2,5 bar (GMR=0.95)

When the superheat of the melt was increased from 200 K to 300 K (Figure 4) the average grain size of the deposits increased from 20 µm to 50 µm. In addition to the general increase of the grain size a region with significantly larger grain sizes of up to 150 µm developed in the centre of the billet, which was caused by secondary grain growth during the cooling of the billets especially after deposition. The heat from the bulk material was removed rather slowly to the environment and to the substrate, so that the temperaiure in the centre section remains on a high level for a considerable amount of time. The location and size of the coarse grained region corresponds to the zone with the high residual temperature, so that this region is generally called the "hot spot". The porosity of the material however decreased with increasing superheat and a material density of up to 99 % especially in the middle of the deposit was determined. Caused by the reduction ofthe porosity an increase in hardness of up to 51 HV was measured.

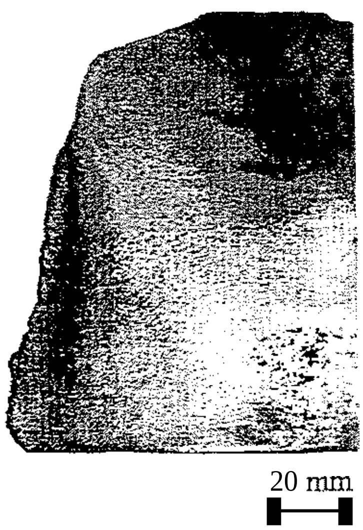
With a further increase of the superheat to 350 K (Figure 5) the grain sizes grew to 60 µm in the outer regions of the deposit, in the "hot-spot"-region grain sizes of even more than 1 mm could be measured. In the zone of the excessive grain growth the average hardness of the deposit decreased to 37 HV. The density distribution of this deposit was more uniform in contrast to the deposits sprayed with a superheat of 200 K and 300 K respectively.



98,2	98,8	98,9	
98,6	99,0	99,2	94,6
96,8	97,3	89,1	76,7

Density Distribution [%]

Figure 5. Microstructure development (left) and density disuibution (right) of a billet, sprayed with ΔT=350K and p=2,5bar (GMR=0.95)



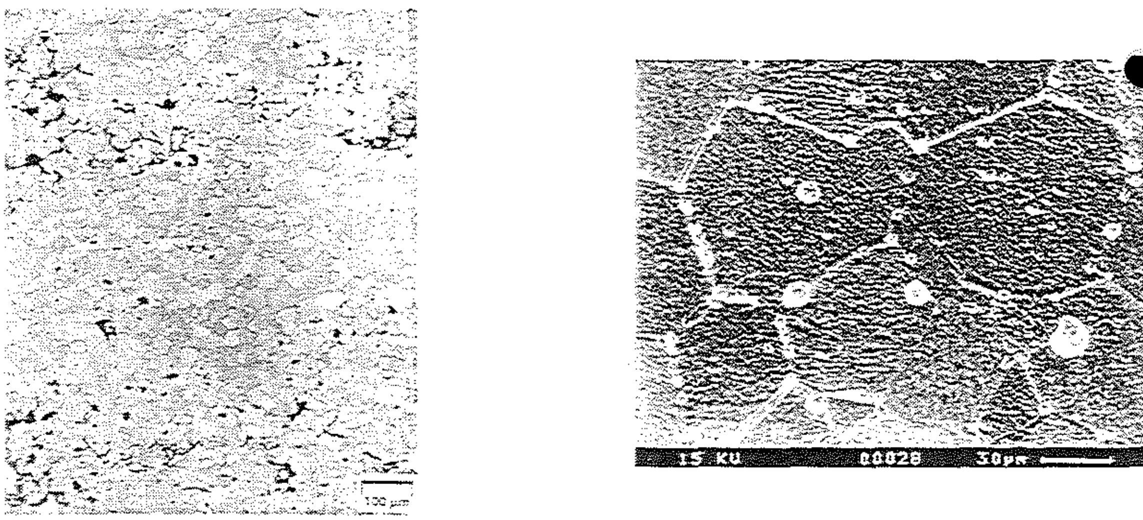
85,6	83,8	90,2	
82,9	82,6	93,9	
74,7	91,3	94,1	65,8
96,1	95,3	84,9	84,4
95,4	89,2	94,7	85,6

Density Distribution [%]

Figure 6. Microstructure development (left) and density distribution (right) of a billet, sprayed with ΔT=300K and p=4bar (GMR=1.35)

A higher gas pressure amounting from 2,5 bar (GMR=0.95) to 4 bar (GMR=1.35) led generally to decreasing grain sizes and increasing porosity in all regions of the deposits. Figure 6 shows the typical microstructure and density distribution of a billet sprayed with a superheat of 300 K and a gas pressure of 4 bar.

