

The columnar to bimodal transition of Al–Cr–Mo–Sc–Zr alloys during laser powder bed fusion

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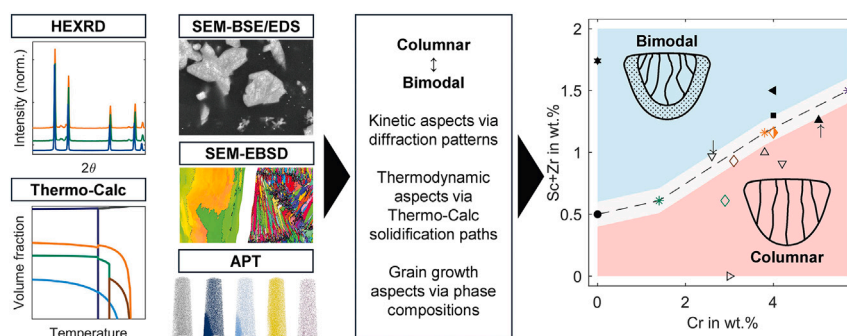
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HIGHLIGHTS

- Al–Cr–Mo–Sc–Zr alloys exhibit either columnar or bimodal microstructures, depending on composition.
- $\text{Al}_3(\text{Sc}, \text{Zr})$ and $\text{Al}_{45}\text{Cr}_7$ compete during solidification from the liquid melt.
- Lattice mismatch of $\text{Al}_3(\text{Sc}, \text{Zr})$ and $\alpha\text{-Al}$ impedes grain refinement.
- At least 11% of Sc and 25% of Zr are captured by $\text{Al}_{45}\text{Cr}_7$ phases.

GRAPHICAL ABSTRACT



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ABSTRACT

Aluminium alloys processed via Powder Bed Fusion using a Laser Beam (PBF-LB) enable complex and lightweight components. Especially high-strength and heat-resistant Al alloys are in high demand for aerospace and motor-sports applications, but the processability of these alloys remains critical due to hot-cracking along columnar grains. Therefore, the microstructural control of PBF-LB alloys is under increasing consideration. Al–Cr alloys have shown promising high-temperature properties and good processability in previous studies despite having a coarse and fully columnar grain structure. In this study, Al–Cr–Mo–Sc–Zr alloys with different compositions are subjected to phase analysis to understand the transition from fully columnar to bimodal grain structures. Synchrotron diffraction, electron dispersive spectroscopy, and atom probe tomography results have shown that three phases are present, irrespective of the alloys' composition: $\alpha\text{-Al}$, $\text{Al}_{45}\text{Cr}_7$, and $\text{Al}_3(\text{Sc}, \text{Zr})$. The introduction of Cr increases the lattice mismatch between $\alpha\text{-Al}$ and $\text{Al}_3(\text{Sc}, \text{Zr})$ and is suspected to hinder grain refinement by Sc and Zr. Various thermodynamic simulations revealed the effect of grain refining elements (Sc + Zr) and Cr on the solidification path. The combination of simulation and experimental investigations led to three hypotheses on the columnar to bimodal transition in Al–Cr alloys. These results will help to further enable the microstructural control of PBF-LB processed alloys.

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1. Introduction

Powder Bed Fusion using a Laser Beam (PBF-LB) is an additive manufacturing technique to build complex metallic components by melting successive layers of powder with a laser. Aluminium alloys are important in the automotive, aerospace and motorsports sectors, and are ideal for PBF-LB applications, e.g., topology optimization, because of their high strength and low density. Especially in aerospace and motorsports, high-strength and heat-resistant alloys are in demand. However, high-strength Al alloys are susceptible to hot-cracking along columnar grain boundaries during the rapid cooling rates of PBF-LB, which limits the application of already available conventional alloys. Previous research focused on improving the processability of 2xxx and 7xxx series alloys by adding grain refining elements such as Sc, Zr, and Ti [1–3].

When 0.7 wt.% Sc is added to cast aluminium, L_{12} Al_3Sc precipitates form first from the liquid and act as nuclei for α -Al [4–8]. Although Zr is a less potent grain refiner, the combination of Sc and Zr reduces the necessary amount of Sc for grain refinement, increases thermal stability and increases age hardening response because of an increased number of smaller $Al_3(Sc,Zr)$ precipitates [4,9–11]. Due to the high cooling rates of PBF-LB, precipitation hardening in Sc-/Zr-modified Al alloys is achieved without quenching after single-step heat treatments and enables high-strength alloys without hot-cracking [5,12].

Scalmalloy® (Al-Mg-Mn-Sc-Zr) was the first Al alloy concept specifically designed for PBF-LB and meets the requirements on a high-strength alloy with ultimate tensile strengths (UTS) > 500 MPa and a good elongation > 8.6% [13]. Though, its tensile strength is significantly reduced at high temperatures [14] and Mg evaporates during laser melting at temperatures beyond 1090°C [15], which causes smoke and spatter [16]. Therefore, Scancromal® (Al-Cr-Mo-Sc-Zr) was developed based on Scalmalloy® in 2019 by Airbus Defence and Space GmbH replacing Mg and Mn with Cr and Mo to prevent evaporation, improve melt pool dynamics, and heat resistance. Cr and Mo were chosen to increase heat resistance due to their low diffusion rates in Al [17]. Additionally, solid solution hardening and corrosion resistance are increased [18]. Sc and Zr enable precipitation hardening and the development of creep resistant Al alloys due to the low diffusion rate of Zr and the low coarsening of L_{12} $Al_3(Sc,Zr)$ precipitates [17]. Additionally, PBF-LB processability is usually improved by adding grain refiners [1–3]. Most of the PBF-LB Al-Cr alloys demonstrated a good processability without hot-cracks, despite having fully columnar grain structures [16,19]. Table 1 serves as an overview for the so far reported mechanical properties and grain structures of Al-Cr alloys, including the alloys used in this study (CR-hi, CR-med, CR-lo). Depending on composition, heat treatment, and process parameters, an UTS up to 514 MPa and elongation up to 30% is possible [20]. UTS of Al-Cr alloys at 200°C remains high, up to 252 MPa [14,18,21]. In comparison, UTS of Scalmalloy® decreases to approximately 160 MPa and Al-Fe(-Mn) alloys reach 239–313 MPa at 200°C [14,22]. Moreover, threshold stress during creep tests at 200°C is at least 5 times higher than for Scalmalloy® [14].

Equilibrium solubility of Cr and Mo in Al is limited to 0.37 at.% [24] and 0.06 at.% [25], respectively. Small amounts of Cr are used for grain refinement and to prevent undesired needle-like AlFeSi phases in Al

Table 2

Overview of relevant phases in rapidly solidified Al-Cr alloys and their crystal systems [24].

Phase	Crystal system	at.% Cr	Ref.
Al_7Cr ($Al_{13}Cr_2$, $Al_{45}Cr_7$)	monoclinic	12.4–13.7	[24,35]
Al_5Cr ($Al_{11}Cr_2$)	monoclinic	15.2–17	[24]
	orthorhombic	16.9–19.2	[36]
Al_4Cr	monoclinic	18.5–20	[24]
	hexagonal	20.6–21.2	[36]

alloys [26,27]. Up to 0.2 wt.% (0.1 at.%) Cr improves tensile strength slightly, but higher amounts lead to the formation of the coarse and detrimental Al_7Cr phase in die-cast Al-Mg-Si-Mn alloys [28]. Rapidly solidified Al-Cr alloys have been investigated earlier to increase solubility up to 5.6 at.% [29,30]. Mechanical properties were improved and found to be stable up to temperatures of 300°C [31]. Earlier studies of rapidly solidified Al-Cr(-X) alloys verified the presence of the stable monoclinic Al_7Cr phase in those alloys, whereas other metastable phases such as Al_5Cr or Al_4Cr were not observed [30–33]. Overall, those phases are closely related to each other [34]. Table 2 gives an overview of relevant phases, their reported structures and Cr compositions.

Control of the microstructure and Columnar to Equiaxed Transition (CET) is a frequently discussed topic in current research [37–41]. Fe- and Ni-alloys develop mostly equiaxed or columnar microstructures, with an intermediate structure depending on solidification front velocity V and temperature gradient G , following classical theories on microstructure development [42–45]. Al alloys, on the other hand, develop three different microstructure types: fully columnar, bimodal and fully equiaxed. Primary phases at the melt pool boundary (MPB) such as oxides or $Al_3(Sc,Zr)$ act as nuclei [46] for equiaxed grains due to the low V and high G at the MPB [47,48]. The number of nuclei is further increased by constitutional supercooling of the melt and facilitates equiaxed grain growth and grain refinement in the MPB region [49]. With increasing V and decreasing G towards the melt pool top, bigger and/or columnar grains grow perpendicular to the solidification front creating the bimodal grain size distribution [47,48,50]. Increasing build plate heating and volume energy density (VED) leading to a decrease of V in PBF-LB processing has been reported to increase the amount of equiaxed grains [37,51]. Regarding grain refining elements, the more Sc, Zr and/or Ti are added to Al-Mn and Al-Mg alloys, the more equiaxed grains are formed [3,52–54]. However, the most important aspect influencing CET is the number density of nuclei [55]. By adding grain refining elements, nucleation sites are added and promote equiaxed grain growth. Even though Al-Cr-Mo-Sc-Zr alloys contain Sc and Zr in comparable amounts to the bimodal Scalmalloy® alloys [56], the Al-Cr alloys are often observed with a fully columnar grain structure (see Table 1).

