Spray-Formed Materials for Low Temperature Superconductors

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0. Abstract

During the production of super-conducting multi-filamentary Nb_3Sn-wires after the bronze method, copper tin billets are extruded and furtheron together with niobium rods co-extruded, drawn and annealed to form the super-conducting Nb_3Sn-phase.

Prior to the introduction of spray-formed high-tin bronze, only cast copper tin billets were available. The cast billets have to be exposed to prolonged homogenisation treatments in order to minimize the segregation formed during solidification. Then they are able to be extruded.

Spray-formed high-tin bronzes have a lot of advantages which are beneficial to the production process of super-conducting Nb_3Sn wire. The microstructure of spray-formed bronze billets is fine grained with significantly reduced microsegregation. Homogeneous intermetallic phase distribution allows the elimination of the initial heat treatment and rises overall process stability during further hot and cold work.

1. Introduction

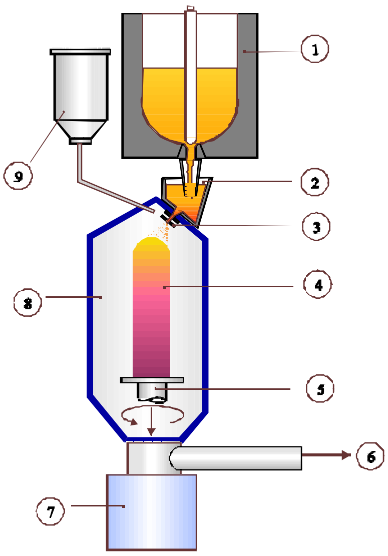
Super-conducting magnets with magnetic field strength up to 22 Tesla are usually low temperature superconductors which run at liquid helium temperature. The super-conducting material is Nb_3Sn, produced by the bronze method. This type of magnets are applied in Nuclear Magnetic Resonance (NMR) spectrometers for analytical applications and in magnets for nuclear physics.

Nb_3Sn is a brittle inter-metallic phase, and so it is not a metallic material which can be produced and brought into the shape of a wire by normal industrial melting, forming and machining processes. It must be produced by co-working of the metals Niobium and bronze until the compound has the shape of a wire. Finally a diffusion annealing process generates the Nb_3Sn super-conducting phase. The bronze serves on one hand as carrier for tin, on the other hand as heat and current carrying material in case of super-conductivity break-down.

This presentation introduces a class of bronzes manufactured by spray forming. This modern way of material manufacturing guarantees bronzes with homogeneous microstructure, with low segregation and with very high Tin content. All these properties favour a high quality of multi-filamentary Nb_3Sn superconductors.

2. Production Process of Bronze for Super-Conducting Nb_3Sn Wire

The Wieland-Werke AG produces high-tin bronzes for super-conducting wires by spray forming. The Osprey process for the spray forming of billets is applied, using a single atomizer (Fig. 1). Deposition rate is 30 kg/min. Growth direction is vertical. The semi-finished product is a billet with diameter between 160 mm and 500 mm and length of 2.2 m. The Wieland spray forming device and process are described in detail in [Mue01], the apdaption of process parameters for spray forming of Cu-Sn-billets in [Mue00].



1. Holding Furnace
2. Tundish
3. Atomizer
4. Billet
5. Withdrawal/rotation unit
6. Exhaust gas
7. Overspray container
8. Spray chamber
9. Particle injector

Fig. 1: Wieland spray forming unit for billets (scheme)

In order to show the long way from material production to the final product the production process of super-conducting wire is illustrated in Fig. 2 in six seperate steps:

1. Spray forming of bronze billet
2. Extrusion and cold drawing of bronze tubes and rods
3. Assembling bronze tubes and niobium rods
4. Co-working of Niobium and bronze (extrusion, cold-drawing, heat treatment)
5. coiling of wire into final shape inside the magnet
6. Generation of Nb_3Sn by final annealing process

