YBa$_2$Cu$_3$O$_7$ coatings based on trifluoro-acetic acid precursors

Proefschrift voorgelegd tot het behalen van de graad van Master in de Chemie door

Koen Vandaele

Academiejaar 2010-2011

Promotor: prof. dr. Isabel Van Driessche (Universiteit Gent)
Copromotor: prof. dr. Bartek Glowacki (University of Cambridge)
Begeleider: Mariusz Mosiadz (University of Cambridge)
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Abstract

YBCO Coated Conductors (CC) are already used for various applications where high magnetic fields and/or high current densities are required. High Temperature Superconducting (HTS) power cables for instance are considered to be the future electricity transport medium for power grids. Additionally, coils consisting of superconducting windings are becoming more and more important. Therefore, long length YBa$_2$Cu$_3$O$_{7-x}$ (YBCO) coated tapes are needed. A promising method to produce those coated superconductors for commercial use is the Trifluoroacetic Acid Metal Organic Deposition (TFA-MOD) method of depositing YBCO coatings onto a textured metal substrate (performed by inkjet printing). This non vacuum method has the advantage of being easily scalable and is of low cost.

Much research has been done on single crystals to obtain understanding of the mechanisms of nucleation and growth (1) (2), but also the influence of heat treatment parameters has been thoroughly studied to produce the highest critical current density ($J_C$) possible (3). Despite this intensive research, there are still many aspects which are not fully understood. Furthermore, by changing the substrate from single crystals to polycrystalline metal tapes, the process parameters have to be modified in order to grow YBCO at lower annealing temperatures (4).

In this thesis, the influence of various heat treatment parameters of YBCO growth was investigated. The fully buffered substrate was coated via the inkjet printing method, which is very advantageous for controlling the coating thickness. This method is also very promising for depositing multifilamentary coatings (5). Instead of trying to achieve high $J_C$ values, in this work, the influence of the annealing temperature, the gas flow rate, the annealing time and the humidity were studied. Hall probe and XRD scans, $T_C$ measurements, optical microscope and SEM images are presented and discussed here.

It was found that reproducible superconducting coatings with a critical current density of 0.2 MA/cm$^2$ can be produced after annealing for 2 h at 730°C, with a gas flow rate of 1.5L/min 200ppm O$_2$ in Ar. The water vapour partial pressure during the annealing was 30 mbar. Under these experimental conditions, no oxidation of the buffered tape occurred.
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PART I

SUPERCONDUCTIVITY &
COATED CONDUCTORS
1 Superconductivity

1.1 History

Superconductivity was first observed by the Dutch physicist, Heike Kamerligh Onnes. In 1911 he discovered that the resistivity of mercury suddenly drops to zero when cooled in liquid helium (boiling point of 4.2K). Although Onnes discovered superconductivity, he also found that a sufficiently strong magnetic field or a sufficiently high current density could destroy the superconducting state, which restricts the usefulness of many superconducting materials (6) (7).

Figure 1: Overview of superconducting materials discovered over the last century (8). Materials with the same symbols represent a family of superconductors. Note the dotted lines, which indicate the boiling point of liquid He (4.2K) and liquid N\textsubscript{2} (77.4K)

In the following years, new low temperature superconducting materials were discovered in various metallic elements. Different families of superconductors are shown in Figure 1.
1.2 Properties of superconductors

1.2.1 The transition temperature

The superconducting transition temperature, $T_C$, is the temperature at which the electrical resistance to direct current totally vanishes (Figure 2). This temperature varies for each superconductor and the sharpness of the transition depends on its purity.

![Figure 2: Superconducting transition in YBa$_2$Cu$_3$O$_{7-x}$ ($T_C = 92K$)](9)

1.2.2 Magnetic behaviour of superconductors

Another important property of superconductors is the fact that the amount of magnetic flux trapped inside cannot change if it is in the superconducting state (perfect diamagnetic material). This means that the flux density does not vary with time or $\dot{B}=0$, which was discovered in 1933 by Meissner and Ochsenfeld. Two theoretical situations are therefore compared to clarify this behaviour (Figure 3). On the one hand, one could consider a "perfect" conductor, which shows a different state of magnetization depending on the sequence by which the sample is cooled and magnetized. However, a superconductor is not just a "perfect" conductor, since it has always the same magnetic behaviour regardless of the way in which this state is achieved (diamagnetic material).
In part (a) of Figure 3, a "perfect" conductor is cooled below its critical temperature without any applied field. At this stage, the resistance is zero and a magnetic field is subsequently applied. Thereby a current in the outer layer of the superconductor is generated, which induces a magnetic field cancelling out the external magnetic field in the interior ($\dot{B} = 0$). After removing the external field, the induced current vanishes and $B$ remains 0 inside. Section (b) shows a "perfect" conductor, which is cooled below its $T_c$ while being magnetized. Consequently the magnetic field inside the remains unchanged. Once the magnetic field is released, the uniform field inside remains present ($\dot{B} = 0$) (10).

Figure 3: Comparison of the magnetic behaviour of a "perfect" conductor (a)(b) and a superconductor (c)(d), depending on the sequence of cooling and applying a magnetic field. (a)(c) The magnetic field is applied after cooling to a temperature below $T_c$. (b)(d) The sample is cooled while a magnetic field was applied already (11)
However, applying the same conditions for a superconductor (c) (d) show that the magnetic field in a superconductor is always zero. This is caused by a surface current which cancels the external field and is conform with the Meissner state of a superconductor. The resulting magnetic state of a superconductor is thereby independent of the sequence of the cycle, which is in contrast with the situation for a "perfect" conductor.

The depth to which the screening currents reach is called the penetration depth $\lambda$. This is only a thin layer of the superconductor which appears to be penetrated by field lines and is temperature dependent. Upon approaching the critical temperature, the superconductor is almost completely penetrated by the external magnetic field.

1.3 Type-I vs type-II superconductors

![Figure 4](image)

Figure 4: Depiction of the magnetization behavior for type-I and type-II superconductors in function of the applied magnetic field (12)

The influence of the magnetic field strength on the magnetization of the superconductor is shown in Figure 4. The red curve corresponds to a type-I superconductor, that remains
superconducting until a critical magnetic field $H_C$ is exceeded. This $H_C$ is the maximum magnetic field which could be created by the super currents at the outer surface of the material in order to cancel the external magnetic field in the interior of the type-I superconductor, and hence can be related directly to $J_C$. Above $H_C$, the type-I superconductor reverts into its normal state ($\dot{B} \neq 0$). Type-II superconductors, on the other hand, cannot be described by a single thermodynamic critical field. Above a lower critical field ($H_{C1}$), the superconductor enters the mixed state, in which the magnetic flux partially penetrates the interior of the material. The flux penetrating the superconductor is quantised as fluxons, with each essentially constituting a small normal "cylinder" (or vortex) while the bulk remains superconducting. Repulsion between these vortices means that they form a flux lattice (the Abrikosov lattice) to maximize their separation. By increasing the field strength, flux penetration becomes increasingly substantial, which means that an increasing number of progressively more closely-spaced vortices are formed. Once the upper critical field ($H_{C2}$) is exceeded, the superconductor is fully in the normal state, due to complete flux penetration (6) (7).

Figure 5 shows the appearance of normal cores (dark grey "cylinders") during the mixed state. $n_s$ stands for the super-electron density in the material and $B$ depicts the magnetic flux density. By increasing the field, the vortex density rises and they gradually start to overlap as the field is further increased.

![Figure 5: Flux penetration in the mixed state for a type-II superconductor under the influence of an external magnetic field (13)](image)
1.4 Flux pinning and the critical current density $J_C$

Considering the situation in which a current is passed through a type-II superconductor in the presence of an external magnetic field, not only exceeding the $H_{C2}$ threshold can return the superconductor to its normal state, but also passing a sufficiently high current can destroy superconductivity.

![Diagram](image)

**Figure 6:** Lorentz forces experienced on the vortices for a superconductor in the mixed state (13)

At a fixed external magnetic field (*Figure 6*), the Lorentz force is proportional to the transport current density, and the flux lattice remains pinned as long as the Lorentz force is balanced by the pinning force. The current density at which the pinning force is exceeded is called the critical current density ($J_C$), above which energy is dissipated (7).

In normal situations, impurities and lattice defects act as these pinning centres, but by introducing artificial pinning centres, such as BaZrO$_3$, a much higher pinning force can be achieved. These defects provide a resistance against the vortex motion, which means that a higher transport current density can pass through the superconductor before overcoming the threshold at which flux motion and consequently energy dissipation occurs (13).

Magnetizing a superconductor can be executed by field cooling and zero field cooling. Firstly, field cooling is accomplished by cooling the superconductor below its $T_C$ in the presence of an external magnetic field. Secondly, zero field cooling means that a superconducting sample below its $T_C$ is subsequently magnetized. It is characteristic of non-ideal superconductors that after magnetization, a residual field remains. This trapped flux is correlated with the critical current density which can be derived as explained in §5.1.
1.5 $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ (YBCO) as High Temperature Super Conductor (HTSC)

1.5.1 Introduction

In 1986 superconductivity in cuprates ($\text{LaBaCuO}$, with a $T_C \sim 30\text{K}$) was discovered, which had been believed to be impossible among scientists. In the following years much research was done on this new family of superconductors and it was found in 1987, by a research group in Alabama and Houston, that $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ ceramics are superconducting below 92K. This discovery was of great importance, since the critical temperature is above the boiling temperature of liquid nitrogen, which is much cheaper and more widely available than helium as a coolant (7).

Later, even higher $T_C$ cuprate superconductors were discovered, the most important ones being $\text{Bi}_2\text{Ca}_2\text{Sr}_2\text{Cu}_3\text{O}_{10}$ ($T_C \sim 110\text{K}$) and $\text{Tl}_2\text{Ca}_2\text{Ba}_2\text{Cu}_3\text{O}_{10}$ ($T_C \sim 125\text{K}$) (7).