While Al-Si, Al-Mg and Al-Mn alloys for PBF-LB are already quite well investigated, the PBF-LB solidification propensities of Al-Cr alloys still need to be uncovered. The microstructure of Al-Cr alloys has been examined in less detail to date. This study, systematically investigates

Table 1

Overview of mechanical properties of Al-Cr alloys. Testing direction is perpendicular (XY) or parallel (Z) to the build direction. XYZ indicates the range of both XY and Z values.

Alloy	This study	Testing direction	Heat treatment	Grain structure	UTS	Elongation	Ref.
Al-Cr5.03-Mn1.56-Zr1.26	–	XYZ	400°C/2 h	bimodal	475–488 MPa	0.2–0.9%	[18]
Al-Cr3.8-Mn1-Zr1	–	XYZ	400°C/2 h	columnar	364–397 MPa	15–17%	[18]
Al-Cr4-Mo1.36-Sc0.78-Zr0.52	–	XY	355–400°C/0.5–1 h	bimodal	486–514 MPa	11–30%	[20]
Al-Cr4-Mo1.6-Sc0.72-Zr0.44	CR-hi	XYZ	330°C/4 h	weakly bimodal	462–478 MPa	2.4–10.2%	[14]
Al-Cr3.1-Mo1.4-Sc0.64-Zr0.29	CR-med	Z	400°C/2 h	columnar	419 MPa	15%	[18]
Al-Cr2.9-Mo1.28-Sc0.3-Zr0.31	CR-lo	XYZ	400°C/4 h	columnar	353–369 MPa	14.1–14.8%	[14]
Al-Cr4-Zr1.5	–	XYZ	400°C/10 h	bimodal	420 MPa	12–15%	[21]
Al-Cr3	–	XYZ	none	columnar	180 MPa	35–40%	[23]

the microstructural characteristics of Al-Cr-Mo-Sc-Zr alloys. Through a combination of multi-scale characterization and thermodynamic simulations, it is revealed how Cr and grain refining elements Sc and Zr interact and influence grain structure. Different alloy compositions are used to evaluate the influence of composition on occurring phases, solidification sequence, and grain structure. A combination of classical phase analysis and phase prediction using Thermo-Calc software provides valuable insights into the solidification process. Three hypotheses on the columnar to bimodal transition are presented based on kinetics, thermodynamics and grain growth. The results of this study will help to further understand the microstructural control of Al-Cr alloys and choose future compositions to achieve the desired combination of a high-strength, heat-resistant and ductile alloy.

2. Experimental

2.1. Materials

Scancromal® (Al-Cr-Mo-Sc-Zr) powders with varying Cr, Mo, Sc and Zr compositions were used in this study. Reasons for the chosen alloy system are explained in Section 1. The influence of these elements on the microstructure was determined by using an overall high, medium and low alloying content (see Table 3). These variations will be denoted as 'CR-hi', 'CR-med', and 'CR-lo' in the following. To compare the Al-Cr and Al-Mg systems, Scalmaalloy® (Al-Mg-Mn-Sc-Zr) powder was used and is listed in Table 3 as 'MG'. Iron and silicon content are displayed for information but remain as inevitable contaminations during material creation (sourced back to the used master alloys).

Cubes of bulk material with an edge length of 10 mm were printed using appropriate parameters to obtain dense samples. During parameter studies, laser power, scan speed, hatch distance and build plate temperature were varied [18,19]. Note that different layer thicknesses (30 µm and 100 µm) and different process gases (Argon and Nitrogen) were used. The layer thickness was increased to improve productivity and Nitrogen was used to enhance economic aspects. Both of these parameters influence the microstructure and are discussed in Section 4.2.6. Further information on powder production, particle size distribution and PBF-LB process parameters is provided in Appendix A Supplementary data S1.

Heat treatments were applied according to aging studies [14,18] for each alloy individually. Peak aged conditions are achieved by aging in air at 330°C for 4 h (CR-hi), at 400°C for 1 h (CR-med), at 400°C for 4 h (CR-lo), and at 320°C for 2 h (MG). Over aged conditions are achieved by aging in air at 330°C for 32 h (CR-hi) and at 400°C for 32 h (CR-lo). To evaluate the phase evolution during heat treatment, an additional batch of CR-hi samples was used after aging at 410°C for 3, 8 and 32 h.

2.2. Thermodynamic calculations

Solidification paths were calculated by one-axis equilibrium simulations using Thermo-Calc Software version 2024a and the TCAL8 and TCAL9 Al-based Alloy Database. To simplify the system, Fe and Si were not considered during the calculations. Furthermore, the tetragonal DO₂₃ Al₃Zr and the monoclinic Al₅Cr phases were excluded from the calculations. DO₂₃ Al₃Zr was not observed during in-situ XRD investigations of Al-Zr powder [5]. Al₅Cr is not expected to form under rapid solidification conditions as it was not detectable during any of our experiments.

A detailed description of the chosen calculation method can be found in Appendix A Supplementary data S2.

2.3. Microscopy

Samples for microstructural observations were cut from as built, peak aged and over aged cubes of solid material, cold embedded in epoxy, grinded and polished. Scanning Electron Microscope (SEM) images in Backscattered Electron (BSE) mode of CR-hi and CR-lo were taken on a Tescan Clara field emission gun SEM using an ultra low energy (L-BSE) detector. Electron Backscattered Diffraction (EBSD) images were captured on tilted samples (70°) using 20 kV voltage. Electron Dispersive Spectroscopy (EDS) analyses were conducted on a LEO 1430 SEM equipped with a Bruker SFlash 6–30 silicon drift detector using 15 kV voltage. In the case of CR-med, a Zeiss Auriga 40 SEM equipped with an Oxford X-Max 50 EDS detector and an Oxford NordlysNano EBSD detector was used.

2.4. Atom probe tomography

Samples for Atom Probe Tomography (APT) were prepared on an FEI Helios Plasma Focused Ion Beam (PFIB) using a Xe source. The APT analysis was then conducted on a Cameca Local Electrode Atom Probe (LEAP®) 5000XR at a base temperature of 40 K, in laser-pulsed mode (25 pJ laser energy, 250 kHz pulse rate), and with a target detection rate of 0.5%. The number of ions per measurement ranged between 21.9 and 30 million.

2.5. Synchrotron high-energy x-ray diffraction

Synchrotron high-energy X-Ray Diffraction (HEXRD) experiments were performed at beamline P07B (Petra III, DESY Hamburg) with a wavelength of 0.14235 Å and slit size of 0.7×0.7 mm². Debye-Scherrer diffraction patterns were recorded using a detector from PerkinElmer with a pixel size of 200×200 µm² and 2048×2048 pixels. Single diffractograms were derived with the pydifas package v24.09.19 [57] after calibration of the experimental setup with diffraction data of a LaB6 standard.

Texture measurements were conducted on machined cylinders of Ø4 mm (peak aged). The cylinders were rotated around the longitudinal Z-axis (build direction) from −92.5° to 92.5° with a step size of 5°. Slices of 5° were also used in the Debye-Scherrer images to provide data for pole figure calculation on a 5°×5° pattern.

3. Results

3.1. Thermodynamic calculations

To get an overview of the possible occurring phases, Thermo-Calc calculations have been performed. Similar solidification paths are visible for the three Al-Cr alloys in one-axis equilibrium calculations (see Fig. 1). Either an Al_xMo_y phase or Al₄₅Cr₇ solidifies first from liquid, followed by Al₃(Sc,Zr), and finally α-Al. The four phases Al₄₅Cr₇, Al₃(Sc,Zr), Al₁₂Mo, and α-Al are always stable below 662°C. Additionally, metastable Al₂₂Mo₅ (orthorhombic) and Al₅Mo (trigonal) appear at higher temperatures.

The four stable phases, their lattice information, solidification temperatures and chemical compositions are summarized in Table 4. The

Table 3

Chemical powder compositions in wt.% (at.%) provided by the powder manufacturer (IPC-OES). The last column shows the corresponding Sc/Zr ratio of each alloy.