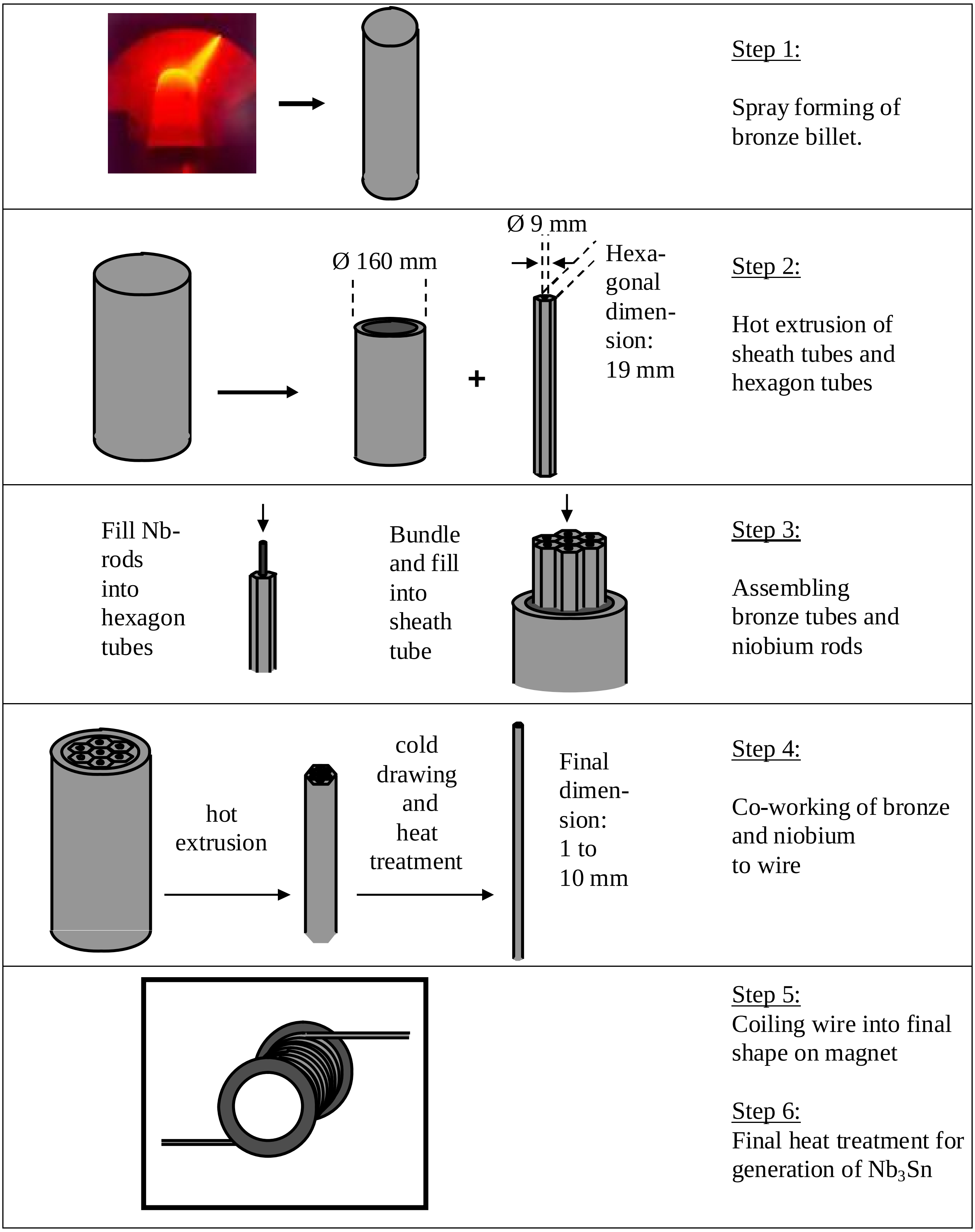


Fig. 2: Production process of bronze for super-conducting Nb_3Sn wire (scheme)

During this process a multi-filamentary composite material is generated. Fig. 3 shows a cross section through a non-stabilized type of superconductor in a production stage after extrusion and before cold-drawing of the niobium-bronze-composite (production step 4). At a first glance 120 hexagonal grey dots surrounded by bronze are visible. Each dot consists of 84 niobium filaments which also are surrounded by a bronze matrix. This matrix has been generated during the extrusion of 84 hexagon tubes of bronze (e.g. hexagonal dimension of 19 mm) filled with niobium rods (e.g. diameter of 9 mm).