1.5.2 Material characteristics

All the high $T_C$ superconducting materials currently used in applications are cuprates, which are classified crystallographically under the perovskite family. The crystallographic structure of YBCO depends on the degree of oxygenation and it is only superconducting in the orthorhombic form. As can be seen in Figure 7, the superconducting phase is formed when YBCO consists of more than 6.4 oxygen atoms per unit. However, the $T_C$ is still very low and only an oxygen content close to 7 results in a high transition temperature. This oxygenation is performed by exposing the material to a pure oxygen atmosphere at an elevated temperature. For an oxygenation degree of $0.0 < x < 0.4$, $\text{YBa}_2\text{Cu}_3\text{O}_{6+x}$ is an insulator (tetragonal), whereas it is superconducting (orthorhombic) for $\sim 0.4 < x < 1.0$ (note that the oxygen content is written here as $O_{6+x}$). In $\text{YBa}_2\text{Cu}_3\text{O}_6$, the chains are oxygen deficient: Cu(1) in Figure 8 is only coordinated by 2 oxygen ions, which results in an insulating structure. By increasing the oxygen concentration, all vacancies get filled until $\text{YBa}_2\text{Cu}_3\text{O}_7$ is formed, which is superconducting (6).
The crystallographic structure, depicted in Figure 8 shows clearly the layered structure. The presence of the CuO\(_2\) planes result in characteristic properties depending on the orientation. The conductivity in the ab-planes for instance is much higher than along the c-axis, which is because of the resistance between the layers of the perovskite structure. This emphasizes the direction dependence of the properties indicating the high anisotropic character of YBCO. In comparison with the fully oxidized perovskite structure, the yttrium layer contains 4 vacancies. Since the crystallographic structure is symmetric in this plane, Y can easily be replaced with a variety of rare earth elements without compromising the superconductivity.

![Graph](image)

**Figure 7:** Depiction of the superconducting transition temperature in function of the oxygen content in YBa\(_2\)Cu\(_3\)O\(_{7-x}\) (14)
Figure 8: Crystallographic structure of YBCO (15). The YBCO unit cell dimensions are ~4Å, ~4Å and ~12Å for the a-, b-, and c-axis directions respectively.
2 YBCO deposition methods

2.1 Introduction

The key objectives of YBCO thin film deposition are to produce coatings with an exact composition over the entire length without impurities and to form epitaxially grown YBCO with only c-axis orientated grains. Multiple deposition methods are described here and are able to produce high quality YBCO thin films.

2.2 Physical vapour deposition methods (PVD)

2.2.1 Evaporation

The physical vapour deposition method of evaporation consists of a vapour source and a vacuum which allows the transport of the material to the heated substrate. Vaporisation of the coating material could be achieved by e.g. resistance evaporation or electron-beam evaporation.

Resistance evaporation makes use of a crucible which has resistive heating elements to provide thermal energy. By varying the heat input, the vapour flux can be varied. However, if an alloy or composite target material is used, different vapour pressures for the elements cause a variation of the stoichiometry in time. This could be avoided by using a method based on flash vaporization to prevent fractionation (16).
A better way to prevent fractionation of the vapour could be using electron-beam evaporation (Figure 9). With this method, the target is rapidly heated with an electron beam, which allows quick evaporation of the target. However, it is still difficult to ensure that the vaporization rates of elements with very different vapour pressures are the same. It is therefore difficult to produce a very complex coating as YBCO, starting from a composite target. Therefore, one normally uses several single element electron beams with a shutter to control the composition of the resulting compound (16).

2.2.2 Sputtering

Sputtering differs from evaporation in the sense that one uses energetic particles, typically ions of an inert gas like argon, to eject the target material. In the simplest approach, a voltage is applied between the substrate and the target, the latter being the cathode, accelerating the argon ions towards the target. In addition to sputtered atoms of the target, ions or atoms can be reflected and electrons can be released, the sputtering yield of the process depending on the energy of the incident particles and on the target. This method provides much more control over deposition than evaporation, as the gas species and pressure, voltage and substrate temperature can all be adjusted to control the flux and energy of the depositing species. Many variants on this basic approach exist: a widely used
sputtering method makes use of a magnetron to increase the argon ionization by accelerating electrons in the region of the target using crossed magnetic and electric fields, and high frequency AC (often radio frequency, RF) can be applied in place of DC to avoid the accumulation of positive charge on the target (16).

2.2.3 **Pulsed laser deposition (PLD)**

Laser ablation or pulsed laser deposition (PLD) uses pulses of coherent light, focused by lenses as shown in Figure 10 and directed on the target, to explosively vaporize the target material. Usually, the target rotates to increase its lifetime and to obtain a constant plume composition in the case of composites. The target can consist of various materials e.g. composites or alloys. It is therefore very convenient to deposit a complex coating such as YBCO with this method. The substrate is located in front of the plume where the vapour sublimes on the heated substrate. This is performed in a vacuum chamber, with the possibility to introduce oxygen (16).

![Figure 10: Pulsed laser deposition system (18)](image-url)
2.2.4 Ion beam assisted deposition (IBAD)

Figure 11: Drawing of the IBAD deposition system showing electron-beam deposition systems to vaporize the target compound and an electron gun focused on the film to provide extra energy (19)

The ion beam assisted deposition (IBAD) method uses conventional physical vapour deposition methods, for example electron-beam evaporation, to vaporize the target materials, while an ion source provides extra energy on the growing film surface by bombarding it with ions. The advantage is that sufficient energy is provided to repair defects, to form a very dense and adherent coating and sputter away impurities. A schematic drawing of the setup is shown in Figure 11. Depending on the design of the system however, Y and Cu are usually vaporized by either an electron-beam or by sputtering, whereas barium (as BaF$_2$) is vaporized via a thermal source. Simultaneously, the heated substrate is bombarded by ions, while the oxygen partial pressure is typically kept as low as 1.3 × 10$^{-6}$bar. In order to control the composition and thickness of the growing film, Rutherford backscattering measurements are often performed in situ. Adjustments of the film composition are performed by varying the arrival speed of the individual elements with shutters (20).
2.3 Chemical Vapour Deposition methods (CVD)

A frequently used method to deposit YBCO coatings is MOCVD (Metal Organic CVD). In principle, metal-organic precursors with the correct ratio are vaporized and grow a well-defined film on a heated substrate. The thin film via this method is produced by the co-pyrolysis of organometallic compounds. The process described in Figure 12 is an example for the fabrication an YBCO coated substrate using the MOCVD method. Therefore, a volatile metalorganic precursor solution of Y, Ba and Cu was used. A homogeneous solution was obtained by dissolving the individual precursor solutions in a solvent. Evaporation occurred in a "Band Evaporator" (21) (22). In this process, a complex system of mass flow controllers fed a band going through two different heating zones. In the first zone, the solution is heated to vaporize the solvent only, whereas the second zone vaporizes the metal organic precursor. In this stage, the solvent vapour was directed to a cold finger to condensate the solvent, while the pure precursor was transported and introduced into the reactor chamber (23).

![Figure 12: MOCVD system for YBCO deposition (24)](image)

Additionally, the use of photo assisted metal organic vapour deposition (activation of the growing film by means of tungsten halogen lamps or a Nd:YAG laser beam) can enhance the deposition rate of highly oriented c-axis grown YBCO films (25) (26).
Another system which makes use of a different approach to form the reactive gas mixture is depicted in Figure 13. Here, the Y, Ba and Cu metal organic precursors in vapour form are produced by heating the solid precursor materials in three individually controlled ovens. The amount of each precursor vapour introduced in the reactor chamber was controlled by varying the argon carrier gas flow. In the reactor chamber, the YBCO film deposition was produced on a heated substrate (25).

2.4 Chemical Solution Deposition techniques (CSD)

2.4.1 Dip coating

A simple method to deposit a solution on a substrate is dip-coating. For continuous coating of long substrates, the substrate is immersed in a bath and very slowly pulled out again using a reel-to-reel winding mechanism. The thickness of the coating depends mainly on the viscosity, total metal-ion concentration and the speed at which the substrate is moved. The setup shown in Figure 14 is used for continuous reel-to-reel coating, whereas small substrates are simply pulled out of a precursor solution in a controlled manner.
2.4.2 **Spin coating**

Spin coating involves depositing a small amount of the precursor solution in the middle of the substrate and spinning it at very high speed. Spreading of the applied solution occurs through centripetal acceleration, which eventually results in a thin film on the surface of the substrate. The coating thickness depends on the properties of the precursor solution such as viscosity, drying rate of the solvent, surface tension, etc.) and the spin process parameters (rotational speed, acceleration, etc.). A schematic representation of the coating technique is given in *Figure 15* (28).

![Diagram of spin coating](image)

*Figure 15: The numbers a to d represent the different stages during spin coating (29)*
Note that this coating technique is limited to small substrates, which is appropriate for the study of YBCO growth on single crystals for instance for instance.

2.4.3 Inkjet printing

2.4.3.1 Electromagnetic micro-valves

Electromagnetic micro-valves are small solenoid valves capable of delivering small volumes of liquid when actuated with a short electrical pulse. The device depicted in Figure 16 consists of a coil with a magnetic slug in the middle, which is connected via a stiff wire to a plunger assembly capped with a rubber plug. At the bottom of the device there is a small ink chamber closed at the bottom with a ruby or sapphire disc containing a small-diameter orifice (in this case 90μm). Pressurised ink is delivered to the ink chamber, which at rest is sealed by the rubber plug. When a pulse of electrical current is applied to the coil, the plunger is raised and a small volume of ink is ejected, the volume depending on the pulse duration (opening time), the applied pressure, the viscosity of the ink and orifice diameter.

Figure 16: Electromagnetic inkjet printing nozzle
2.4.3.2 Piezoelectric printheads

In piezoelectric printheads, a piezoelectric element is used to deform the ink chamber when a voltage is applied. Typically the volume of the chamber is slightly reduced by deflecting its roof or walls inward with one polarity of the applied voltage, forcing ink out of the chamber, and this is reversed to draw new ink into the chamber from an ink manifold. This technology allows much smaller ink chambers and orifices to be used than electromagnetic micro-valves, allowing many nozzles to be packed into a single compact printhead and allowing smaller droplets (typically 10pL) to be formed, which can increase the resolution of printing patterns or decrease the thickness and improve the uniformity of a continuous coating. However, more care needs to be taken with ink development, since the small ink channels can easily be blocked if particles are present in the ink, and the small ink channels and small negative operating pressure place tighter constraints on the suitable ink viscosity and surface tension.
3 Ink synthesis for the CSD method via the sol gel approach

3.1 Introduction

Although vacuum techniques have proven that high quality Coated Conductors (CC) (see §4) can be fabricated, chemical solution deposition (CSD) techniques are widely recognized as a very promising route to produce low-cost long-length coated conductors. Precise control of the stoichiometry and composition of the solution can be achieved with this approach. An important advantage of CSD is the fact that the coating components are homogeneously distributed in the ink because of mixing at the molecular level. In addition, additives as dopants or polymers can easily be incorporated in the coating by mixing with the ink.