With the exception of the "hot-spot" region an average grain size of 35 µm was measured. In spite of tbe high porosity the average hardness amounted to 64 HV which is attributed to the fine-grained structure. Furthermore, a fine layered microstructure could be observed (Figure 6) which reflects the characteristic cyclic growing of these billets during deposition. The boundaries of the layers consist of lines of interconnected irregular pores as illustrated in Figure 7 (a). This was typical for copper billets sprayed with a gas pressure of 4 bar corresponding to a GMR of 1.35. The porosity occurs when the liquid fraction of the spray cone is insufficient to fill interstices between subsequent layers. In addition banding appears when the time between rotation over a particular area allows the original surface to solidify. Similar observations have been documented by numerous investigators 14-61.



(a) (b)

Figure 7. Appearances of porosity: (a) Optical micrograph of porosity caused by a deposition process with small fraction of liquid; (b) scanning electron micrograph of gas porosity

Another type of porosity of sprayed pure copper becomes obvious by scanning electron microscopy as it is shown in Figure 7 (b). The formation of spherical pores. especially at the grain boundaries arises from entrapped atomisation gas and is attributed to the general lack of solubility of nitrogen in copper alloys. The gas-related porosity may be reduced by adding an alloying element that reacts with the atomisation gas. Hence, the alloying element hehaves as a gathering agent for the entrapped gas and thereby prevents the formation of gas pores. The effective elimination of nitrogen caused porosity in copper alloys by zirconium has clearly been demonstrated by several groups involved in spray casting [6, 7].

A phenomenon observed for sprayed pure copper billets is shown in Figure 8. During spray forming a conical region of insufficient compaction grew up symmetrically to the top of the deposit. The surface morphology looks like a "cauliflower"(Figure 8 (a)). Scanning electron microscopy exhibits an abrupt transition from the sufficiently deposited material to the "cauliflower"-region (Figure 8 (b)) which contains a high fraction of completely solidified particles (Figure 8 (c)). A comparison with the spray forming behaviour of different steels where no "cauliflower" could be observed lead to the suggestion that the "cauliflower"-formation may be supported by the high thermal conductivity of pure copper.