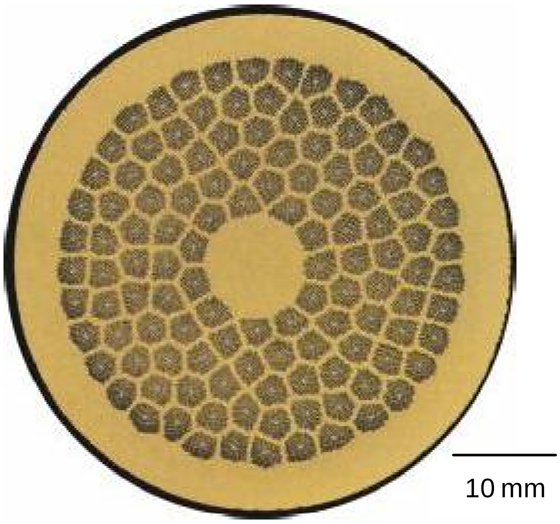


Fig. 3: Cross-section through superconductor wire in production stage after hot extrusion. Bronze matrix contains 120 x 84 = 10080 Nb-filaments, with courtesy to Vacuumschmelze GmbH Co KG, Hanau, Germany.

The following production steps are numerous cold-drawing steps and heat treatments. The dimensions of niobium filaments and bronze channels finally reach the size of 5 to 20 µm.

3. Requirements to High-Tin-Bronze Semi-Finished Material

The manufacturers of super-conducting wire need a good workability of the tin-carrying bronze. By means of forming processes the tin is brought as near as possible to the niobium. The final heat treatment lets tin diffuse to the niobium and transfers both into the Nb_3Sn phase. Accordingly the manufacturers state two main requirements to the semi-finished bronze material:

- Good hot and cold workability.
- Suitable high tin content (> 13%) and homogeneous tin distribution.

4. Advantages of Spray-Formed High-Tin Bronze

The requirements to the material are a challenge to the material manufacturer. Bronzes produced by casting processes have a high tendency to grain growth, tin-segregation and precipitation of the inter-metallic delta-phase, a copper-tin-phase with 32 to 33 % tin. These two effects are detrimental to the further production processes of the super-conducting material. Cast bronzes therefore have to be time and cost intensively heat treated before being suitable to the production process.

Spray-formed high-tin bronze billets fulfil the requirements concerning homogeneity and workability. This chapter shows the advantages of spray-formed bronze in comparison to cast material.

4.1 Grain Structure

Advantage 1:
The grain structure of spray-formed material is very fine and homogeneous, which favours good workability.

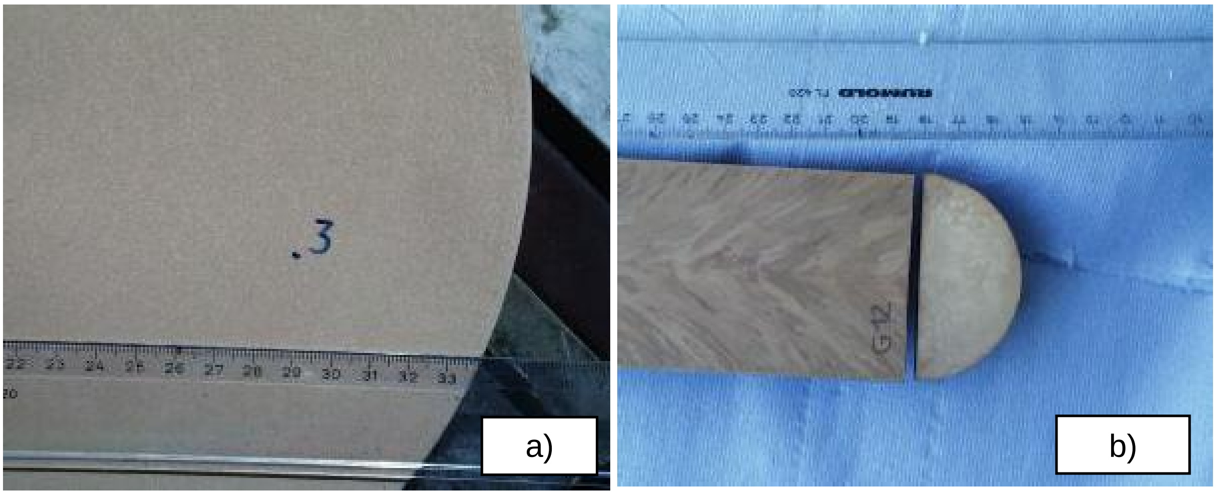


Fig. 4 illustrates the different grain structures between spray-formed and cast bronzes. While spray-formed bronze shows fine homogeneous grains (Fig 4a), the grains in cast bronze are coarse and inhomogeneous (Fig. 4b).