An important technique used for ink preparation for CSD is the sol-gel approach, in which the term sol-gel stands for sol-gelling. The technique uses a precursor solution consisting of all the cationic species which is transformed into a semi-solid state via a sequence of chemical or physical interactions. During solvent evaporation, the solution transforms gradually from a viscous solution into a transparent, homogeneous, amorphous gel. Neither crystalline phases nor precipitates are formed: the semi-solid is considered as a 3D gel network, which is kept together by covalent bonds or physical interactions, depending on the sol-gel type (30).

Three different sol-gel methods to produce YBCO coatings were described by Kakihama and classified as the colloidal sol-gel route, inorganic route and organic sol-gel route (30). The colloidal network of dispersed colloidal particles in a liquid is stabilised by weak Van der Waals interactions and electrostatic forces, often regarded as the physical gel route. The inorganic and organic types, on the other hand, are usually considered as chemical routes as chemical reactions take place between the precursor materials. The inorganic sol-gel route is subsequently divided into the alkoxide gel method and the metal-chelating sol-gel method.
3.2 Colloidal sol-gel

Gels in this method are obtained by dispersing the colloidal particles (typical diameters of 1-100nm) in a liquid medium and subsequently gelling by electrostatic or steric interactions between the colloidal particles. Interparticle interactions in the fluid here are mainly physical forces on surfaces such as van der Waals forces and electrostatic forces (30).

3.3 Inorganic sol-gel route

3.3.1 Hydrolysis of metal alkoxides

The hydrolysis of metal alkoxides results in the formation of an inorganic polymeric oxide network. These polymeric strands, regarded as constituting the gel, are formed by hydrolysis and condensation reactions of the precursor solution. The chemical reactions of the hydrolysis of a metal alkoxide $M(OR)_n$ where M is a metal ion and R an alkyl group is shown below. On addition of water, the metal alkoxides hydrolyze, with splitting of an alcohol substituent (Reaction 1). The formation of the network occurs through condensation by dehydration (Reaction 2) and dealcoholation (Reaction 3) (30).

\[
M(OR)_n + xH_2O \rightarrow M(OH)_{x} (OR)_{n-x} + xROH \quad \text{Reaction 1}
\]

\[
-M - OH + HO - M - \rightarrow - M - O - M - + H_2O \quad \text{Reaction 2}
\]

\[
-M - OH + RO - M - \rightarrow - M - O - M - + ROH \quad \text{Reaction 3}
\]

The reactions occurring during the condensation result in the formation of the inorganic polymeric oxide network. Factors such as the molar ratio of water to alkoxides, solvent nature, temperature and pH influence the hydrolysis, condensation and polymerization reactions. Optimization of the reaction conditions is therefore required (30).

More complications are encountered if multicomponent gels need to be formed, because the hydrolysis does not take place simultaneously for two or more different alkoxides. Consequently, the degree of homogeneity of the obtained gel strongly depends on both the
mixing level of the different alkoxides in the precursor solution and also the reactivity of each metal alkoxide species towards water. These problems can however be avoided by utilizing chemically modified alkoxides to control the rate of hydrolysis of the different precursor materials. The original alkoxides are thereby modified with carboxylic acids or β-diketonates as additional ligands. For example, two of the RO-ligands of M(OR)₄ can be changed by acetic acids to slow down the rate of hydrolysis. In this way, it is possible to obtain a gel with the different cations homogeneously distributed in the inorganic polymeric oxide network (30).

The perovskite films and buffer layers in coated conductors are often produced via this method. Drawbacks, however, of this method are the sensitivity of the starting material to moisture and its cost (10).

3.3.2 Amorphous metal-chelate route

Advantages of the metal-chelate sol-gel method are the low cost of the metal salts and the ease of handling this starting material. Furthermore, various possibilities exist for the chelating agent, such as ethylene diamine tetraacetic acid (EDTA), citric acid, propionic acid, etc., which form complexes with the metal ions resulting in a metal-chelated starting solution without any precipitation. By slow evaporation of the solvent (either water or organic), a viscous or glassy gel network is formed (30).

It is noteworthy that a precursor solution containing simple inorganic metal salts (for example nitrates) in the absence of any organic complexants does result in a homogeneous solution at atomic level, but a heterogeneous mixture of precipitates would be formed upon complete evaporation of the solvent. This constraint can however be overcome by usage of acidic organic chelating agents for instance. The basic idea of this approach is to reduce the concentration of free-metal ions in the precursor solution by the formation of soluble chelate complexes. Strong chelating agents, e.g. EDTA, citric acid and TFA, are often used in the synthesis of YBCO thin films, which result in a better stability of
the precursor materials over a wider range of experimental conditions (temperature, pH and higher total ion metal concentrations) (30).

3.3.2.1 Chelating agents for the metal-chelate sol-gel method

TFA route

Although the MOD method reduces the production cost for coated conductors, critical current densities of 1MA/cm$^2$ are rarely exceeded if carboxylic chelating agents are used. This is because stable BaCO$_3$ tends to form, causing a deterioration of the $J_C$ of the YBCO films. In addition, nucleation of nanocrystallites occurs during pyrolysis, causing the growth of randomly oriented YBCO. To avoid this, one has to control simultaneously the temperature and oxygen partial pressure to decompose BaCO$_3$ completely (30).

One could overcome the problem of BaCO$_3$ formation by using trifluoroacetates as chelating agents, which forms BaF$_2$ after pyrolysis rather than barium carbonate. This method was first introduced by Gupta et al. (31). Compared with acetic acid, TFA has a much higher stability as an anion because of the high electronegativity of fluorine, withdrawing electron density from the oxygen atoms. Consequently, solutions with a much higher total metal-ion concentration can be achieved without any precipitation because of the high chelating power of TFA.

Figure 17: Equilibrium reaction of TFA with the protonated and deprotonated form. The deprotonation of TFAH is favored because of the electron withdrawing power of fluorine (32)
Two procedures are used to prepare the YBCO precursor solution. One could dissolve YBa$_2$Cu$_3$O$_x$ powder in TFA to synthesise inks with the exact 1:2:3 ratio for Y, Ba and Cu (schematic procedure depicted in Figure 18). Using this synthesis route, water and impurities can easily be removed by trifluoroacidic acid anhydride, which binds water. Washing with methanol and vaporizing the solution in a rotary evaporator results in a very pure precursor solution.

**Figure 18**: Synthesis route for the preparation of YBCO-TFA ink in methanol
Another approach consists of the starting products $Y(Ac)_3$, $Ba(Ac)_2$ and $Cu(Ac)_2$, which are dissolved in diluted TFAH. An advantage of this route is the fact that ink with off stoichiometry can be synthesized. However, the preparation of a completely pure coating solution is impeded because of the strong hydrogen bond formation between fluorine, water and acetic acid. Here methanol is utilized to remove any excess of solvent, impurities and water. The synthesis route is shown in Figure 19.

**Figure 19:** Synthesis procedure for the preparation of the precursor solution TFA-MOD (33)
Advanced TFA route

In the advanced TFA-MOD method, Cu-TFA is usually replace by Cu-naphthenate (34) (35). The main reason for doing this is to reduce the amount of fluorine in the process and to decrease the time needed for pyrolysis. Only copper is replaced because it breaks down to CuO during the pyrolysis, which reacts directly with Y-Ba-O-F and H₂O during annealing (33). It is therefore not necessary to have copper present as Cu-TFA which is more harmful and requires a long pyrolysis.

Water based route

The usage of environmentally friendly processes is encouraged worldwide and it is particularly desirable to use water as a solvent. Water based precursor solutions are considered safe for handling and inexpensive. Short chain inorganic salts can be dissolved in water and some acid. The dissolved cations are stabilized in solution by means of stabilizing agents such as triethanolamine (TEA). A semi-solid gel is subsequently formed during mild heating of the precursor solution (36) (37) (38) (39).

3.4 Organic sol-gel method

The last method, termed as the organic sol-gel route, forms gel networks starting from a precursor solution containing the homogeneously distributed chelated metal ions and organic monomers. The gel is then formed upon polymerisation of the monomers with the metal-chelates homogeneously distributed. A variant of this technique is the usage of coordinating organic polymers for the metal and a suitable solvent. Evaporation of the solvent converts the highly viscous precursor solution into a thermoplastic gel.
4 YBCO Coated Conductors (CC)

4.1 Introduction

YBCO superconductors can either be fabricated as bulk material or as thin film. As film, a substrate acting as support is required to provide the necessary strength and rigidity to the coated conductor. To obtain superconducting coatings, it is important that the YBCO grains are epitaxially grown (see §1.5.2). Therefore it is required that textured substrates are used.

The term Coated Conductors (CC) involves that an YBCO coating is deposited onto a textured substrate. This substrate is always provided with buffer layers which can either be the origin of texture or transfer the texture from the underlying metal tape. The current carrying region is then the epitaxially grown YBCO layer, following the texture of the buffered substrate. For industrial applications, such as the fabrication of coils made by winding superconducting "cables", long length superconductors are required. Therefore, the YBCO superconducting layer need to be part of a rigid architecture. The simplified structure of a section of such arbitrary called superconducting cable is illustrated in Figure 20. Note that for industrial applications also a conducting cap layer is deposited onto the YBCO coating to enable a continuous current flow if it for any reason cannot be conducted by the YBCO layer itself.