Alloy	Cr	Mo	Mg	Mn	Sc	Zr	Fe	Si	Al	Sc/Zr ratio
CR-hi	4.00 (2.16)	1.60 (0.47)	–	–	0.72 (0.45)	0.44 (0.14)	0.11 (0.06)	0.07 (0.07)	bal.	1.6 (3.2)
CR-med	3.1 (1.66)	1.4 (0.41)	–	–	0.64 (0.40)	0.29 (0.09)	0.18 (0.09)	0.07 (0.07)	bal.	2.2 (4.4)
CR-lo	2.90 (1.55)	1.28 (0.37)	–	–	0.30 (0.19)	0.31 (0.09)	0.13 (0.06)	0.05 (0.05)	bal.	1.0 (2.1)
MG	–	–	3.73 (4.16)	0.42 (0.21)	0.73 (0.44)	0.30 (0.09)	0.14 (0.07)	0.10 (0.10)	bal.	2.4 (4.9)

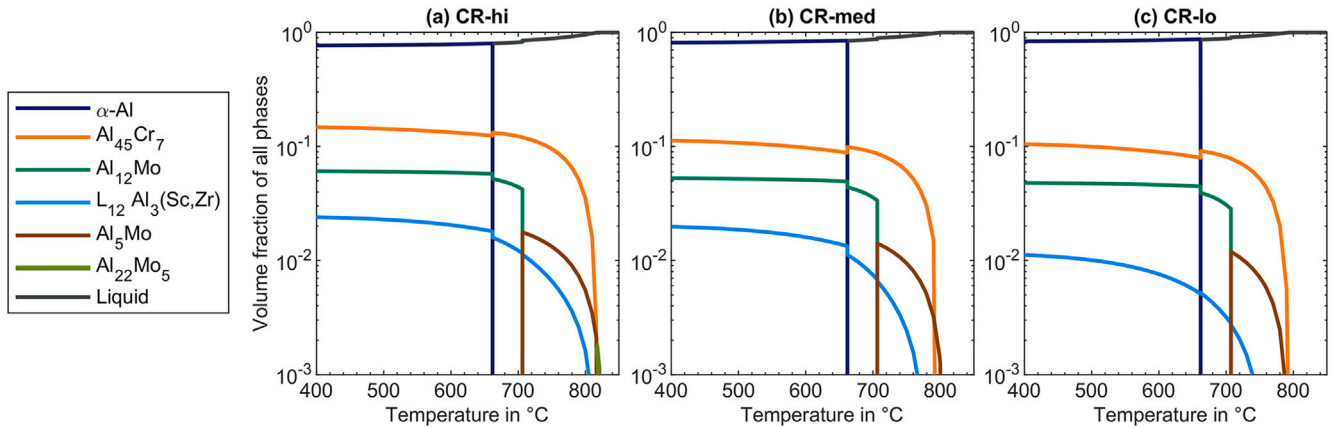


Fig. 1. Thermo-Calc one-axis equilibrium calculations of (a) CR-hi, (b) CR-med, and (c) CR-lo. Tetragonal D_{023} Al_3Zr and monoclinic Al_5Cr were excluded (see Section 2.2).

Table 4

Stable phases, their lattice information, volume fractions, and compositions for CR-hi, CR-med, and CR-lo derived from Thermo-Calc one-axis and single equilibrium calculations.

Crystal system	Space group, lattice	Alloy	Volume fraction φ (%)	Solidification temperature	Composition (at.%)				
					Al	Cr	Mo	Sc	Zr
α -Al	225, cubic	-hi	76.5	662°C	99.98	0.02	< 0.01	< 0.01	< 0.01
		-med	81.5	662°C	99.95	0.04	< 0.01	0.01	< 0.01
		-lo	83.6	662°C	99.95	0.04	< 0.01	< 0.01	< 0.01
$\text{Al}_{45}\text{Cr}_7$	12, monoclinic	-hi	15.0	816°C	86.54	13.46	–	–	–
		-med	11.3	790°C	86.54	13.46	–	–	–
		-lo	10.5	793°C	86.54	13.46	–	–	–
$\text{Al}_3(\text{Sc,Zr})$	221, cubic	-hi	2.4	810°C	75.00	–	–	19.22	5.78
		-med	2.0	770°C	75.00	–	–	20.44	4.56
		-lo	1.1	750°C	75.00	–	–	16.56	8.44
Al_{12}Mo	204, cubic	-hi	6.1	706°C	92.31	–	7.69	–	–
		-med	5.2	706°C	92.31	–	7.69	–	–
		-lo	4.8	707°C	92.31	–	7.69	–	–

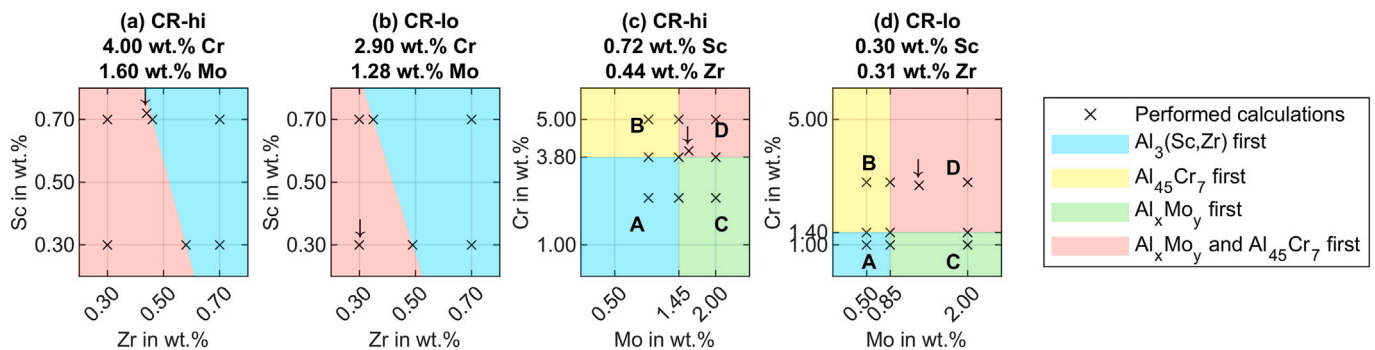


Fig. 2. Solidification maps of CR-hi and CR-lo with (a,b) variations of Sc and Zr and (c,d) variations of Cr and Mo. The different regions A–D indicate if either $\text{Al}_3(\text{Sc,Zr})$ or other phases are formed first from liquid. Arrows indicate the experimentally investigated compositions. Tetragonal D_{023} Al_3Zr and monoclinic Al_5Cr were excluded (see Section 2.2).

composition and solidification temperature of these phases are almost unaffected by the alloy content. However, some differences in $\text{Al}_{45}\text{Cr}_7$ and $\text{Al}_3(\text{Sc,Zr})$ will be described in the following.

Calculated solidification temperatures of $\text{Al}_{45}\text{Cr}_7$ and $\text{Al}_3(\text{Sc,Zr})$ are generally higher with a higher alloy content. The temperature difference between the solidification of $\text{Al}_3(\text{Sc,Zr})$ and $\text{Al}_{45}\text{Cr}_7$ is 6, 20, and 43°C for CR-hi, -med, and -lo, respectively. Therefore, the higher the alloying content, the closer the solidification-temperatures of $\text{Al}_3(\text{Sc,Zr})$ and $\text{Al}_{45}\text{Cr}_7$.

Calculated composition of $\text{Al}_3(\text{Sc,Zr})$ is also affected by the alloy content. The amount of Sc + Zr is always 25 at.%, but the individual Sc

and Zr composition is based on the alloy's Sc/Zr ratio. For example in CR-hi, the Sc/Zr ratio in at.% is 3.2 for the nominal alloy composition and 3.3 for the calculated composition of $\text{Al}_3(\text{Sc,Zr})$.