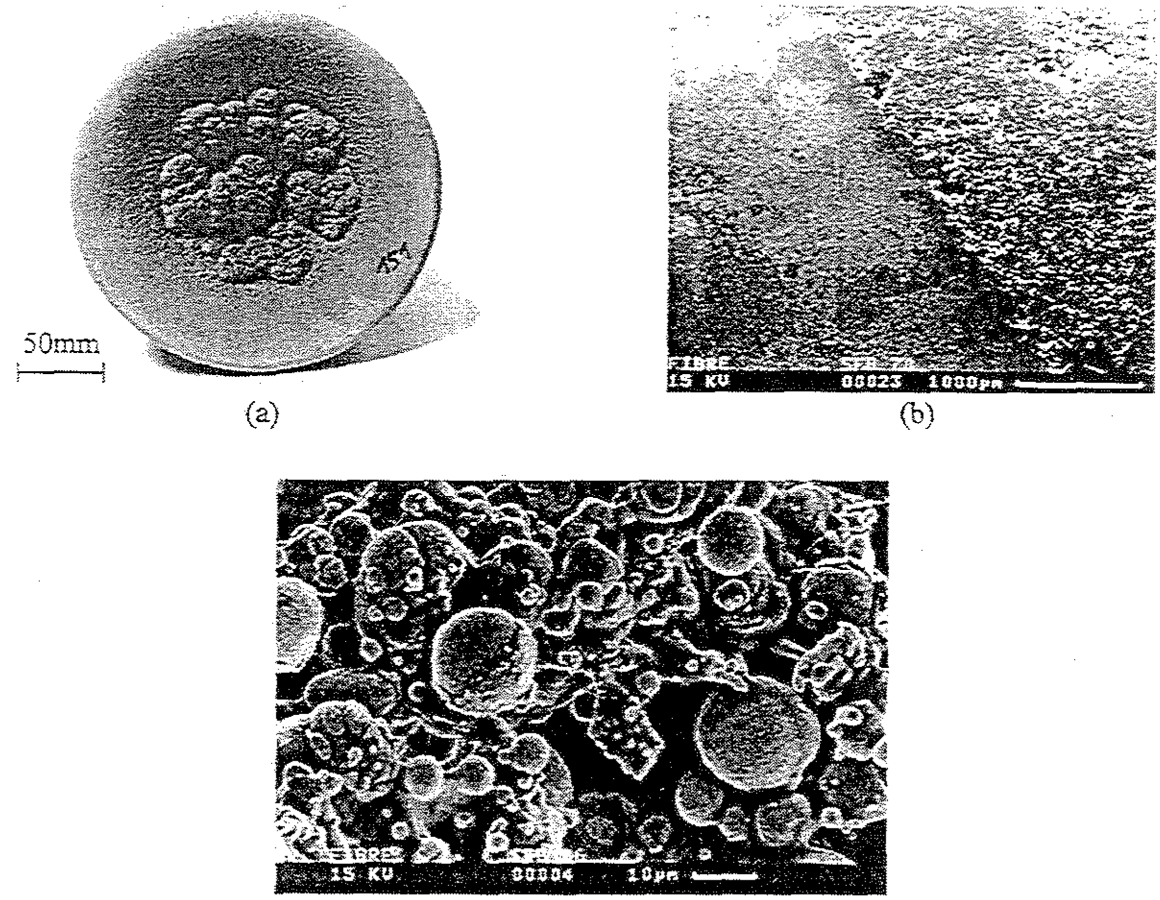


Figure 8. Surface morphology of the „cauliflower"-phenomenon (a); scanning electron micrographs of the transition from the completely deposited material (left) to the "cauliflower"-region (nght) (b) and its high fraction of solidified particles (c)

Initial investigations [8] showed, that in addition to the core process parameters the specific process technology, e.g. the configuration and motion of the substrate or the scanning of the atomisation nozzle influence the "cauliflower"formation decisively. Increasing the superheat of the melt and/or decreasing the gas/metal-ratio reduced the "cauliflower" regions within the billets but did not prevent it completely. Only after a supplementary geometrical rearrangement of the substrate related to the spray cone combined with an adjusted transverse substrate motion during deposit growing led to improved results. Furthermore, the scanning of the atomisation nozzle supported a more uniform deposit growth which counteracted the "cauliflower" formation.

SOME SPECIALITIES OF FLAT PRODUCTS

Although not being the main topic of these investigations, some aspects and results of spray forming of flat products will also be presented to demonstrate the considerable influence of the product geometry. In comparison with sprayed formed billets flat products are characterised by a high ratio of surface to volume so that the microstructure development is more critically determined by the heat transition from the bulk material to the substrate and the upper free surface. Therefore, flat products tend to develop higher porosity in the cooler peripheral regions (Figure 9 (b)), an effect, which has also been found for aluminium and steel strips [9, 10].