Figure 20: Multilayered structure of an YBCO CC, consisting of the basic components: metal tape + buffer layer(s) + YBCO coating and often also a conducting cap layer (required for industrial applications) (40)
4.2 Substrate characteristics

4.2.1 Single crystal substrates

Single crystals are ideal substrates on which to investigate the different processes occurring during YBCO nucleation and growth. They can be readily prepared with low densities of impurities and crystallographic defects, and a flat surface for deposition, allowing the influence of processing parameters on the superconducting properties to be easily investigated without contributions from substrate variations. The absence of grain boundaries and effectively perfect crystalline orientation also encourages good epitaxial growth and texture, typically producing YBCO coatings with much higher critical current densities.

Some frequently used single crystals for YBCO thin films are LaAlO$_3$ (LAO), SrTiO$_3$ (STO), Yttrium Stabilized Zirconium (YSZ) and Ag, most of which have appropriate lattice mismatch with YBCO to avoid the need for a buffer layer and can tolerate an annealing temperature exceeding 800°C. Note that YSZ is almost always provided with a CeO$_2$ buffer layer, because of its high lattice mismatch with YBCO.

4.2.2 Metal based substrates

Three types of metal substrates which are commonly used for YBCO coated conductors are biaxially textured Ni-alloy tape, stainless steel tape and Hastelloy tape (nickel based alloy). Of these, only appropriately rolled Ni-alloy tapes are textured; the other substrates need a textured buffer layer to be deposited (usually by IBAD). YSZ is often used as buffer layer to coat untextured metal tapes.

The crystallographic uni-axial texture in Figure 21 is obtained by annealing only. Equal orientations for the a-axes of the grains in bi-axially textured tapes, on the other hand, are produced by heavy rolling. This involves the deformation of the original tape up to 95%. The bi-axial texturing is subsequently obtained by annealing the rolled Ni-alloys up to
1000°C for 2h. This results in the formation of sharp ⟨100⟩ cube texture after recrystallisation. Electropolishing subsequently reduces the roughness of the surface to about 1µm, which is necessary for epitaxial YBCO growth. In addition, the cube texture which is required to achieve high critical current densities is also beneficial for better mechanical properties (41).

Figure 21: Effect of rolling on the texture (42)

To fabricate high $J_C$ coated conductors, it is necessary to achieve a low grain boundary misorientation: the superconducting planes of YBCO are oriented parallel with the plane of the substrate (43) and good coupling between the grains is required to achieve high critical current densities over a long length. The linking between grains depends on the [001] tilt, [100] tilt and [100] twist boundaries and it is therefore important to fabricate RABiTS with a low angle grain boundary distribution. Figure 22 shows the influence of the tilt in different directions on the critical current density. This reveals that the ratio between $J_C$ (boundary) and $J_C$ (grain) drops very quickly with increasing misorientation angle. Consequently, long length superconducting tapes with a high misorientation angle for any of the axes will reduce the total current carrying capacity drastically. The a-axis and b-axis tilt (also out of plane misalignment) can be quantified using a rocking curve scan, whereas the x-axis tilt of in plane misorientation is measured using pole figures.
4.3 Buffer layers

If Ni-alloy tapes are used to fabricate coated conductors, buffer layers are required to prevent oxidation of the substrate and Ni diffusion into the YBCO film, which could destroy the superconducting properties entirely, during heat treatment. The purpose of the buffer layers is therefore to act as a chemical barrier between the substrate and the deposited YBCO film. The choice of the buffer layer however is not trivial, because three important requirements have to be met. Firstly, the buffer layer should be dense and block both oxygen diffusion into the substrate and Ni diffusion to the YBCO film. Secondly, the buffer layer has to be able to transfer the texture of the substrate to the YBCO film because epitaxial growth is necessary. Consideration of the lattice parameters of the substrate, buffer layer and YBCO film is therefore important. Finally, a similar thermal expansion coefficient for the different materials of the coated conductor is important to reduce stresses caused by temperature variations.
Some frequently used buffer layers are yttrium stabilized zirconium $\text{Y}_2\text{O}_3$-$\text{ZrO}_2$ (YSZ), CeO$_2$, La$_2$Zr$_2$O$_7$, Gd$_2$Zr$_2$O$_7$, etc. (Figure 23). Most desirable is the usage of only one buffer layer, but it is difficult to meet all the requirements, so it is usually necessary to employ two different buffer layers.

### 4.4 Important achievements of YBCO Coated Conductors

#### Table 1: Overview of the performance of YBCO thin films produced via different methods (46)

<table>
<thead>
<tr>
<th>Author, Year</th>
<th>$d$ (µm)</th>
<th>Substrate</th>
<th>Method</th>
<th>$J_C$ (MA/cm$^2$)</th>
<th>Remark</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gupta et al., 1988 (31)</td>
<td>1.0</td>
<td>YSZ</td>
<td>TFA</td>
<td>0.001</td>
<td>Used BaF$_2$ to prevent carbon contamination</td>
</tr>
<tr>
<td>McIntyre et al., 1990 (47)</td>
<td>0.3</td>
<td>STO</td>
<td>TFA</td>
<td>1.1</td>
<td>O$_2$ in gas stream to stabilize tetragonal YBCO phase</td>
</tr>
<tr>
<td></td>
<td>Thickness d (μm)</td>
<td>Substrate</td>
<td>Deposition Technique</td>
<td>Laminates/Coatings</td>
<td>Notes</td>
</tr>
<tr>
<td>------------------</td>
<td>------------------</td>
<td>-----------</td>
<td>----------------------</td>
<td>--------------------</td>
<td>-------</td>
</tr>
<tr>
<td>Smith et al., 1988 (48)</td>
<td>1.0</td>
<td>LAO</td>
<td>TFA</td>
<td>1.0</td>
<td>Low pH$_2$O during nucleation of YBCO; first thick high $J_C$ film</td>
</tr>
<tr>
<td>Araki et al., 2001 (32)</td>
<td>0.172</td>
<td>LAO</td>
<td>TFA</td>
<td>11.6</td>
<td>Dehydrated solution (SIG method); highest reported $J_C$ for MOD</td>
</tr>
<tr>
<td>Dawley et al., 2003 (49) (50)</td>
<td>0.18</td>
<td>LAO</td>
<td>TFA</td>
<td>2</td>
<td>Low p(O$_2$) decomposition, DEA additions for faster decomposition</td>
</tr>
<tr>
<td>Tokunaga et al., 2004 (35)</td>
<td>1.48</td>
<td>CeO$_2$/IBAD-Gd$_2$Zr$_2$O$_7$/Hastelloy</td>
<td>Advanced TFA-MOD</td>
<td>2.1</td>
<td>Cu(TFA)$_2$ replaced with Cu-naphthenate; multi-layers</td>
</tr>
<tr>
<td>Clem et al., 2005 (51)</td>
<td>0.6</td>
<td></td>
<td></td>
<td>4</td>
<td>DEA-addition; multiple coatings and rapid decomposition</td>
</tr>
<tr>
<td>Xu et al., 2005 (52)</td>
<td>0.6</td>
<td>Y$_2$O$_3$/YSZ/CeO$_2$/Ni-W RABITS</td>
<td>Advanced TFA-MOD</td>
<td>2.4</td>
<td>Y and Cu-TFA replaced with trimethylacetates; high $J_C$ single coat</td>
</tr>
<tr>
<td>Nakaoka et al., 2005 (34)</td>
<td>0.2</td>
<td>LAO</td>
<td>Advanced TFA-MOD</td>
<td>5.7</td>
<td>Optimization of reduced fluorine TFA-based process</td>
</tr>
<tr>
<td>Rupich et al., 2006 (53), (54)</td>
<td>1.5</td>
<td>CeO$_2$/YSZ/Y$_2$O$_3$/Ni-5%W RABITS</td>
<td>TFA</td>
<td>3</td>
<td>Nanoparticle doped TFA-based coated conductor, multiple coat, 100m</td>
</tr>
<tr>
<td>Eickemeyer et al., 2010 (55)</td>
<td></td>
<td>CeO$_2$/YSZ/Y$_2$O$_3$/Ni-9%W RABITS</td>
<td>PLD</td>
<td>1.1</td>
<td>Nonmagnetic substrate tape for YBCO-coated conductors</td>
</tr>
</tbody>
</table>

Table 1 presents some important changes in production of YBCO CC via the TFA MOD approach. Note that some examples are produced by other techniques. The coating thickness d, the substrate and the deposition technique are added if those were reported.
PART II

EXPERIMENTS

The influence of heat treatment parameters on pyrolysed YBCO TFAH films by inkjet printing
5 Measurement techniques

5.1 Hall probe

A Hall probe scan was used to map the trapped magnetic field in the YBCO coated conductors. An estimate of the critical current density $J_C$ was derived for each sample from the region with the highest trapped magnetic field. This measurement technique is based on the Hall effect as illustrated in Figure 24. The charge carriers of the current passing through the plate (Hall sensor) are forced to move to the sides of the conductor under the influence of the external magnetic field. A potential difference is thereby built up between both sides of the sensor. Consequently, the magnetic field, which should vary linearly with the measured voltage, can be determined if a known current is passed through the Hall sensor.

![Schematic representation of the Hall effect](image)

**Figure 24:** Schematic representation of the Hall effect (56)

The Hall measurements were always performed before other characterisation to reduce the chance of scratching the tape, which would significantly reduce the trapped field by reducing the scale of macroscopic current flow or percolation paths (57). *Figure 25 shows*
the Hall probe setup with the Hall sensor attached to an XYZ positioning system. The tape was cooled by immersing it in liquid nitrogen and subsequently magnetized with a coil generating a magnetic field of about 0.1T. This zero field cooling (ZFC) method leads to the critical state in which current density equal to $J_C$ flows around connected regions creating a trapped field profile (58). The trapped field was scanned using a Hall probe of dimension 0.1 x 0.1 mm with a scan height of 0.2 mm and step size also of 0.2 mm.

An estimate of the critical current density can be obtained by considering the field produced by the critical state in a circular thin film. This is equivalent to a uniform current density of $J_C$ circulating around the axis of a disk.

$$B_0(x) = \frac{1}{2\pi \mu_0} \int_A x A(x, a)$$

Equation 1
The peak field $B_0$ on the axis perpendicular to the surface is given by Reaction 1, whereby $x$ is the height of the hall probe above the surface, $a$ is the radius of the current disk, $f$ is a correction factor to take account of the increase in field due to a magnetic substrate and $\mu_0$ the vacuum permeability. A constant estimate of $f = 0.6$ was used based on a numerical model of the current disk and assuming a permeability for the Ni-W substrate of between 20 and 50. (59) Rearranging Reaction 1 gives Reaction 3, the surface critical current density (A/m) with the critical current density given by $J_C = J_S/b$, where $b$ is the film thickness.