Sc and Zr are often added as grain refiners in Al alloys, but the authors assume that $\text{Al}_3(\text{Sc,Zr})$ must form first from the liquid to actually act as a grain refiner. Because of the fully columnar and bimodal reported grain structures of Al-Cr-Sc/Zr alloys, additional one-axis calculations were performed with varying Sc and Zr concentrations but fixed Cr and Mo concentrations of the alloys of interest. The results are summarized in the solidification maps in Fig. 2(a,b). These maps visualize two regions, depending on Sc and Zr content, where either

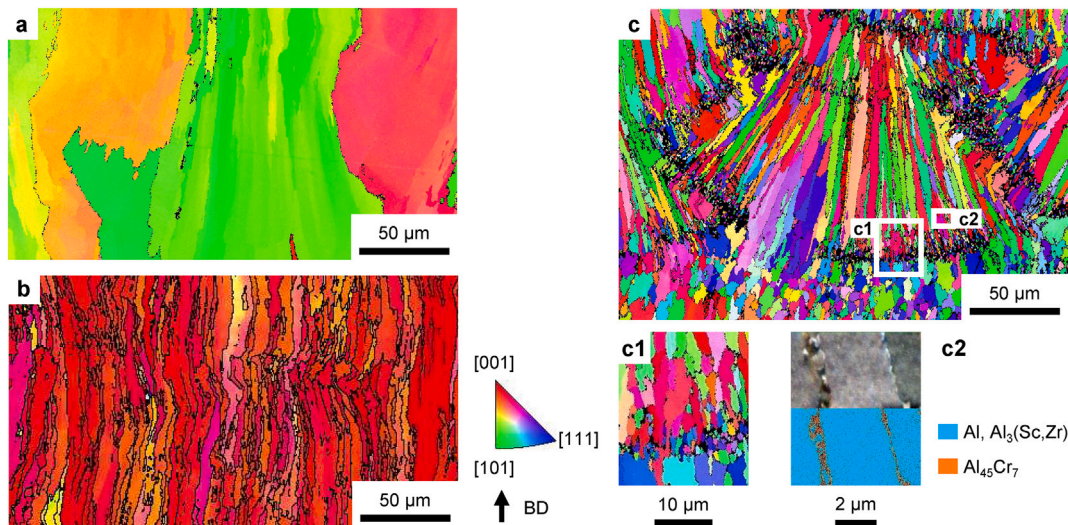


Fig. 3. EBSD images of (a) CR-lo, (b) CR-med, and (c) CR-hi. CR-lo and CR-med show a completely columnar grain structure, while CR-hi has a weakly bimodal grain structure. (c1) Additional image of smaller grains of CR-hi at a MPB. (c2) ARGUS image and phase map verify the $\text{Al}_{45}\text{Cr}_7$ GBP.

$\text{Al}_3(\text{Sc,Zr})$ (blue region) or another phase (red region, $\text{Al}_{45}\text{Cr}_7$, $\text{Al}_{22}\text{Mo}_5$, or Al_5Mo) is formed first from the liquid. The experimentally investigated alloy compositions are indicated by arrows and are both positioned in the red region where $\text{Al}_3(\text{Sc,Zr})$ is not formed first. Unlike CR-lo, CR-hi is close to the boundary between the two regions. Since the boundary between the blue and red regions differs between CR-hi and CR-lo, the other alloying elements (Cr and Mo) must have an influence on the solidification sequence as well.

To verify the influence of Cr and Mo, further calculations with varying Cr and Mo concentrations have been performed and provide the four regions in Fig. 2(c,d):

- A: $\text{Al}_3(\text{Sc,Zr})$ is formed first
- B: $\text{Al}_{45}\text{Cr}_7$ is formed before $\text{Al}_3(\text{Sc,Zr})$
- C: Al_xMo_y (Al_5Mo , Al_{12}Mo , $\text{Al}_{22}\text{Mo}_5$) is formed before $\text{Al}_3(\text{Sc,Zr})$
- D: all phases from B and C are formed before $\text{Al}_3(\text{Sc,Zr})$

This confirms that not only Sc and Zr but also Cr and Mo concentrations influence whether the grain refining $\text{Al}_3(\text{Sc,Zr})$ phase or an $\text{Al}_{45}\text{Cr}_7$ and/or Al_xMo_y phase forms first from liquid. Again, CR-hi is close to the critical Cr content of 3.8 wt.% that marks the boundary between regions C and D, where $\text{Al}_{45}\text{Cr}_7$ is formed before $\text{Al}_3(\text{Sc,Zr})$. CR-lo is clearly above its critical Cr content of 1.4 wt.%.

3.2. Microscopy

EBSD images of CR-lo and CR-med (Fig. 3a,b) show a completely columnar grain structure with pronounced epitaxial grain growth where individual melt pools cannot be identified. Although not very pronounced, CR-hi has directly visible melt pools due to a weakly bimodal grain structure (Fig. 3c), with some smaller grains on MPBs (see Fig. 3c1), and less epitaxial grain growth. All three alloys are textured with [100] and [101] as preferred orientations, with CR-lo and CR-med exhibiting stronger texture than CR-hi.

For reasons of readability and clarity, Fig. 4 provides a schematic representation of the melt pool with its phases and their designations as used in the rest of the text.

SEM-BSE images of CR-hi and CR-lo are provided in Fig. 5 as representatives of bimodal and columnar grain structures, respectively. Similar phases are visible in both as built and over aged conditions: A combination of finely dispersed equiaxed dendrites of different sizes appears at MPBs and columnar grains are visible within the melt pools (see Fig. 5a–d).

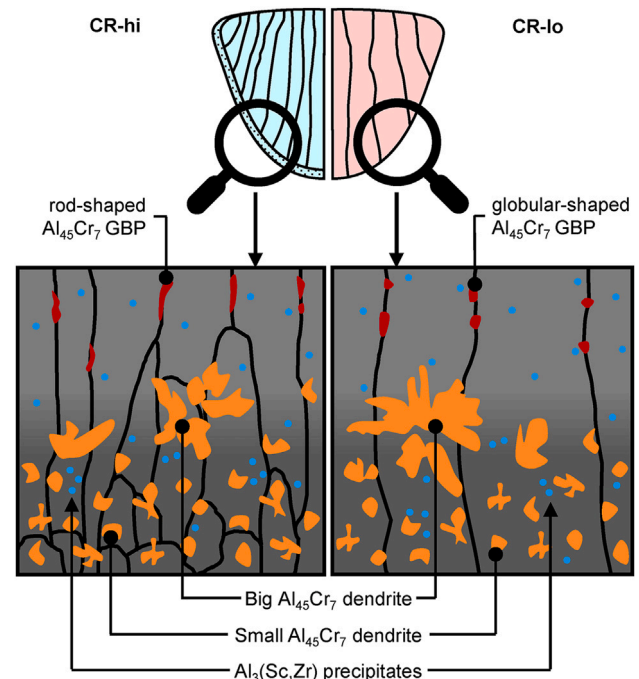


Fig. 4. Overview of the phases in weakly bimodal CR-hi and the fully columnar CR-lo. The difference in shape of GBPs between CR-hi and CR-lo becomes clear after over aging. Colour of the phases matches the indicating arrows in BSE-images in Fig. 5. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

A closer look at the columnar grains and their grain boundaries (Fig. 5e–h) reveals bright grain boundary phases (GBP, red arrows) that grow during aging and become more globular-shaped in the case of CR-lo (Fig. 5h) and more rod-shaped in the case of CR-hi (Fig. 5f). Those GBPs are always surrounded by a darker α -Al matrix (green arrows). With the use of EBSD phase maps (example Fig. 3c2), GBPs and equiaxed dendrites could be verified as $\text{Al}_{45}\text{Cr}_7$. This is in agreement with Thermo-Calc results in Section 3.1 and will be confirmed by HEXRD and APT in the following sections.

Examples of the $\text{Al}_{45}\text{Cr}_7$ dendrites using a higher magnification are given in Fig. 5(i,j) (orange arrows). The dendrites' diameter ranges from