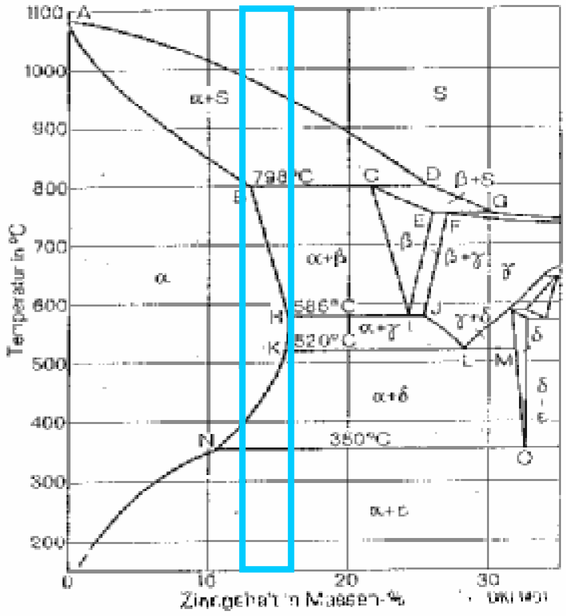
Fig. 4: a) Spray-formed 13.5%-tin bronze with fine and homogeneous grain structure, grain size about 60 µm, and b) continuous cast 12%-tin bronze with course and inhomgeneous grains

4.2 Intermetallics and Microsegregation

Fig. 5 shows the equilibrium phase diagram of copper-tin. The composition range of commercially available high-tin bronze is between 13 and 16 % tin. It is marked grey in Fig. 5. According to the phase diagram the maximum solubility of tin in copper is at a temperature of 520 to 580 °C and amounts to15.8 wt-%. In industrial practice an amount of max. 13.5 % is soluble only if using the spray forming process. At higher tin content a second phase, the precipitation of intermetallics, the delta-phase with 32 – 33 wt-% Sn, is unavoidable. This is due to slow diffusion at 580°C. Cast bronzes show delta-phase formation already at tin contents of about 5 %. Advantage No. 2 is claimed as:

Advantage 2:
The spray forming process is able to generate single phase bronze material with a tin content up to 13.5 %. This guarantees a good hot and cold workability.

Fig. 6 shows a comparison of the micro-structures of a spray-formed 13.5% tin-bronze after hot extrusion (Fig. 6a) and cast 12%-tin bronze (Fig. 6b). Spray forming generates a nearly delta-free microstructure at 13.5% tin content (Fig. 6a). In contrast, the cast material contains a lot of delta-phase between the dendrite arms, although the tin content is only 12 % (Fig. 6b).



Punkt	Temp. °C	Zinngeh. Mass.-%
A	1 083	0
B	798	13,5
C	798	22,0
D	798	25,5
E	755	25,9
F	755	27,0
G	755	30,6
H	586	15,8
I	586	24,6
J	586	25,4
K	520	15,5
L	520	27,0
M	520	32,4
N	350	11,0
O	350	32,55

Fig. 5: Equilibrium phase diagram Cu – Sn [DKI65]