A perfect superconducting sample tape would have an approximately conical trapped field profile resulting from a single disk of current. In reality the ability to sustain a macroscopic current might be confined just to one or more smaller regions of the coating, typically leading to a single peak in trapped field surrounded by other irregular smaller peaks. Reaction 3 is therefore used only to give an approximate estimate of $J_S$. The estimate of $J_C$ has a further error contribution due to the uncertainty in the thickness $b$ of the film.

The minimum size of a fully connected superconducting region that could be detected using the Hall probe method was approximately 1mm assuming a minimum $J_C$ of 0.2MA/cm$^2$. This was found by calculating the radius of a current loop from Reaction 1 that gives a peak field equal to the minimum detectable field of the Hall probe (resulting from noise and drift). Therefore the Hall probe technique is ideal for identifying macroscopic superconducting percolation paths but cannot detect superconductivity if the percolation paths are small.

The film thickness was assumed to be 500 μm for all tapes, which was previously measured for coatings printed using the same printing parameters. An estimation of the $J_C$ was made based on Reaction 3, in which $B_0$ and the radius $a$ were derived from the measured results. To estimate the $J_C$, the superconducting area was first defined by

\[
A(x,a) = \ln \left[ \sqrt{1 + \left( \frac{a}{x} \right)^2 + \frac{a}{x}} \right] - \left[ 1 + \left( \frac{a}{x} \right)^2 \right]^{-1}
\]

Equation 2

\[
J_S = \frac{2fB_0}{\mu_0 A(x,a)}
\]

Equation 3
reading the dimensions on the axis as indicated in Figure 26. Consequently, the radius $a$ was calculated by assuming that the peak is circular. A rough estimate of the $J_c$ can thereby be obtained.

Figure 26: Top view of a typical graph derived from the data obtained by Hall measurements. The dotted line shows the border of the tape and the bold line defines the region which is used to estimate the $J_c$.
5.2 Inductive $T_C$ measurements

Whereas Hall probe scans provide information about macroscopic continuous current carrying regions, AC inductive $T_C$ measurements were used to determine the superconducting transition temperature. The use of inductive $T_C$ measurements is complementary with Hall probe scans and resistive $T_C$ measurements, since the information in this method is obtained from intra-grain percolation paths, rather than from inter-grain percolation paths as for the latter techniques (60).

Imperfections such as pores, cracks, normal phases (including non-superconducting YBCO phases), high angle grain boundaries and other YBCO defects are the main causes of non-percolating macroscopic paths. As mentioned in §5.1, superconducting regions smaller than 1mm$^2$ cannot be detected with the Hall sensor. The use of this inductive method, on the other hand, enables us to generate shielding currents inside the specimen regions which do not contribute to the transport current and can be detected with the receiving coil (60).

The superconducting transition temperatures in the coated tapes were measured by applying an alternating voltage of 1V rms and 320Hz over the drive coil (Ø 3.22mm), which was located above the region of interest. The induced voltage in the receiving coil was measured as a function of temperature, from which the $T_C$ value could be deduced (Figure 27). The measurement was performed using an EG&G model 5210 lock-in amplifier, the drive signal being generated by its internal oscillator.

The inductive $T_C$ measurements were conducted above the region which appeared to be superconducting concerning Hall probe. If the coated tapes were not superconducting, the $T_C$ at the middle of the tape was measured. Note that the obtained results cannot be generalised for the entire area and care should be taken with the interpretation.
In §7, the amount of YBCO coating contributing to the superconducting transition as indicated in Figure 28 is also called the amplitude of the transition, which is calculated as \( (V_1 - V_2)/V_1 \).

**Figure 27:** Drawing of the inductive probe for critical temperature measurements (61)

**Figure 28:** Typical graph showing the superconducting transition obtained from inductive \( T_C \) measurements.
5.3 X-Ray Diffraction

X-Ray Diffraction (XRD) analysis provides the ability to identify the crystallographic structure by passing X-rays of known wavelength ($CuK_\alpha = 154$ pm) through the sample. The penetrating character of this radiation enables the X-rays to interact with the atoms of the sample and a unique pattern of reflections is thereby obtained (10).

All the XRD techniques used are based on Bragg's Law (Equation 4), in which $n$ stands for the order of diffraction, $\lambda$ is the wavelength of the incident ray, $d$ is the inter-planar spacing for a particular set of lattice planes and $\theta$ is the angle between that crystal plane and the diffracted beam.

$$n\lambda = 2dsin\theta$$  \hspace{1cm} \text{Equation 4}

As described in §4.2.2, the texture of the produced YBCO layer is very important to obtain superconducting properties. Therefore, the Bragg-Brentano setup ($\theta$-2$\theta$ setup), rocking curves and pole figures are three different XRD techniques, which are normally used to examine the YBCO coatings. However, pole figures were not conducted in this work. Firstly, a $\theta$-2$\theta$ scan from 5 to 60° was executed with a Philips X'Pert PW1730 diffractometer using unfiltered $CuK_\alpha$ radiation. To minimize the variation in measured intensity of the typically 1cm$^2$ sample, divergence and anti-scatter slits of 1/2° and a 0.3mm receiving slit were used (62). The XRD data were analysed with Philips Highscore Plus software to identify the different phases, crystal structure and preferred orientation. Using the same device, the rocking curve of YBCO (005) was acquired and the out-of-plane grain misalignment was assessed based on Full Width at Half Maximum (FWHM) value (10).
5.4 Scanning Electron Microscopy (SEM)

SEM provides sample images with high magnification. The coating morphology could thereby be assessed. EDX (Energy Dispersive X-ray spectroscopy) spectra were obtained with the same device and were used to identify variations in the elemental composition.

Figure 29: Schematic representation of the SEM setup (63)

Figure 29 depicts the basic elements of an SEM device. The used JEOL 5800LV SEM instrument utilizes a tungsten filament as electron gun. The produced thermal electrons are subsequently accelerated towards the anode (15kV potential difference). The electron beam can be manipulated and focused using electromagnets ("electron lenses"). The focused electron beam hits the sample on the moving stage in the vacuum chamber, and secondary electrons (SE), backscattered electrons (BSE) and characteristic X-rays are
generated. The low energy SE (<50eV) are generated by elastic scattering within the first few nm of the sample and provide only morphological information. The BSE are formed by multiple elastic and inelastic collisions, which means that only the high energy electrons of the incident beam are able to escape from further in the sample. Images made from BSE have a lower resolution, but they do represent better the elemental composition of the material. During the electron bombardment on the sample, electrons of the inner shells are also kicked away, leaving a vacancy. Relaxation by electron transfer from a higher energy level results in the production of characteristic X-rays, which reveals the chemical composition of the material. This technique is termed EDX and stands for energy-dispersive X-ray spectroscopy (10) (64).

5.5 Optical microscopy

The thin film samples were examined with an optical microscope in bright field mode using a Zeiss Axiotech Reflected Light Microscope. The digital images were analysed with Image-Pro Plus software.
6 Experimental details

6.1 Chemicals used

Yttrium barium copper oxide (YBCO, YBa$_2$Cu$_3$O$_{6.9}$, 99.90%) orthorhombic powder was obtained from SSC Inc. and desiccated in a vacuum furnace at 150°C for 24h.

Anhydrous acetone (DMK, CH$_3$COCH$_3$, 99.99%), methanol (MeOH, CH$_3$OH, 99.99%) and isopropanol (IPA, (CH$_3$)$_2$CHOH, 99.90%) were purchased from Fisher Scientific. Note that methanol was rectified just before usage.

Trifluoroacetic acid (TFAH, CF$_3$COOH, 99.99%) and trifluoroacetic anhydride (TFAA, (CF$_3$CO)$_2$O, 99.99%) were obtained from Sigma-Aldrich and used as supplied.

6.2 Ink preparation

The YBCO precursor solution (ink) was prepared by dissolving desiccated YBCO powder (vacuum furnace at 150°C for 24h) in a stoichiometric amount of TFAH with distilled DMK (dimethyl ketone) as a solvent. TFAH was added drop-wise at room temperature while stirring. The mixture was subsequently refluxed at 70 °C with vigorous stirring, giving a blue solution after about 24h. Next, removal of water was performed by adding TFAA drop-wise until the colour changed to green. Once green, the solution was cooled down to room temperature with gentle stirring. Pure N$_2$ was used as an inert atmosphere during the whole synthesis.

The excess of TFAH together with DMK was removed in a rotary evaporator giving a viscous dark green gel. This procedure was repeated three times for further purification of the precursor solution. Anhydrous MeOH was used to dilute the gel and adjust the concentration of the final solution to 1.08M total metal ion concentration.

Finally the transparent green solution was filtered through a 1 μm glass microfiber filter to ensure that no particles of dust or other contaminants remained to block the inkjet printing.
equipment. The ink was stored under pure N$_2$ in glass vials and did not show any signs of precipitation over several months.

6.3 Substrate

Highly textured Ni-5%W tape with double La$_2$Zr$_2$O$_7$ (LZO) buffer layers and a CeO$_2$ cap layer was used as a fully chemical solution deposited (CSD) rolling assisted biaxially textured substrate (RABiTS) derived from reel-to-reel dip-coating (Zenergy Power GmbH, Germany). The FWHM of the LZO (200) reflection (omega scan) of the buffer layer was 4.85°, while the FWHM of the CeO$_2$ (400) reflection of the was 5.29°.

The buffered tape was chemically cleaned in IPA in an ultrasonic bath for 10min before each deposition and used as soon as possible to prevent degradation of the wettability.

6.4 Inkjet printing

The electromagnetic inkjet printing method was used to deposit the YBCO ink on the fully buffered tapes. The print head was mounted on a computer controlled XY positioning system (Figure 30) and was connected to a pressurized ink reservoir. The nozzle and printing system are controlled by an in-house made software program.

In order to get a complete covering of the buffered tape, it was important to use the correct spacing between the positions at which the droplets were released. Droplets were dispensed in a square lattice with 0.9mm spacing between each droplet release location as shown in Figure 31.