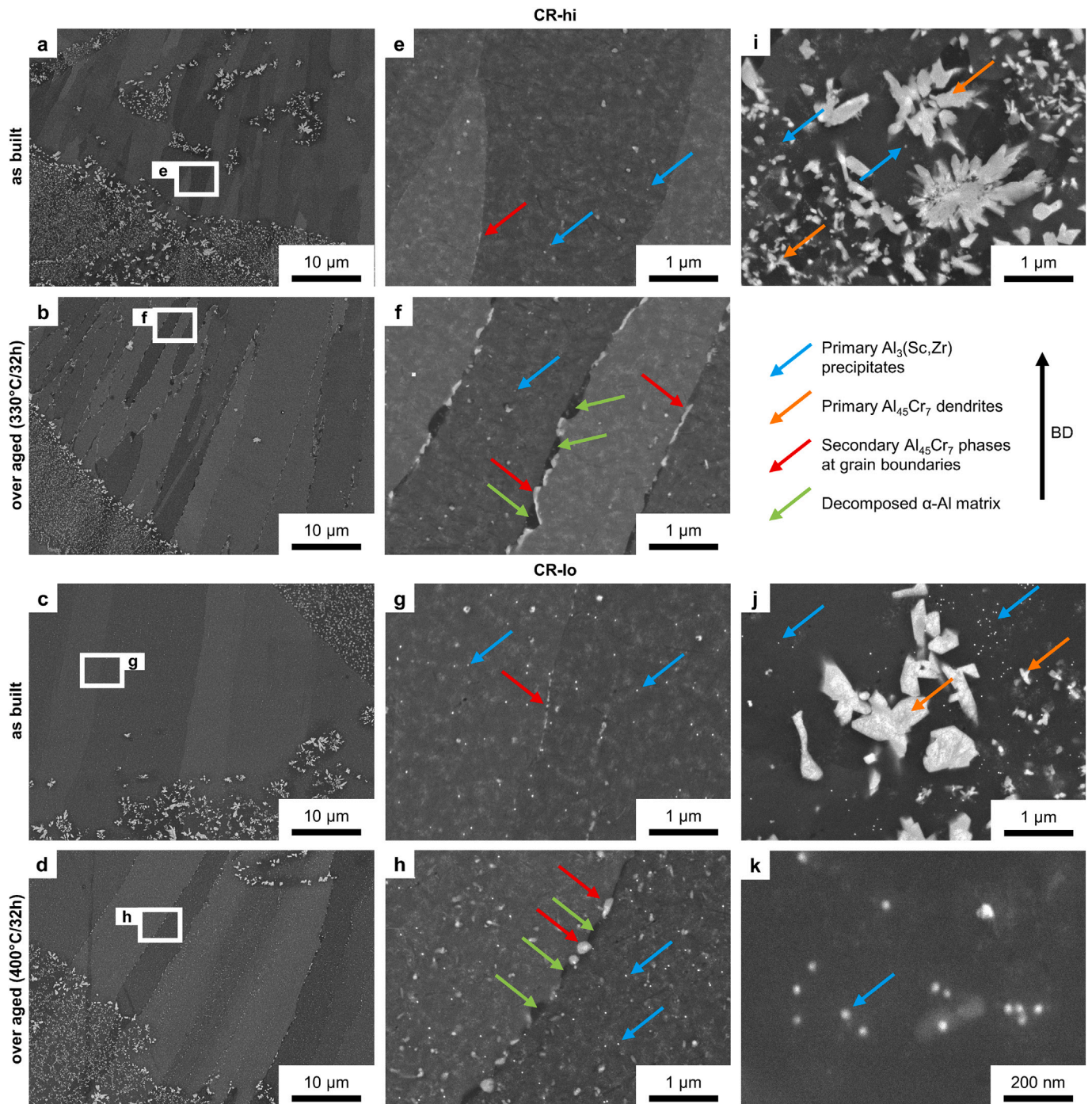


Fig. 5. SEM-BSE images of CR-hi and CR-lo in as built and over aged condition. (a–d) Overview of MPBs and columnar grains within the melt pool. (e–h) $\text{Al}_{45}\text{Cr}_7$ GBPs that coarsen during aging and become more rod-shaped in case of CR-hi and globular-shaped in case of CR-lo. (i,j) Primary equiaxed dendrites at MPBs are present, irrespective of alloy and heat treatment. (k) Example of $\text{Al}_3(\text{Sc,Zr})$ precipitates. BD indicates build direction.

less than 100 nm up to approximately 3 μm and their shape varies from small, delicate, and flowery to big, blocky, and snowflake-like. EDS measurements of the big dendrites (see Fig. 6a) showed a concentration mainly of Al, about 3.3 at.% Cr, and 1.0 at.% Mo, irrespective of the alloys' composition. Small amounts of Sc (0.07–0.35 at.%) and Zr (0.07–0.11 at.%) are also present in the dendrites, with CR-lo having the lowest Sc concentration in agreement with its lower alloying content. Heat treatment does not change the dendrites' composition (see Fig. 6b). Overall, there is no significant difference between the three alloys before and after aging regarding phase composition.

$\text{Al}_3(\text{Sc,Zr})$ precipitates appear small in size (≤ 50 nm), bright, and spherical (blue arrows) in both columnar and MPB regions and are assumed to be primary precipitates because of their size and shape. They are evenly distributed within the melt pool, but tend to occur in clusters next to large $\text{Al}_{45}\text{Cr}_7$ dendrites at MPBs (example Fig. 5k).

Chemistry of the Al matrix via EDS has also been determined for CR-hi at different positions and after different heat treatments (see Fig. 6c,d). Darker regions in BSE images between $\text{Al}_{45}\text{Cr}_7$ dendrites at MPBs contain less Cr (about 1.0 at.%) and Mo (about 0.2 at.%) compared to columnar grains (Cr about 1.7 at.%, Mo about 0.5 at.%)

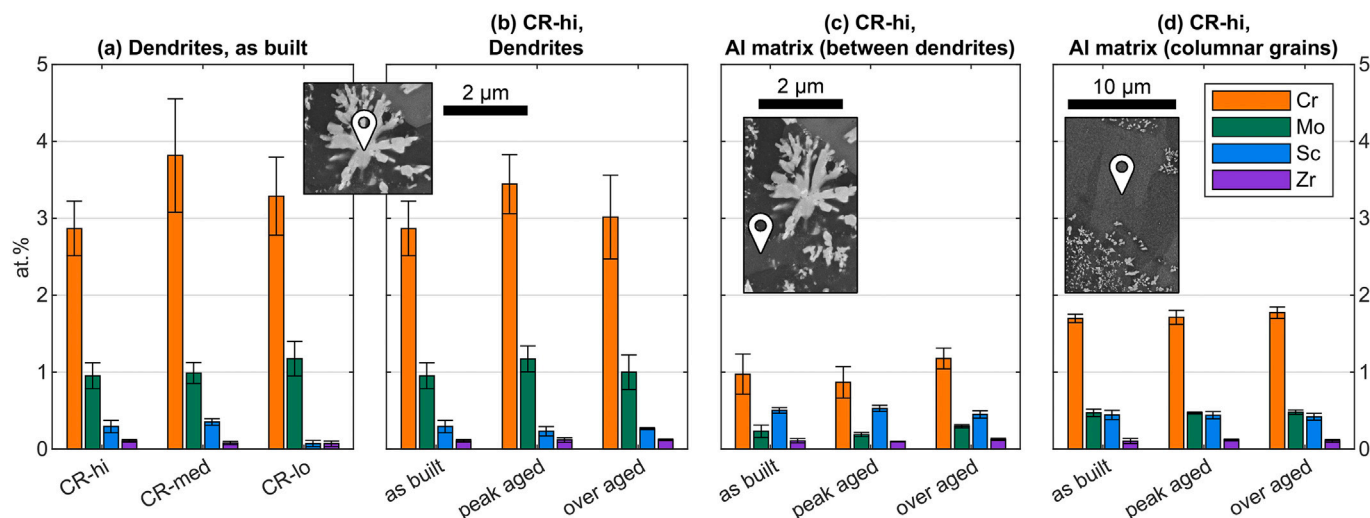


Fig. 6. Chemistry determined by EDS point measurements. (a) Comparison of equiaxed dendrites in CR-hi ($n = 5$), CR-med ($n = 2$), and CR-lo ($n = 5$) in as built condition. Comparison of (b) equiaxed dendrites ($n = 5$), (c) Al Matrix (between dendrites, $n = 3$), and (d) Al Matrix (columnar grains, $n = 5$) after different heat treatments in CR-hi. Error bars indicate standard deviation. Balanced by Al.

because of the partitioning between the Al matrix and $\text{Al}_{45}\text{Cr}_7$. Sc and Zr concentrations of the Al matrix are always close to the nominal alloy composition indicating a homogeneous solution and precipitation distribution. Heat treatments had no significant effect on the EDS results of the Al matrix. The same observations have been made for CR-lo in [Section A Supplementary data S3](#) with lower concentrations following the lower alloy composition.

3.3. Atom probe tomography

To get a more precise result on the compositions observed in [Section 3.2](#), APT analysis was conducted on as built and peak aged samples of CR-med. Only CR-med was used for APT analysis, because Thermo-Calc and EDS results in the previous sections showed no significant difference in composition between the three alloys. For both heat-treated conditions, one sample in the region of the small dendrites on MPBs and one sample in the region of the big dendrites on MPBs were prepared as indicated in [Fig. 7\(a,d\)](#). The results of the exact phase compositions are obtained from 1D concentration profiles and are summarized in [Table 5](#).

$\text{Al}_{45}\text{Cr}_7$ dendrites were solely surrounded by the Al Matrix in as built condition ([Fig. 7a–c](#)). Sample 1 contained one 20 nm-sized dendrite with a significantly higher Sc (1.03 at.%) and Zr (0.42 at.%) concentration compared to the nominal alloy composition. Sample 2 contained a dendrite of at least 80 nm with almost no Sc and Zr (≤ 0.06 at.%). After peak aging, no significant change in composition was observed for a bigger dendrite (120 nm, [Fig. 7f](#)). No dendrite was observed in peak aged sample 3. As a result, the Cr (10.62–12 at.%) and Mo (1.31–1.87 at.%) concentrations of the $\text{Al}_{45}\text{Cr}_7$ dendrites are similar regardless of size and heat treatment. However, the size of the dendrites affects the Sc and Zr concentrations: Small dendrites contain 2.6 times as much Sc and 4.7 times as much Zr as the nominal alloy composition.