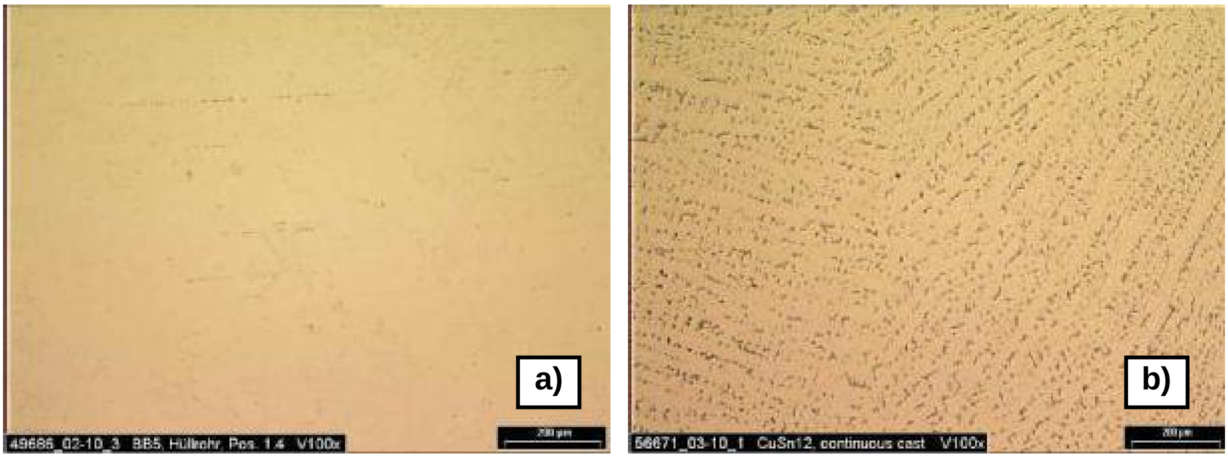


Fig. 6: a) Micro-structure of spray-formed 13.5%-Sn bronze, hot extruded into shape of sheath tube, material is nearly single phased, longitudinal section, b) Micro-structure of continuous cast 12%-Sn bronze

The customer's requirement for an increasing tin content led to the development of 15.5 % tin-bronze. As mentioned above the precipitation of inter-metallic delta-phase with 32 to 33 % tin becomes unavoidable, even if the phase diagram suggests that single-phased bronze without delta-phase should be possible. The difference in micro-structure between cast and spray-formed bronze with 15.5 % tin is illustrated in Fig. 7. Cast materials show the typical dendrite structure of a dual-phase material (Fig. 7a). The tin-rich delta-phase is connected through the complete material. Hot forming process can not abandon this. Cold forming processes are not possible. In opposite, in the spray-formed material the delta-phase particles are homogeneous distributed at the triple-points of the matrix grains (Fig. 7b). Fig. 8 shows this structure after hot extrusion into shape of a sheath tube. No connections between the isolated inter-metallics exist. This phenomenon guarantees a good cold workability. It is summarized in terms of advantage No. 3:

Advantage 3:
Spray-formed dual-phase bronze with a tin content up to 16% has less delta-phase and smaller particle sizes than cast bronze. Delta-phase distribution is very homogeneous. Good hot and cold workability is guaranteed.

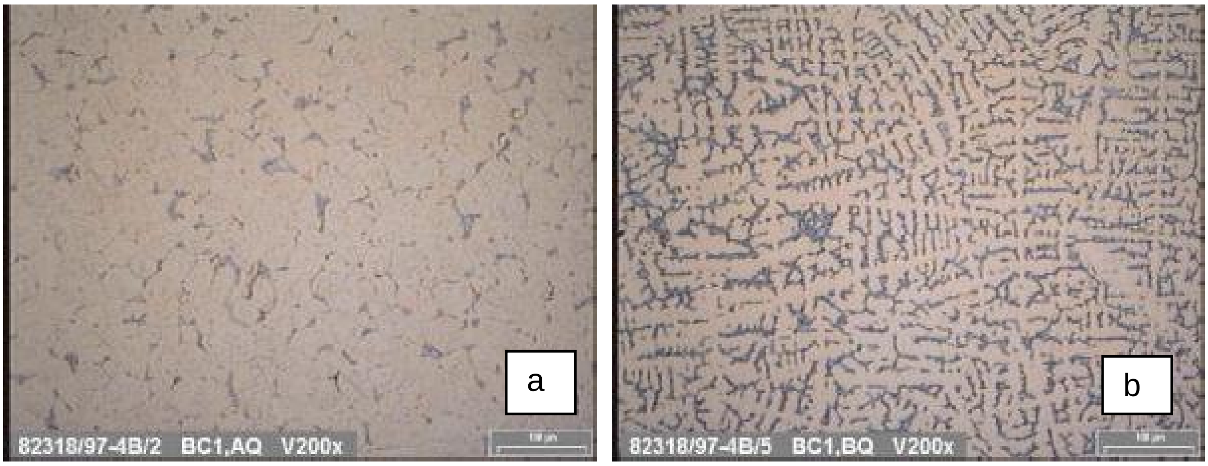


Fig 7: Microstructure of 15.5 %-tin bronze produced by a) spray forming and b) die casting.