The cleaned tape was placed on a magnetic plate to ensure an entirely flat surface. Subsequently, the printing environment was flushed with N$_2$ gas until a relative humidity below 20% was achieved. The tape was cooled to about 10°C. Using a nozzle opening
time of 500 µs, applying a pressure of 0.16bar and using the described printing pattern, a fully covered tape could be produced with a coating thickness of about 500nm after the full heat treatment (this was previously measured for a tape printed under the same conditions). The raster pattern for printing was previously optimized for Ce$_{0.8}$Gd$_{0.2}$O$_2$ and the same parameters were adopted here for printing YBCO ink (65).

**Figure 30**: Electromagnetic nozzle and printing setup

**Figure 31**: Square pattern used as printing array (spacing of 0.9×0.9mm) (65). The black arrows depict the movements of the plotter (the coating was formed row per row, perpendicular to the length of the tape). The grey rectangle represents the tape
6.5 Heat treatment

6.5.1 Pyrolysis

The pyrolysis was previously optimized and it was found that crack-free coatings could be produced using the described printing settings and pyrolysing the tape according to the heat treatment shown in Figure 32. Note that superconducting coatings could only be produced with the provided pyrolysis heat treatment, rather than using the highly cited "long pyrolysis" for TFA-MOD thin films (66). A similar observation to ours was published by Matsuda et al. for coated PLD-CeO$_2$/IBAD-Gd$_2$Zr$_2$O$_7$/Hastelloy tapes (67).

![Figure 32: Typical pyrolysis heat treatment profile (measured), used for all the tapes](image)

The tape was dried for 20min after printing at a temperature below 15°C and a relative humidity below 20%, ensuring a slow evaporation rate of the solvent, before executing the pyrolysis. The dried tape on an alumina tile was placed in the middle of the heating zone with a type K thermocouple set up under it. The temperature was increased to 325°C at a rate of 1°C/min while the furnace was flushed with O$_2$ gas (1.5L/min). The furnace was...
cooled down with the same rate. As can be seen from the dotted line in Figure 32, the gas was passed through a water bubbler (25°C) from 40°C till 100°C (during cooling), which provided a water vapour pressure of approximately 0.031 bar. Note that the water vapour pressures were not measured but obtained from tables, representing the temperature and pH_{2}O relationship. (68)

6.5.2  Annealing

After the pyrolysis, the tape was cut into smaller parts 1cm long to anneal separately. Before undergoing the second heat treatment, it was checked whether the tapes were crack-free by using optical microscope.

Figure 33: Typical heat treatment for the annealing of pyrolysed tapes (measured)
For all experiments, the furnace was flushed with either O$_2$ or 200ppm O$_2$ in Ar at a speed of 1.0L/min, 1.5L/min or 2.5L/min. The temperature was ramped up from room temperature at a rate of 5°C/min to the annealing temperature, which was varied from 695 to 815°C. The samples were annealed for 0.5, 1, 2 or 3h (time at the maximum temperature) and then cooled down at a rate of 5°C/min. Oxygenation of the YBCO coating in a pure oxygen atmosphere was performed at 450°C for 4h. After this, the sample was further cooled at a rate of 5°C/min to room temperature. As depicted in Figure 33, the dotted line which represents the water vapour pressure shows that the 200ppm O$_2$ in Ar gas mixture was humidified by passing it through a water bath once the sample temperature exceeded about 270°C and switched back to the dry gas mixture at the end of the annealing (end of the first temperature plateau). Water bath temperatures of 15, 25, 35, 50 and 70°C were used, which correspond to a water vapour pressure of 0.017, 0.031, 0.056, 0.122 and 0.308bar respectively.
7 Results and discussion

7.1 Printing of the substrates

Although the investigation of the printing parameters were not the focus of this work, the influence of temperature at which the buffered tapes were printed on the coating quality was studied. It was observed that the best pyrolysed tapes were obtained if the ink was printed at an environmental temperature between 5 and 10°C, which reduced the evaporation rate and resulted in smoother coatings compared with the coatings printed at room temperature.

It is important to mention that the superconducting coating properties were highly dependent on the coating quality after printing. This was caused by two problems. Firstly, the relatively large droplets ejected from the electromagnetic inkjet did not always fully merge. Those disconnected droplets gave rise to an uneven surface, which during the heat treatment tended to crack at the thickest coating regions, whereas the thin coatings areas did not. It was observed from inductive Tc measurements that significantly more secondary phase (broader transition and lower superconducting volume fraction) was formed at the edges of the coating than in the middle of the coated tape. It has also been reported that the sol-gel morphology after deposition influences the amount of randomly oriented YBCO, which subsequently deteriorates the epitaxial YBCO growth, so this was in agreement with our observations (69). Secondly, although the tape was washed in isopropanol before printing, the buffered tape exposed a different wetting behaviour between each batch and even within a batch. Moreover, since the cleaning, printing and drying steps were not fully automated, the coatings may have been deposited each time under slightly different conditions. It was also observed with optical microscopy that uncoated buffered tapes contained many cracks in the buffer layer, which can only have a negative impact on the epitaxial YBCO growth and diffusion effects.

Figure 34 shows the dependence of the YBCO morphology on the region in the tape. It shows that much more needle-shape crystals structures or randomly oriented YBCO are formed at the edges, than in the middle of the tape (33). Note that the chemically deposited buffer layers (see §6.3) did not reach the edges of the tape. About 90% of the width was
coated, whereas only 60% of the width had a constant coating thickness, which could be seen from the colour profile (visually observed). Hence, it is expected that this effect is caused by difference in thickness of the buffer layers, however, a clear conclusion concerning this issue cannot be made.

Figure 34: Top view of the graph which depicts the trapped magnetic field of a 2cm long coated tape, measured with the Hall probe. SEM pictures are presented for different regions in the tape. Note that the contrast comes from the difference in atomic number (YBCO is black, confirmed via EDX)
7.2 Investigation of the annealing temperature

Figure 35 shows the $\theta$-2$\theta$ scans from the samples annealed at different annealing temperatures. From 760°C onwards, significant oxidation of the substrate occurred. With increasing annealing temperature, the intensity of the YBCO (00l) peaks rose almost over the entire range. However, also the amount of green phase ($Y_2$BaCuO$_5$) rose considerably with increasing annealing temperature. An overview of the data provided in this graph is shown in Figure 36.

![Figure 35: XRD patterns of the $\theta$-2$\theta$ scans of samples annealed at different temperatures (shown at the right of the graph). Note that the curve at 730°C is the tape with the best superconducting performances]
The YBCO (003) peak intensity in Figure 36 reaches a local maximum around 728°C. However, the most c-axis oriented coatings were obtained around 785°C. In addition, the coatings produced in this temperature region showed a very low FWHM, with a minimum of 4.08° for 785°C. Note that all the intensities presented and discussed here are normalised against the Ni5%W (200) peak intensity, which is the most intense peak of the substrate.

![Graph showing relative intensity of the YBCO (003) peak and FWHM of the YBCO (005) peak versus annealing temperature.](image)

**Figure 36**: Relative intensity of the YBCO (003) peak for samples heat treated at different annealing temperatures (left axis). The FWHM of the YBCO (005) peak is shown on the right axis.

A semi-quantitative indication of the amount of BaF$_2$ present in the annealed tape is shown in Figure 37 for data obtained from XRD scans and EDX analysis. The same broad trend for both curves is observed, showing that the amount of BaF$_2$ dropped quickly when the annealing temperature increased. The more reliable variable for phase identification is likely to be the normalised XRD intensity, which shows that high BaF$_2$ residues were measured for the tapes annealed at 695 and 700°C. This value dropped quickly for the following temperatures until virtually no BaF$_2$ could be identified at and above 760°C. EDX analysis also confirms that at and above 760°C no fluorine atoms could be identified.
Figure 37: Indicators of the amount of unreacted BaF$_2$ present after the heat treatment for the tapes annealed at different annealing temperatures according to XRD data (left axis) and EDX data (right axis).

The measured $T_C$ values (Figure 38) show that no transition occurred above 77.4K for the samples annealed at 695 and 700°C. Those annealed between 700°C and 734°C showed a high $T_C$ with small transition width. At higher annealing temperatures, the transition width remains much the same. Note that the transition temperature decreased again above 785°C. Apart from the two samples annealed at 695 and 700°C, the amplitude of the transition did not change significantly over the studied temperature range.
Figure 38: Transition temperatures measured by inductive $T_C$ measurements for samples heat treated at different annealing temperature (left axis). The bottom dashed curve shows the beginning of the transition, while the upper one depicts the end of the transition. The solid line in the middle shows the transition temperature itself. The right axis refers to the amplitude of the transition, which is considered to be a measure for the superconducting volume fraction of the measured area.

Figure 39 shows that at higher temperatures, more green phase was formed. From about 772°C onwards, the ratio between the green phase intensity and the YBCO (003) peak intensity increased significantly.

As seen from the inductive and Hall probe measurements, the samples annealed at 695 and 700°C are not superconducting and therefore trap no magnetic flux (Figure 39). The best superconducting coatings seem to be produced when annealed around 728°C, reaching a maximum of 0.14MA/cm$^2$. Above that region, the estimated critical current altered until 785°C and should be repeated to find a clear correlation between the amount of green phase estimated $J_C$ at varying different temperatures. It is clear, however, that exceeding that temperature resulted in non superconducting coatings.
Figure 39: Ratio of the green phase intensity ($Y_2BaCuO_5$) against the YBCO (003) intensity for samples heat treated at different annealing temperature (left axis). The estimated critical current density is shown on the right axis.

The SEM images in Figure 40 show that the samples annealed at low temperatures consist of many needle-shaped structures. Small YBCO (not very clear however) grains could be identified in the samples annealed below 760°C. The samples annealed in the higher temperature region show large grains and small pores. However, needle-shaped crystals were still present above that temperature. White-grey particles, identified as CuO via EDX, were observed on the surface of the samples over the entire examined temperature range, but they were most notable in the higher temperature region.
It is expected that two competing processes took place during the investigation of the heat treatment, since the highest c-axis oriented YBCO phase was formed at 785°C with a very low FWHM, while good superconducting coatings were only obtained if annealed around 728°C. Note that more YBCO phase was formed (higher YBCO (003) intensity), with a better orientation (lower FWHM) at high annealing temperatures, but that simultaneously more oxidation of the buffered tape and green phase formation occurred.