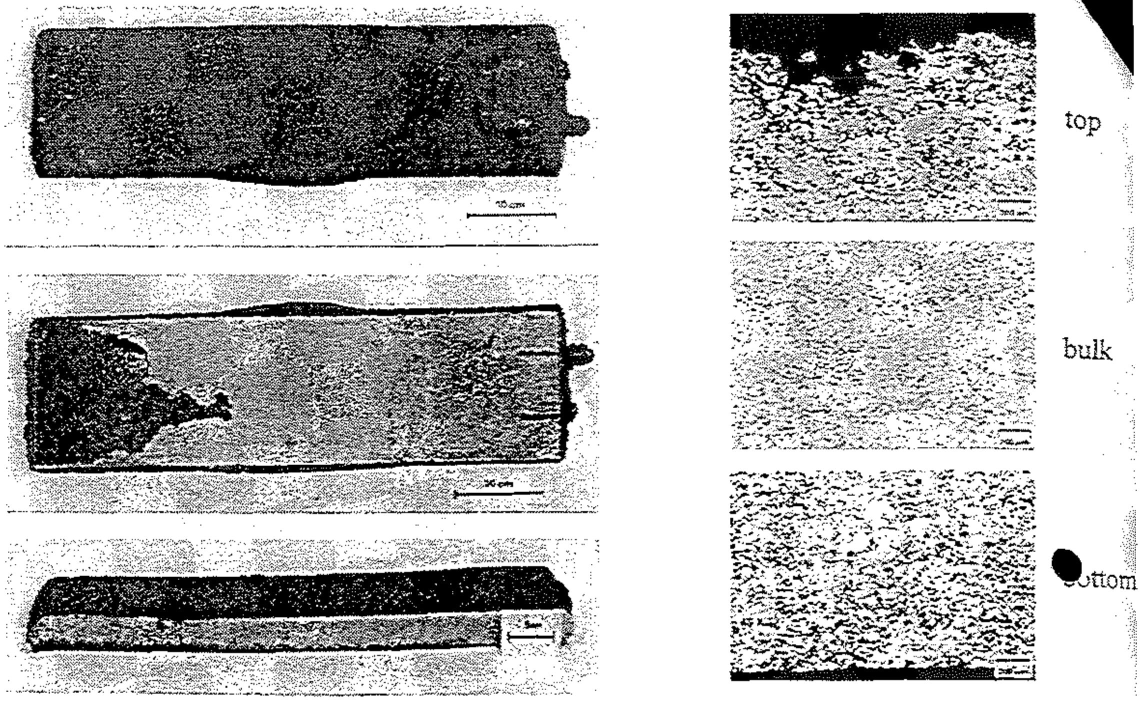


Figure 9. Spray formed copper strip (a) and the porosity distribution within the as-sprayed structure of pure copper (b)

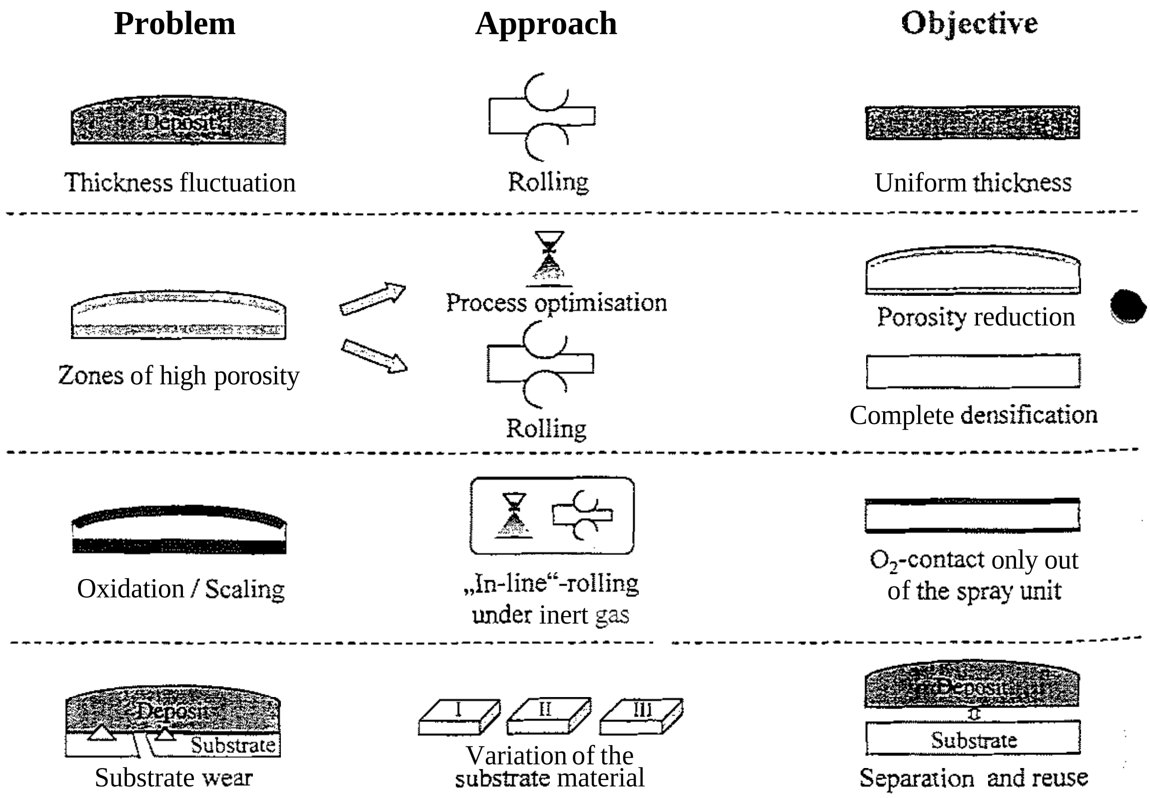


Figure 10. Schematic description of the deficits of spray formed *flat* products and approaches to quality improvement