Secondary $\text{Al}_3(\text{Sc,Zr})$ precipitates appeared in peak aged condition in both samples with an even distribution and a size of approx. 4 nm ([Fig. 7d–f](#)). They consist mainly of Al and Sc (24.37–29.69 at.%) with small fractions of Zr (0.12–1.15 at.%), Cr (0.72–0.99 at.%) and Mo (0.72–1.46 at.%). Comparing the compositions of secondary $\text{Al}_3(\text{Sc,Zr})$ precipitates, Sc concentration is slightly higher next to $\text{Al}_{45}\text{Cr}_7$ dendrites (29.69 at.%) and slightly lower in the absence of $\text{Al}_{45}\text{Cr}_7$ dendrites (24.37 at.%). Zr concentration behaves inversely. Additionally, one bigger (approx. 40 nm) primary $\text{Al}_3(\text{Sc,Zr})$ precipitate appeared in sample 2. This primary precipitate has a reduced Cr concentration (0.15 at.%)

and similar Mo, Sc, and Zr concentrations in comparison to secondary precipitates.

The Al matrix next to $\text{Al}_{45}\text{Cr}_7$ dendrites ([Fig. 7b,c,f](#)) is poor in Cr and Mo, similar to EDS results in [Section 3.2](#). In the absence of those dendrites ([Fig. 7e](#)), the Al matrix composition is close to the nominal alloy composition. The difference in Cr and Mo next to and in the absence of the dendrites confirms that the dendrites solidify first and consume Cr and Mo from the remaining liquid. Regarding Sc and Zr, the same observation as for $\text{Al}_3(\text{Sc,Zr})$ precipitates can be seen for the Al matrix: The highest Zr concentration (1.78 times the nominal composition) was observed in the absence of $\text{Al}_{45}\text{Cr}_7$ dendrites (sample 3) and the highest Sc concentration (1.48 times the nominal composition) was found to be next to $\text{Al}_{45}\text{Cr}_7$ dendrites even after heat treatment. A possible reason for this counteracting distribution of Sc and Zr will be discussed in [Section 4.2](#).

3.4. Synchrotron high-energy x-ray diffraction

An overview of the performed HEXRD measurements for CR-hi (orange) and CR-lo (green) in as built, peak aged and over aged conditions is given in [Fig. 8\(a\)](#). For both Al-Cr alloys, three phases explained all of the peaks very well during Rietveld refinement: α -Al, $\text{Al}_{45}\text{Cr}_7$ and $\text{Al}_3(\text{Sc,Zr})$. Nevertheless, the Al_xMo_y phases and Al_5Cr phase, predicted by Thermo-Calc in [Section 3.1](#), might be present in small fractions. The diffractogram section of over aged CR-hi in [Fig. 8\(b\)](#) demonstrates the experimental (orange) and refined (red, dashed) intensities as well as the contribution of the monoclinic $\text{Al}_{45}\text{Cr}_7$ (black).

To compare the Al-Mg and Al-Cr alloying systems, an additional measurement of MG (blue) was conducted and is shown in [Fig. 8\(c\)](#). It is noteworthy that the Al diffraction angles of MG are lower than those of Al-Cr alloys and will be discussed in [Section 4.2.1](#). The derived α -Al lattice parameters of as built CR-hi, CR-lo, and MG are given in [Table 6](#).

A closer look at the α -Al peaks of CR-hi after heat treatment at 410°C for up to 32 h ([Fig. 8d](#)), shows a slight shift towards lower angles with increasing heat treatment duration. This can be explained by a reduction of Cr in the supersaturated solid solution.

Another effect of heat treatment in [Fig. 8\(d\)](#) is the increase in $\text{Al}_{45}\text{Cr}_7$ intensity. As shown in BSE images in [Fig. 5\(e–h\)](#), there are small $\text{Al}_{45}\text{Cr}_7$ GBPs that grow during heat treatment. Because of this growth, the higher volume fraction and size of these phases lead to higher peak intensities. Further details on this will be explained in [Section 4.1.2](#).

$\text{Al}_3(\text{Sc,Zr})$ precipitates grow during heat treatment and subsequently change from coherent (as built) to incoherent (over aged), thus there

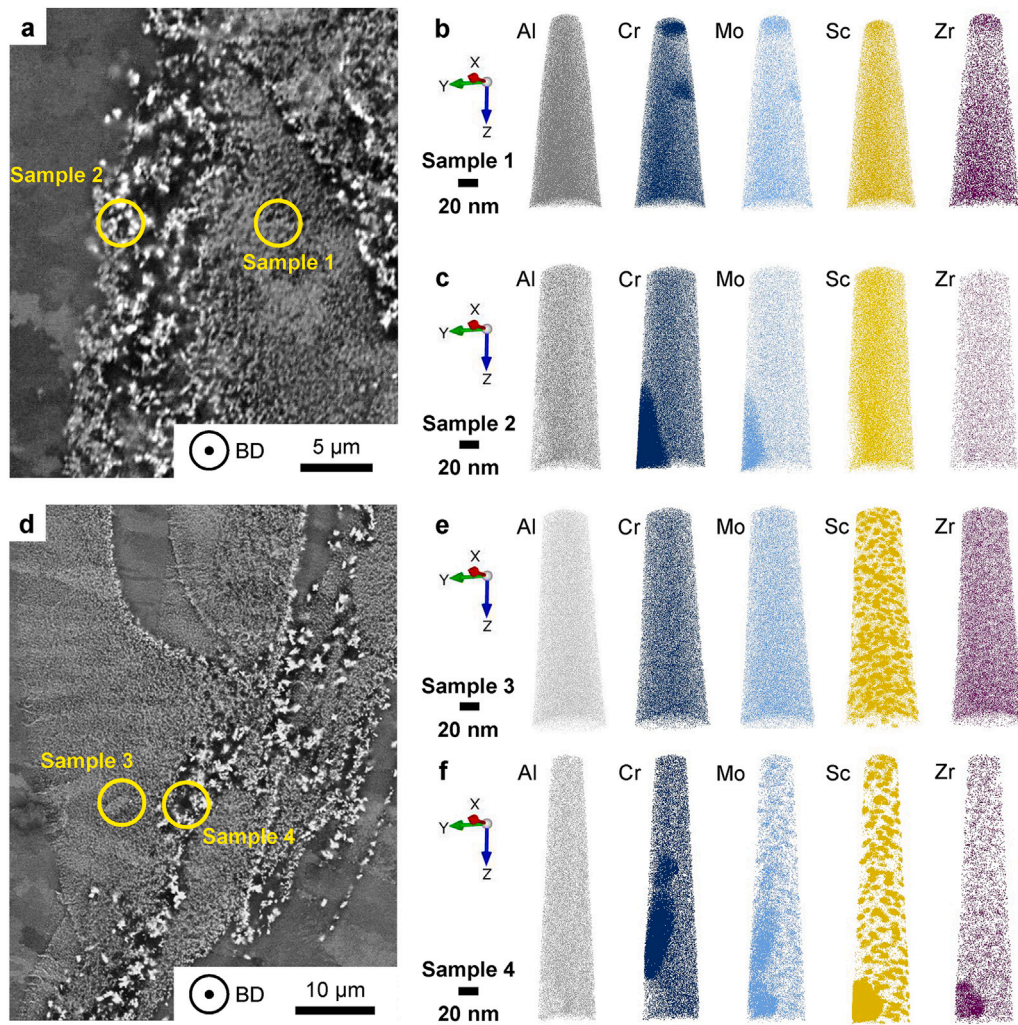


Fig. 7. SEM-BSE images and reconstructed volume of APT CR-med samples in (a–c) as built and (d–f) peak aged condition. Two regions were chosen to examine (b,e) the small and (c,f) big $\text{Al}_{45}\text{Cr}_7$ dendrites at MPBs. BD indicates build direction.

Table 5

Chemical composition (at. %) extracted from APT 1D concentration profiles of the Al matrix, $\text{Al}_{45}\text{Cr}_7$ dendrites, and $\text{Al}_3(\text{Sc,Zr})$ precipitates in CR-med. Additionally, the nominal alloy composition of CR-med powder is provided.