The measured $T_c$ values (Figure 38) show that no transition occurred above 77.4K for the samples annealed at 695 and 700°C, which means that no superconducting YBCO phase was formed. XRD and EDX data (Figure 37) revealed that those samples had a
significantly higher fraction of BaF$_2$ than the tapes annealed above 700°C, which was reported to be a measure for the progress of the YBCO formation (70). Furthermore, as could be observed, low annealing temperatures resulted in more a-axis grown YBCO (needle-shaped crystals), which caused more pores and reduced the superconducting volume fraction. Our observations are consistent with the YBCO phase diagram (Figure 41) showing that a much higher proportion of a-axis oriented YBCO should be formed than c-axis oriented YBCO below 700°C for the atmosphere used.

Above 700°C, superconducting phase was formed in all the coatings, whereas the Hall probe could not identify any macroscopically detectable percolation paths in the tapes annealed above 772°C. In addition, relatively large amounts of green phase were formed above that temperature. It is therefore assumed that the grains were insulated from each other by Y$_2$BaCuO$_5$. Another disadvantageous influence on the current carrying performance is the fact that the substrate got significantly oxidized above 760°C (see Figure 35). This presumably caused diffusion of Ni into the YBCO coating, which subsequently decreased the transition temperature from 785°C onwards.

It could be seen from the SEM images in Figure 40 that the YBCO grain size was influenced by the annealing temperature. Larger grains and fewer pores were formed at higher annealing temperatures, whereas the small grains were observed below 760°C. Particularly the tapes annealed at 700 and 713°C were very porous.

Consistent with our observations, Solovyov et al. published that the grain size strongly affects the $J_C$ (71). Although the difference in grain size in our study was not as marked as in the reported work, similar results were obtained. Solovyov et al. reported that a drastic reduction of the $J_C$ of large grains (~5µm) was observed, caused by the accumulation of secondary phase precipitates close to the grains and accumulation of non-superconducting phases in the grain boundaries of grains larger than ~10µm. Consequently, small grains would benefit the grain connectivity and $J_C$ value. Note that the biggest observed grain size in this work was only about 2.5µm.

Studying the influence of the annealing temperature on the superconducting properties showed that 728°C ($J_C = 0.14$MA/cm$^2$) was the best annealing temperature.
Figure 41: YBCO phase diagram showing the dependence of the formed phases on the temperature and oxygen partial pressure (72). Note a1: a-axis oriented YBCO; c2: c-axis oriented YBCO; c1: strong c-axis oriented YBCO; m1: YBCO melting line. The red bold line represents the investigated region, whereas the green one will be investigated in further research.

7.3 Investigation of the gas flow rate

In this investigation, an annealing temperature of 728°C was used, which was shown to be the best temperature to obtain the highest Jc.

The top curve in Figure 42 shows that a very small amount of superconducting phase was formed for gas flow rates of 0.5 and 1L/min. The intensity was more than doubled using
1.5L/min which was also the highest YBCO (003) intensity obtained in this set of experiments. A higher gas flow rate then 1.5L/min slightly reduced the intensity again.

The same trend was followed almost exactly for the critical current density estimated from Hall probe measurements in Figure 42. Both $J_C$ values are very low for the first two lowest gas flows, while a maximum estimated $J_C = 0.14\text{MA/cm}^2$ was reached for 1.5L/min. Increasing the flow rate from 1.5 to 2.5L/min reduced the critical current density to half of its value.

**Figure 42:** Relative intensity of YBCO (003) peak for different gas flow rates used during the annealing (left axis). The estimated critical current density (from Hall probe measurements) is shown on the right axis.
Figure 43: Inductive Tc measurements for samples annealed at 728°C and varying gas flow rate.

Figure 43 shows that the transition temperature of the YBCO coating was only slightly influenced by the gas flow rate. However, the amplitude of the transition varied drastically for each of the experiments: the ratio of the induced voltage at low temperatures to that above Tc can be related approximately to the superconducting volume fraction in the sampled region. Below the superconducting transition temperature (Tc) of the tape annealed with a flow rate of 1.0L/min, it was estimated from Figure 43 that about 60% of the material was superconducting (resulting in a Jc of 0.035MA/cm²), about 95% was superconducting for 1.5L/min (resulting in a Jc of 0.14MA/cm²) and average 35% for 2.5L/min (resulting in a Jc of 0.062MA/cm²). Note that although the amplitude of transition was lower for 2.5 than 1L/min, the corresponding estimated Jc value is higher for 2.5 than 1L/min.

Xu et al. reported that a low gas flow rate causes an accumulation of HF in the coating, which suppresses nucleation and also badly affects the YBCO growth rate (73). The results obtained confirm this trend, since the intensity of the YBCO (003) reflection for 0.5 and 1L/min was much lower than for higher values. It can thereby be assumed that a threshold
of just above 1L/min was required to remove the HF sufficiently quickly to produce highly textured coatings.

By increasing the gas flow rate, water vapour was supplied more quickly, which influences the YBCO growth rate (see §7.5). Chen et al. studied the influence of the flow rate on the microstructure, texture and $J_C$ (74). They showed that the ratio of a-axis/c-axis oriented grains rose if the flow rate exceeded 2L/min, while the YBCO texture and reflections of the YBCO planes were reduced slightly. Although their studied range was much larger than in the work reported here, most of the results presented are in agreement with those reported by Chen et al. However, it is not clear what exactly causes the reduction of the superconducting volume, relative intensity of the YBCO(003) reflection and the estimated $J_C$ when the gas flow rate was increased to 2.5L/min.

7.4 Investigation of the annealing time

A gas flow rate of 1.5L/min, which was used already for the investigation of the annealing temperature, resulted in the highest estimated $J_C$ and is therefore further used here.

As depicted in Figure 44, the YBCO (003) intensity almost tripled when the annealing time was increased from 0.5 to 2h. Increasing further caused a sharp decrease in intensity.

A similar trend was observed again for the estimated $J_C$ (Figure 44). The maximum estimated critical current density doubled when the annealing time was increased from 0.5 to 2h and longer annealing times deteriorated the superconducting performance significantly.
Figure 44: The relative intensity of YBCO (003) for samples annealed at 728°C for increasing annealing times is depicted at the left axis. The estimated critical current density is shown on the right axis.

Figure 45 reveals that the tape annealed for 0.5h showed only a very shallow and broad superconducting transition. The other samples all had a $T_C$ value between 89K and 90K, so little variation of this property was measured for the different annealing times. However, the width of transition for the tape annealed for 3h was slightly higher than for 1 and 2h. In addition, a difference in amplitude was observed between the several tapes. Concerning the results in Figure 45, about 85%, 6%, 4% and 14% of the material did not contribute to the superconducting transition for 0.5, 1, 2 and 3h annealing respectively.
Figure 45: Transition temperature measured via inductive $T_C$ measurements for samples annealed at 728°C for different periods.

Figure 46: Ratio of the greenphase intensity ($Y_2BaCuO_5$) against the YBCO (003) intensity for samples heat treated for different periods (left axis). The estimated critical current density is shown on the right axis.
Figure 46 shows that little variation of the green phase fraction appeared as the annealing time was varied. The minimum was obtained after 2h, corresponding with the maximal $J_C = 0.18 \text{MA/cm}^2$. Increasing the annealing time from 2 to 3h caused a doubling of the green phase ratio.

The SEM images in Figure 47 show that needle-like structures were formed for all the performed experiments in this set. However, they are more abundant for longer annealing times.

![SEM images of the samples annealed at 728ºC for respectively 0.5, 1, 2 and 3h](image)

**Figure 47**: SEM images of the samples annealed at 728ºC for respectively 0.5, 1, 2 and 3h

Note that the area which was superconducting was very small if annealed for 0.5h, but this increased as the annealing time was increased.

The best superconducting performance was obtained when the coated tape was annealed for 2h at 728ºC, resulting in an estimated $J_C$ of 0.18MA/cm² (*Figure 44*). Further increasing the annealing time reduced both the YBCO (003) intensity and the estimated critical current density. In all likelihood, a combination of an increased amount of green phase and a
higher abundance of a-axis grown YBCO resulted in a lower $J_C$ and reduced YBCO (003) intensity. Concerning the curve of 0.5h in Figure 45, one could expect that there was almost no trapped flux because of the very low amplitude of transition. However, the estimated critical current density is $0.09\,\text{MA/cm}^2$ which is similar with the estimated $J_C$ of $0.08\,\text{MA/cm}^2$ for 3h annealing. This indicates the impact of randomly oriented YBCO on the critical current. Although the small amount of superconducting YBCO phase formed after 0.5h, it is expected that during the early stages of the YBCO formation very little a/b-axis oriented YBCO was formed, whereby that the phase was almost pure, resulting in the relatively high $J_C$. The sample annealed for 3h, on the other hand, showed the lowest $J_C$ in this set for a slightly higher YBCO (003) intensity than after 0.5h. It is assumed that the influence of the a/b-axis grown YBCO crystals caused the fall of YBCO (003) intensity, which together with an increase of the green phase fraction compared with 2h annealing (Figure 46) resulted in the significant deterioration of its $J_C$ value. Note that sampling effects might have influenced the results.

The SEM images of the tapes annealed for different periods show that both a-axis and c-axis grown YBCO were formed under the experimental conditions studied (75). Since the needle-like structures are more abundant when annealing for longer durations, no pure c-axis grown YBCO could be formed at $728^\circ\text{C}$ using a gas flow rate of 1.5L/min and a water vapour pressure of 0.031bar. Further research is therefore required to find measures to reduce the growth of a-axis grown YBCO at a low annealing temperature (see §7.6).

### 7.5 Investigation of water vapour pressure

An annealing temperature of $728^\circ\text{C}$, gas flow rate of 1.5L/min and an annealing time of 1h with a varying water bath temperature were used here.