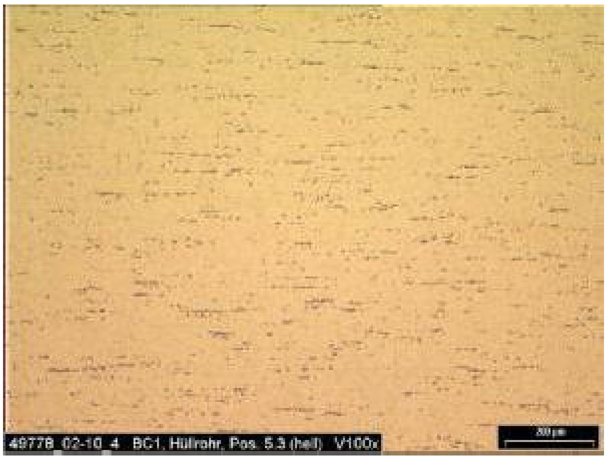


Fig. 8: Microstructure of spray-formed 15.5%-tin bronze after hot extrusion into shape of sheath tube (longitudinal section). Compare with fig. 5a (13.5%-tin bronze, spray-formed and extruded into shape of sheath tube).

4.3 Inverse Segregation

Cast materials usualy show macrosegregation with enrichment of elements which are components of the low melting phases in the center of the cast billets. In continuous cast bronzes inverse segregation is observed, which can be explained by the metallo-static pressure of the liquid metal above the not completely solidified material. This pressure displaces the residual molten metal. Considering the bronze phase diagram, the residual melt has a high tin content. This tin rich residual melt flows through channels between the solidified dendrites into the direction of the billet surface. Finally it solidifies by forming (oder zuerst ∃-hase?) beta-phase and transfers to delta-phase during cooling down. Thus the tin concentration at the billet surface is considerably higher than in the centre. The tin concentration differences reach values in the order of 2 to 9 %. This phenomenon in high tin bronze has been described in detail in [Mue00]. The inverse segregation is not removable by heat treatment [Die67]. Fig. 9 shows a plot of tin-concentration versus the location inside a continuous cast bronze billet with 8 % tin and with a diameter of 7 inch (178 mm).

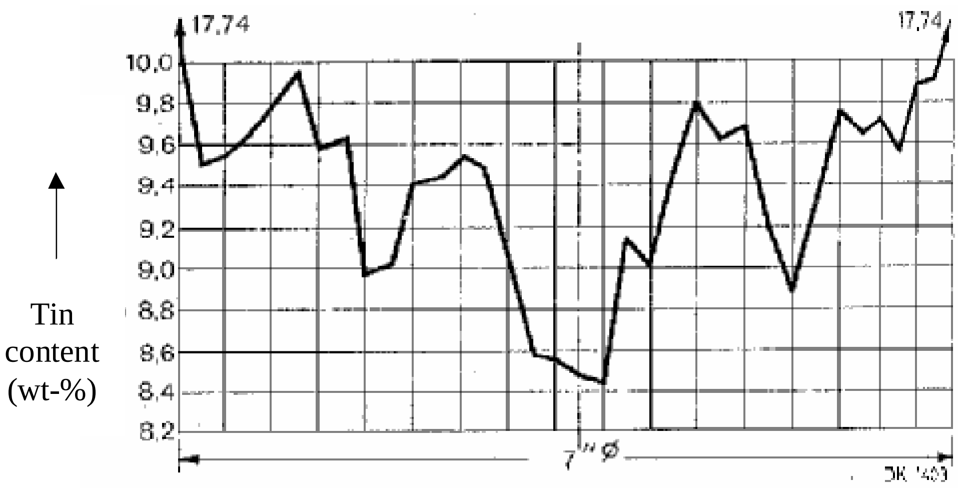


Fig. 9: Tin concentration gradient in continous cast 8%-tin bronze billet, diameter 178 mm, cross section [DKI65].

During spray forming process metallo-static pressure does not exist. Although an inverse segregation is observed. The driving forces for this inverse segregation phenomenon are assumed to be the centrifugal forces of the rotation of the billet during the spray forming process. The detailed explanation is given in [Mue00]. If spray conditions are optimized, inverse segregation is reduced to a tin concentration difference of less than 1 wt-% inside the billet. Fig. 10 shows a concentration plot of a spray-formed 12%-tin bronze at optimized spray parameters. Inverse segregation is limited to 1 wt-% tin.