Phase	Sample	Heat treatment	Size	Comment	Cr	Mo	Sc	Zr	Al
Nominal alloy composition					1.66	0.41	0.40	0.09	bal.
Al matrix	2	as built	–	next to big $\text{Al}_{45}\text{Cr}_7$	0.55	0.10	0.50	0.02	bal.
	4	peak aged	–	next to big $\text{Al}_{45}\text{Cr}_7$	0.42	0.13	0.59	0.03	bal.
	1	as built	–	next to small $\text{Al}_{45}\text{Cr}_7$	0.44	0.14	0.59	0.06	bal.
	3	peak aged	–	in absence of $\text{Al}_{45}\text{Cr}_7$	1.38	0.38	0.26	0.16	bal.
$\text{Al}_{45}\text{Cr}_7$ dendrites	1	as built	20 nm	small	10.62	1.72	1.03	0.42	bal.
	2	as built	≥ 80 nm	big	12.00	1.31	0.06	0.04	bal.
	4	peak aged	≥ 120 nm	big	11.36	1.87	0.04	0.09	bal.
Primary $\text{Al}_3(\text{Sc,Zr})$	4	peak aged	≥ 40 nm	next to big $\text{Al}_{45}\text{Cr}_7$	0.15	1.14	26.01	0.62	bal.
Secondary $\text{Al}_3(\text{Sc,Zr})$	3	peak aged	4 nm	in absence of $\text{Al}_{45}\text{Cr}_7$	0.99	1.46	24.37	1.15	bal.
	4	peak aged	4 nm	next to big $\text{Al}_{45}\text{Cr}_7$	0.72	0.72	29.69	0.12	bal.

should be a visible diffraction peak at least in over aged condition. An increase in intensity is indeed observed at the diffraction angles $2\theta = 6.63^\circ$ and $2\theta = 6.92^\circ$, but it is also attributed to the aforementioned $\text{Al}_{45}\text{Cr}_7$ intensity increase. Unfortunately, the small volume fraction and size of $\text{Al}_3(\text{Sc,Zr})$ precipitates seem to make them difficult to detect. CR-lo shows similar behavior from as built to over aged condition in Fig. 8(e), but the intensities do not increase as much by over aging.

Pole figures of peak aged samples are provided in Fig. 9. MG and CR-hi show a moderate texture with a maximum multiple of

random distribution (mrd) of 1.5 and 2.5 in the build direction (Z), which is an expected range for additively manufactured Al alloys. CR-lo is also textured in the build direction but rotated by 25° to the Z-axis and the maximum mrd is significantly higher (8.7). The stronger texture of CR-lo is consistent with EBSD measurements in Fig. 3 and the tilted texture was observed in EBSD measurements of a previous study at lower magnifications over multiple melt pools [14].

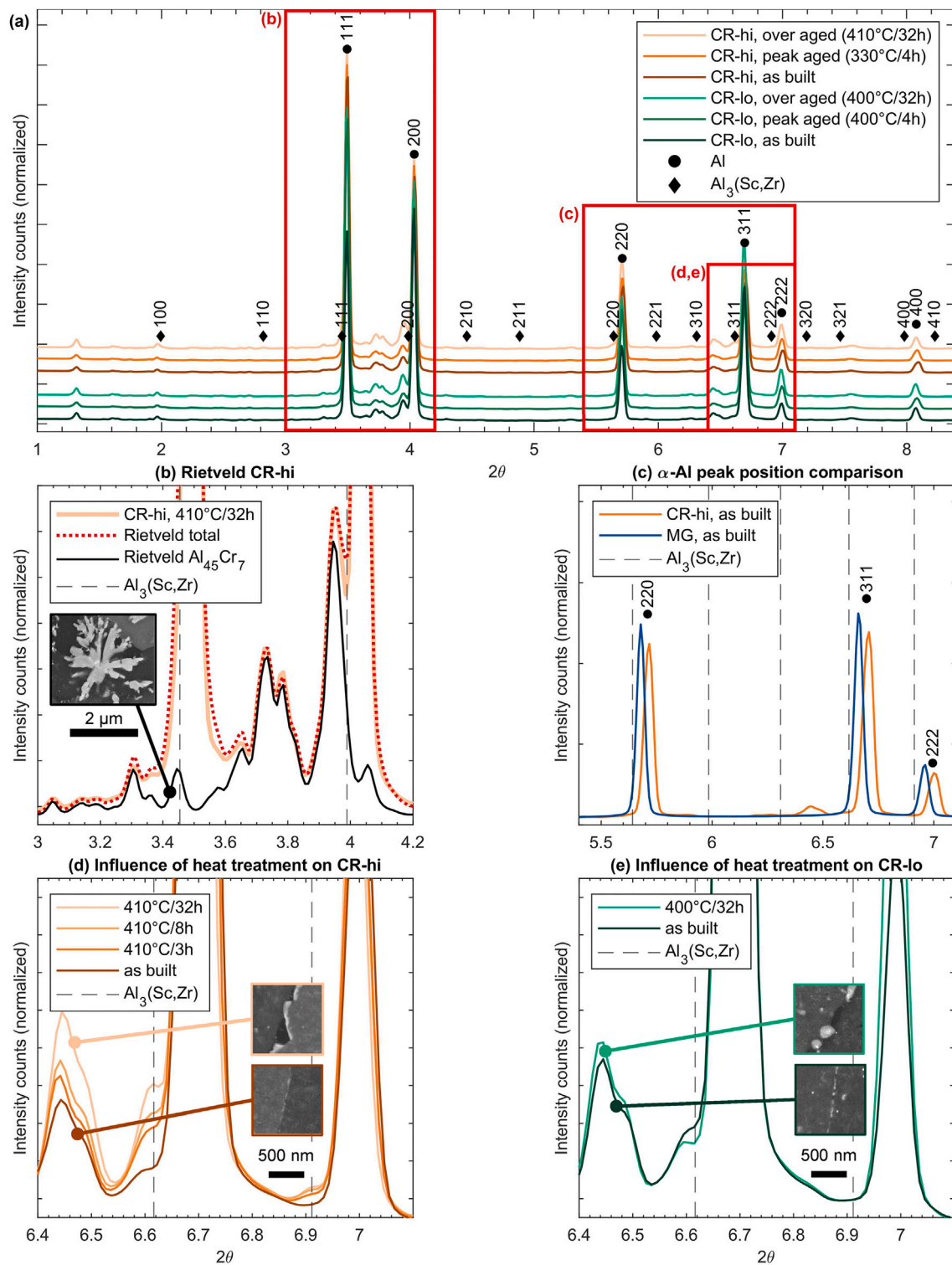


Fig. 8. (a) Overview HEXRD results of CR-hi and CR-lo in as built, peak aged and over aged condition. (b) Contribution of $\text{Al}_{45}\text{Cr}_7$ to diffraction pattern of CR-hi. (c) α -Al peak position of CR-hi and MG. (d,e) Influence of heat treatment on CR-hi and CR-lo. Note that the image of heat treated GBP in (d) is an example and excerpt from Fig. 5(f) (over aged at 330°C).

4. Discussion

4.1. Phase analysis

The occurring phases in the three Al-Cr-Mo-Sc-Zr alloys were evaluated using EDS, APT, and HEXRD measurements alongside with Thermo-Calc calculations. Compositional differences are summarized in Fig. 10

and a detailed description for α -Al, $\text{Al}_3(\text{Sc,Zr})$ precipitates, $\text{Al}_{45}\text{Cr}_7$ dendrites and GBPs is given in the following subsections.

4.1.1. α -Al

The composition of α -Al by Thermo-Calc in Table 4 has been predicted with a very low fraction of Cr (0.02–0.04 at.%) and almost no

Table 6
 α -Al lattice parameter a in as built condition derived from Rietveld analysis.

Alloy	a
CR-hi	4.037 Å
CR-lo	4.044 Å
MG	4.062 Å

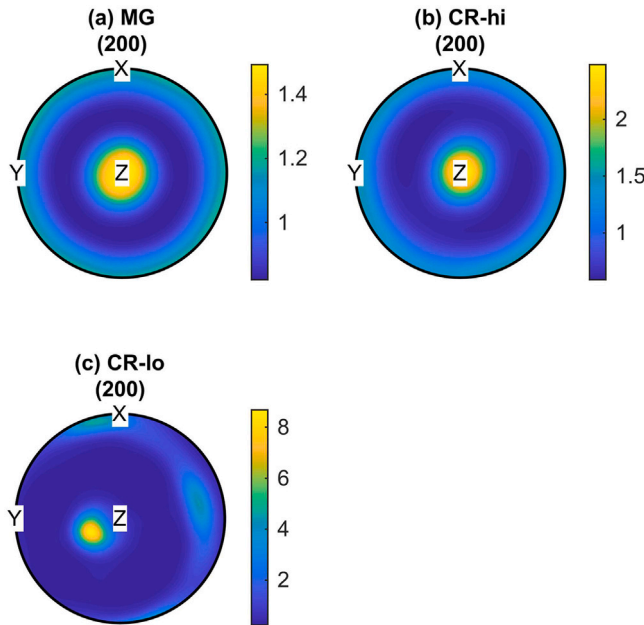


Fig. 9. (200) pole figures from HEXRD results of (a) MG, (b) CR-hi, and (c) CR-lo in peak aged condition. Z-direction is parallel to the build direction. Colorbars indicate mrd.

Mo, Sc and Zr (≤ 0.01 at.%). The low Cr and Mo concentrations predicted by Thermo-Calc result from the equilibrium calculation method and the low solubility of Cr in Al (max. 0.37 at.% [24]) and Mo in Al (max. 0.06 at.% [25]). The high cooling rates of PBF-LB should increase the solubility of Cr and Mo in Al. This was confirmed by APT measurements of the concentrations in the matrix (Section 3.3) and lattice parameters derived from HEXRD diffraction patterns (Section 3.4) and will be described in the following.