The top curve in Figure 48 shows that the intensity of the YBCO (003) peak reached a maximum at a water vapour pressure of about 0.03bar. Increasing the humidity of the gas
from about 0.06 to 0.12bar did not much affect the YBCO (003) intensity, but it did fall significantly as a water vapour pressure of 0.31bar was used.

The estimated \( J_C \) (bottom curve in Figure 48) is zero for the lowest water vapour pressure. At a slightly higher humidity, the maximum \( J_C \) of 0.14MA/cm\(^2\) was already obtained for \( \text{pH}_2\text{O} \approx 0.03\text{bar} \). Increasing the humidity caused a slight \( J_C \) drop for \( \text{pH}_2\text{O} \approx 0.06 \) and 0.12bar and felt to zero upon approaching 0.31bar.

**Figure 48:** The intensity of YBCO (003) normalized against the Ni5%W intensity for samples annealed with different water vapour pressures at 728°C is shown on the left axis. The estimated critical current density is shown on the right axis.
Figure 49: Transition temperatures measured by inductive $T_C$ measurements for samples heat treated at 728°C with different water partial pressures.

Although the tape annealed with a water vapour partial pressure of about 0.02bar could not trap any magnetic flux, its curve in Figure 49 shows that some superconducting material was present, but the transition was very broad and appears to represent only a modest volume fraction of superconducting material. An approximate pH$_2$O of 0.03bar resulted in the highest $T_C$ of 89.4K, with amplitude of about 93%. Apart from the transition amplitude which was about 87%, a similar curve was obtained for the experiment with pH$_2$O $\approx$ 0.06bar. Increasing the humidity more caused a further reduction of the fraction of the coating contributing to the superconducting transition. For pH$_2$O $\approx$ 0.12bar, the transition amplitude dropped to $\pm$81% and the $T_C$ value also shifted to a lower temperature, with a much broader transition. No superconducting transition was observed for pH$_2$O $\approx$ 0.31bar.
Figure 50: Ratio of the greenphase intensity ($Y_2BaCuO_5$) against the YBCO (003) intensity for samples heat treated with a different water vapour pressure (left axis). The estimated critical current density is shown on the right axis.

Figure 50 shows an indication of the amount of green phase as a function of water vapour pressure. Up to 0.12bar, the amount of green phase did not change much with water vapour pressure, however, the fraction increased dramatically if the gas was humidified further. As might be expected, the estimated $J_C$ followed almost the opposite trend.
Figure 51: The amount of unreacted BaF$_2$ present after the heat treatment for the tapes annealed with different water vapour partial pressures obtained from XRD data (left axis) and EDX data (right axis).

*Figure 51* depicts the presence of BaF$_2$ after annealing. A similar trend is observed for both analysis methods, however, XRD results show that no BaF$_2$ was present if pH$_2$O exceeded 0.031 bar, whereas EDX analysis show that the F/Ba ratio does not reach zero with increasing humidity. The F/Ba ratio does not alter much from 0.4 between a water vapour partial pressure of 0.056 and 0.308 bar. This might mean that fluorine was present in another phase, however, evidence therefore was not found.

Note that F atoms are light, and consequently the error of EDX analysis is higher in comparison with Cu atoms for instance. XRD analysis on the other hand, obtains the signals from a bigger area of analysis (1cm$^2$), whereas this is only a few µm$^2$ for EDX. Hence the XRD data is considered more reliable.
Figure 52: SEM images of the samples annealed at 728°C, 1.5L/min gas flow rate and respectively a water vapour pressure of (a) 0.017bar, (b) 0.031bar, (c) 0.056bar, (d) 0.122bar and (e) 0.308bar. The temperatures under the images are those of the water bath through which the gas was passed to humidify.
The SEM images depicted in Figure 52 reveal that slightly more needle-shaped crystals were grown when the humidity during annealing was higher. There were also more cracks (confirmed by EDX) present in the samples annealed with a higher water vapour pressure.

It was reported that an increasing water vapour pressure causes faster crystal growth (76) (77). An indication for the progress of the YBCO formation in our work was the intensity of the BaF\textsubscript{2} reflection obtained from XRD scans and the F/Ba ratio from EDX analysis (Figure 51). In agreement with reported data, here it was also seen that an increase of the water vapour pressure speeds up the YBCO growth rate, indicated by the rapid drop of the F content if the humidity during annealing was increased. As a result of this, the epitaxial growth was less strong due to the quick nucleation and growth. An indication therefore was the intensity drop of the YBCO (003) reflection when pH\textsubscript{2}O exceeded 0.031bar. But although it was reported that the texture deteriorated above a water vapour partial pressure of 10\%, this was not observed in our study (77). Here the FWHM of the YBCO (005) rocking curve did not show any significant deterioration when the water vapour pressure was increased.

Figure 48 shows that a certain water vapour pressure threshold needed to be exceeded to get superconducting coatings, because there was no transition measured for pH\textsubscript{2}O = 0.017bar, whereas a very sharp transition was observed when the water vapour pressure was 0.031bar and higher.

With increasing humidity, the amplitude of the transition dropped gradually, which indicates that more secondary phases were formed. XRD studies showed that the amount of green phase was very high at pH\textsubscript{2}O \approx 0.31bar. It is therefore expected that the increased Y\textsubscript{2}BaCuO\textsubscript{5} fraction both caused the reduction in formed c-axis grown YBCO phase and the estimated J\textsubscript{C}.

More cracks were present in the samples annealed with a higher water vapour pressure. This phenomenon was also observed when the influence of the coating thickness and humidity on the critical current density were investigated (78). Since the growth rate increases with higher water vapour pressures, the rate of HF release would also have been
higher, which is consistent with forming a more porous structure. It is expected that this quick crystal growth gave rise to stresses and resulted in cracking of the coating.
7.6 Future work & recommendations

The YBCO coatings produced in this work were printed at reduced temperatures (5-10°C) which benefited the formation of smooth and unwrinkled films. However, this process has not been completely optimized yet. In addition, it was found that the printing quality strongly affected the YBCO coating properties. Differences in thickness caused unequal growth rates and influenced the amount of randomly oriented YBCO. Castaño et al. reported that the deposition quality strongly affects macroscopic segregation (69). An uneven surface for instance enhances secondary phase formation, and deteriorates epitaxial YBCO growth. So far, the tapes were coated with an electromagnetic nozzle, but in future work the coatings will be deposited with a piezoelectric device to obtain more uniform coatings. Also the influence of the deposition temperature will be further investigated and optimized.

The pyrolysis was previously optimized to produce crack-free coatings. Although superconducting coatings could be made using this heating profile (Figure 32), it is thought that a few adaptations to that heat treatment profile may be beneficial to increase the superconducting performance of the YBCO films. It can be seen in Figure 40 that, particularly for low annealing temperatures, many pores were formed. One of the contributions therefore is the high heating rate (particularly for the 200-250°C temperature region) and thereby rapid release of gases during pyrolysis. The influence of the heating rate during pyrolysis was investigated by Su et al. and micro-pores were already observed when the heating rate in the temperature region 200-250°C exceeded 0.17°C/min, while we used 1°C/min from room temperature to 325°C (66). This problem can be overcome by changing the ink nature as described in §3.3.2.1 (advanced TFA-MOD) and published in (35). Thereby, high performance YBCO coatings can be fabricated with a fast pyrolysis heat treatment. Additionally, it was reported that the characteristics of the crystalline nanoparticles are determined during the pyrolysis and influence the J_c (67). Further improvements therefore need to be implemented to improve the density and microstructure.

Concerning the annealing procedure, superconducting coatings could be produced at 728°C. Above this temperature, it was assumed that poor grain connectivity caused by secondary phase formation around the grain boundaries destroyed the macroscopically
superconducting properties, even though microscopically small YBCO phase regions were present (identified with inductive $T_C$ measurements). Additionally, oxidation of the substrate was significant above 760°C. Hence, it is desirable to reduce the temperature at which highly textured YBCO was formed (around 785°C) to the temperature where the highest estimated $J_C$ was obtained (around 728°C). Concerning the YBCO phase diagram in Figure 41, it may be possible to form epitaxially grown highly oriented YBCO grains at an annealing temperature of 730°C and an oxygen partial pressure of 20ppm. Araki et al. already reported the fabrication of superconducting YBCO coatings at a low annealing temperature (725°C), using a reduced oxygen partial pressure (125ppm). A $J_C$ of 0.81MA/cm² was measured for YBCO deposited onto a CeO$_2$(sputtered)/YSZ(IBAD) buffered Hastelloy tape (70).
8 Conclusions

Process parameters of the heat treatment and their influence on the YBCO phase formation and the superconducting properties have been studied. Fully buffered Ni-5%W tapes (FWHM of 5.29° for the CeO$_2$ (400) reflection) were coated using an electromagnetic micro-valve based inkjet printer.

A previously optimized pyrolysis heat treatment decomposed the precursor material, resulting in crystalline CuO, Y$_2$O$_3$ (or/and Y-O-F) and BaF$_2$ (or/and Ba-O-F) phases (33) (79).

The influence of the annealing temperature, gas flow rate, annealing time and water vapour pressure were studied separately. The best experimental conditions of each previous set were used in the next one. The biggest improvement of the $J_C$ could be made by optimizing the annealing temperature and annealing time. The best superconducting sample was produced if the coated tape was annealed at 728°C for 2h, with a gas flow rate of 1.5L/min and water vapour pressure of 0.031bar. No oxidation of the metal substrate was observed in this temperature region. The formed YBCO phase showed a sharp superconducting transition at a temperature of 89.5K, with an estimated critical current density of 0.18MA/cm$^2$ (or a surface current $J_S = 9A/cm$) and a FWHM of YBCO (005) reflection of 4.97°. To remove the formed HF sufficiently quickly during YBCO formation, a flow rate of at least about 1.5L/min was necessary to obtain high $J_C$ values. For 1h annealing time, a water vapour pressure threshold of 0.031bar was required to form any YBCO phase.

The performed research has provided much information and it is strongly believed that the method used here will produce high $J_C$ coated conductors if the recommendations are implemented. In future work, the coatings will be deposited with a piezoelectric printing device to obtain more uniform coatings. To reduce the temperature at which highly-textured epitaxial YBCO can be obtained, the concept of annealing under a reduced oxygen partial pressure will be investigated.
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PART III

DUTCH SUMMARY