As for the spray formed billets the amount of porosity could be minimised by increasing the superheat of the melt and decreasing the gas/metal-ratio. While the bulk section of a flat product may be sprayed pore free, the porosity at the surfaces ofthe flat products couldn't be avoided by changing the process parameters alone. An approach for further improvement is the use of substrate materials with low heat conductivity and evenly heated Substrates, while complete densification may only be achievable by an additional rolling process. The large surface fraction of flat products and the high porosity of the outer regions also imply a danger of excessive oxidation of the product. Generally this would prevent the achievement of a high quality product even by post-processing, so that a hot rolling step under inert gas "in-line" with the spray process has to be developed [10]. As can be seen in Figure 9 (a), a further problem for flat products is the fluctuation of the cross section i. e. the height and the width of the deposits caused by a mismatch of spray cone and deposit movement. The described problems and approaches to their solving are schematically summarised in Figure 10.

CONCLUSIONS

The development of the microstructure and the amount of porosity of spray formed <u>pure</u> copper billets are very sensitive to the variation of the most important process parameters, the superhear of the melt and the gas pressure. A fine grained microstructure can be achieved with a low superheat of the melt and a high gas pressure, but both settings result in a high amount of already solidified particles in thc spray cone causing a higher porosity. The formation of porosity in sprayed pure copper can only be minimised by the variation of relevant process parameters but not prevented completely. Up to now pore-free copper deposits could only be achieved by adding specific alloying elements. Due to their higher share of surface areathe development of the microstructure of flat products is determined to a large extent by the heat fluxto the substrate and to the environment. Especially the porosity of the peripheral regions cannot be eliminated completely by optimisation of the process parameters alone but may lead to the establishing of suitable post processing steps, e.g. "in situ" hot rolling under protective atmosphere to achieve good product qualities.

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REFERENCES

[1] E.J. Lavernia, Y. Wu, *Spray Atomisation and Deposition*, John Wiley & Sons Ltd., Chicester, UK, 1996

[2] S. Annavarapu, D. Apelian, A. Lawley, "Processing effects in spray casting of steel strip", *Metallurgical Transaction A*, Vol. 19A, 1988, p. 3077-3086

[3] D. Apelian, A. Leatham, G. Gillen, "Near net shape manufacturing via the osprey process", *Processing of Structural Metals by Rapid Solidification*, Orlando, Florida, 1986, p. 107-125

[4] S. Annavarapu, R.D. Doherty, "Evolution of Microstructure in Spray Casting", *International Journal of Powder Metallurgy*, Vol. 29, No. 4, 1993, p. 331-343

[5] R.D. Payne, A.L. Moran, C.J. Madden, P. Kelley, "An Optical Roughness Sensor for Real-Time Quality Measurement", *Journal of the Minerals, Metals & Materials Society*, Vol. 43, No. 10, 1991, p. 18-21

[6] W.G. Watson, "Thermal and Microstructural Characterization of Spray Cast Copper Alloy Strip", *First International Conference on Spray Forming*, Swansea, UK, 1990; p. 23.01-23.20

[7] S. Ashok, "Evolution of Microstructure of Cu-4wt%Zr Alloy Formed by Spray Casting", *International Journal of Rapid Solidification*, Vol. 7, 1993, p. 283-293

[8] N. Jordan, H. Harig, "Sprühkompaktierte Kupferbasis-Werkstoffe – Stand der Forschungs- und Entwicklungsarbeiten", *Kolloquiumsband "Sprühkompatieren"*, Vol. 3, 1998, p. 31-52

[9] M.G. Chu, "Microstructure of Aluminium Alloy Deposits Produced by Spray Forming Using a Linear Nozzle", *Third International Conference on Spray Forming,* Cardiff, UK, 1996, p. 27-35

[10] E. Brinksmeier, M. Schünemann, Th. Brockhoff, "Spray Forming and Rolling of Low Carbon Steel", *Production Engineering,* Vol. 6, No 1,1999, p. 7-10