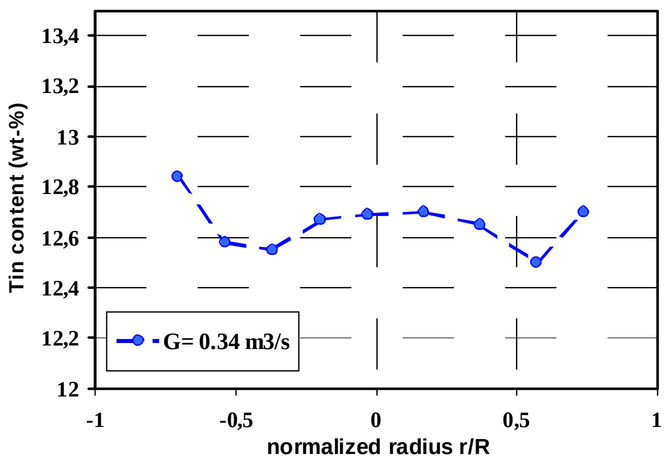


Fig. 10: Tin concentration gradient in spray formed 12%-tin bronze at optimized spray parameters [Mue01]

Advantage 4:
Spray-formed high-tin bronze does not show classical inverse segregation of continuous cast bronze. Tin content inside spray-formed billets varies maximum only about 1 wt-%. Homogenous tin distribution guarantees good hot and cold workability.

4.4 Unnecessary Initial Heat Treatment

Advantage 5:
Spray-formed high-tin bronze billets have a low tin concentration gradient and homogenous delta-phase distribution. A heat treatment before the deformation processes is ***not*** *necessary.*

Cast bronze billets require to be extensively heat treated in order to remove undeformable delta-phase structures and tin concentration differences. Because inverse segregations are not removable [Die67] expensive casting techniques are applied to minimize the concentration gradients.

4.5 Processes Stability

On one hand process stability in forming process is dependent on the application of the suitable material-specific forming parameters which should not exceed the workability limits of the material. Otherwise crack formation will occur.

On the other hand the homogeneity of the material, namely grain and precipitation structure, contributes to process stability. As presented in the previous chapters, the properties of spray-formed high-tin bronzes have many advantages which benefits also to the process stability.

Special consideration must be given to delta-phase particles. During ongoing cold forming the delta-phase particles of 16%-tin bronze are cracked during deformation. Ductile matrix fills the spaces between the crack surfaces and the particles orientate with their longer side parallel to wire axis (see Fig. 11).

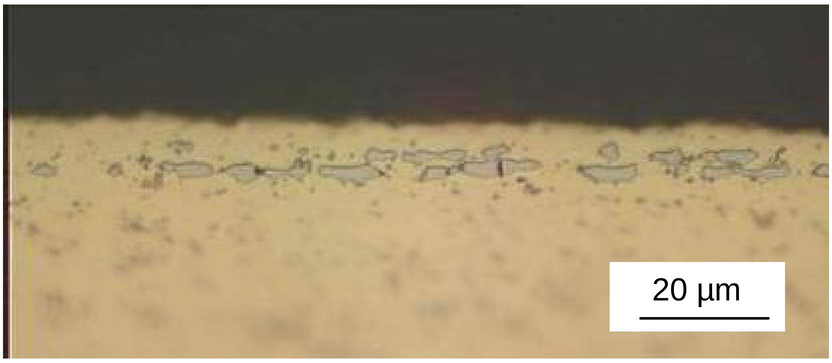


Fig. 11: Delta-phase particels during forming (forming direction horizontal)

5. Summary

Spray-formed high-tin bronzes have various advantages compared to cast high-tin bronzes. The grain structure of spray-formed material is fine and homogeneous. The spray-formed tin bronzes with tin contents up to 13.5 % tin are single-phased. Those with tin content of more than 13.5 % have a homogeneous distributed and easy deformable structure of small delta-phase particles. Inverse segregations are minimized to 1 % tin concentration difference across the billets. All these advantages are beneficial to a good workability and to process stability as well as they help to simplify the production process, e.g. help to make initial heat treatment unnecessary. So they contribute to reduce production cost.

6. References

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[Mue00] H.R. Müller, S. Hansmann, K. Ohla, *Influence of Process Parameters on Segregation and Porosity in Spray-formed Cu-Sn-billets*, Intern. Conf. On Spray Deposition and Melt Atomization, SDMA 2000, Bremen – Germany, June 26.-28., 2000, 205-218.

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