APT measurements of the Al matrix on CR-med showed a concentration of 0.42–1.38 at.% Cr, 0.10–0.38 at.% Mo and 0.02–0.16 at.% Zr (see Table 5) with the highest value in the absence of the $\text{Al}_{45}\text{Cr}_7$ dendrites. These APT results are in good agreement with EDS measurements, which showed a higher Cr and Mo concentration in the Al matrix at columnar grains and a lower concentration between the $\text{Al}_{45}\text{Cr}_7$ dendrites at MPBs. On the contrary, Sc concentration was lower in the absence of the $\text{Al}_{45}\text{Cr}_7$ dendrites (0.26 at.%) and higher than the nominal alloy composition next to $\text{Al}_{45}\text{Cr}_7$ dendrites (≥ 0.5 at.%). Consequently, α -Al is rich in Cr, Mo and Zr in the middle of the melt pool in columnar grains and rich in Sc at MPBs (see Fig. 10a).

Evaluating lattice parameters of α -Al derived from HEXRD diffraction patterns is another method to determine Cr and Mo concentrations. McConnell and Partridge [30] proposed Eq. (1), to describe the relationship between the lattice parameter a in Å and Cr concentration c_{Cr} in at.% of Al-Cr alloys.

$$a = 4.0494 - 0.0083 \cdot c_{\text{Cr}} \quad (1)$$

Lattice parameters of as built CR-hi (4.037 Å) and as built CR-lo (4.044 Å) were extracted from Rietveld refinement. According to Eq. (1),

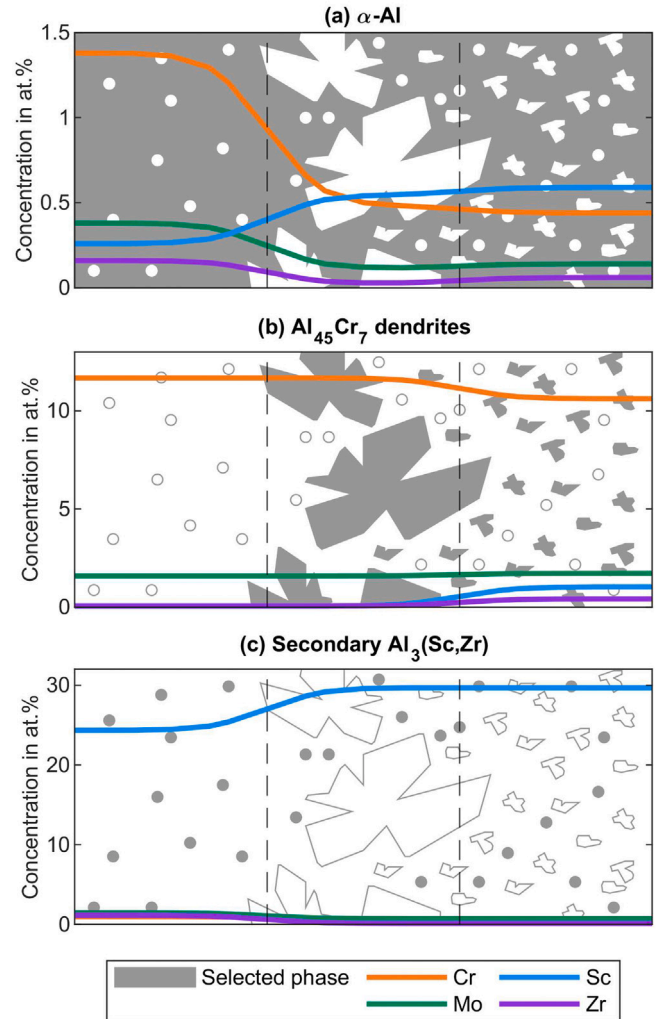
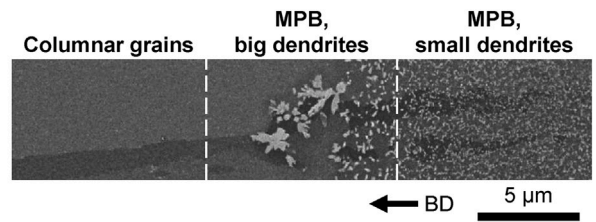


Fig. 10. Schematic composition of (a) α -Al, (b) $\text{Al}_3(\text{Sc,Zr})$ precipitates, (c) $\text{Al}_{45}\text{Cr}_7$ dendrites at MPBs based on APT results for CR-med.

the average Cr concentration of α -Al can be estimated as 1.50 at.% (CR-hi) and 0.65 at.% (CR-lo). These calculated Cr concentrations are in good agreement with the range of Cr concentrations measured via APT in CR-med.

4.1.2. $\text{Al}_{45}\text{Cr}_7$ dendrites and precipitates

The primary equiaxed dendrites can clearly be identified as $\text{Al}_{45}\text{Cr}_7$ due to the results from Thermo-Calc, EBSD, APT and HEXRD investigations in this study. Rietveld fit of the HEXRD diffractograms worked well with $\text{Al}_{45}\text{Cr}_7$ [34,35,58] and the chemical composition by APT of the equiaxed dendrites is consistent with the predicted composition by Thermo-Calc. The only difference is the substitution of some Cr with Mo because of the continuous solution and similar lattice structures of Cr and Mo [59]. Escorial et al. [29] and Sanchez et al. [31] already reported this phenomenon and the existence of $\text{Al}_{13}(\text{Cr}_{0.9}\text{Mo}_{0.1})_2$

in rapidly solidified Al-Cr3-Mo0.3 alloys,¹ which is very similar to the composition of the equiaxed dendrites in this study. Therefore, it seems reasonable that the stoichiometry of the equiaxed dendrites in this study is also $\text{Al}_{13}(\text{Cr}_{0.9}\text{Mo}_{0.1})_2$.

Composition of the $\text{Al}_{45}\text{Cr}_7$ dendrites is not significantly influenced by heat treatment, size, or alloy composition, with one exception: Sc and Zr concentrations of the smaller dendrites are slightly higher (see Fig. 10b). More details on this aspect follow in Section 4.2.3.

Other AlCr and AlMo phases have been predicted by Thermo-Calc as well but were not detected during any of the performed EDS, HEXRD, or APT measurements. It is unlikely that Al_5Cr is present in the investigated alloys because: (i) The Cr concentration of Al_5Cr would be 15.2–19.2 at.% [24,36], up to 5.8% more than that of $\text{Al}_{45}\text{Cr}_7$, which does not fit the APT results. (ii) Diffraction patterns of the Al_5Cr [60,61] did not contribute to an improvement of the Rietveld refinement. $\text{Al}_{22}\text{Mo}_5$ [62] and Al_5Mo [63,64] might be possible in small fractions, but overlapped with the many peaks of the monoclinic $\text{Al}_{45}\text{Cr}_7$ in the diffraction patterns and could not be proven with certainty. The same applies to Al_{12}Mo [65] and it has been reported that a higher Mo concentration might be necessary to develop this phase [29]. Additionally, no phase rich in Mo but poor in Cr was detected during EDS measurements.

GBPs could be verified as $\text{Al}_{45}\text{Cr}_7$ by EBSD phase maps in Fig. 3. This is supported by Escorial et al. [29], who described $\text{Al}_{45}\text{Cr}_7$ phases less than 100 μm in size on grain boundaries in rapidly solidified Al-Cr3-Mo0.3 alloys. Escorial et al. [29] also stated that heat treatments above 400°C led to the decomposition of α -Al and the formation of 10 nm $\times$ 100 nm needle-like precipitates that coarsen and become round with further heat treatment duration. This observation is in agreement with this study, where coarsened rod-shaped precipitates appear in over-aged CR-hi at lower aging temperatures (330°C, Fig. 5f) and coarsened globular-shaped precipitates appear in CR-lo at higher aging temperatures (400°C, Fig. 5h). The rod-shaped precipitates were associated with reduced ductility in an earlier study [19]. This negative effect might be overcome by a slight increase in aging time or temperature to obtain more globular-shaped precipitates similar to CR-lo.

The HEXRD intensity increase of $\text{Al}_{45}\text{Cr}_7$ in Fig. 8(d,e) can be explained by the decomposition of the Al matrix described in the previous paragraph. The decomposition is clearly visible in Fig. 5(f,h), where the matrix around bright GBPs becomes darker than the columnar grains. The weaker intensity increase of CR-lo must be a result of the alloys' lower Cr content. A less strong oversaturation of the matrix means less decomposition and fewer GBPs. This is supported by an Al-Cr2.6-Sc-Zr alloy that did not show any GBPs even after heat treatment [18] and must mark a maximum Cr content between 2.6 and 2.9 wt.% to avoid GBPs.

4.1.3. $\text{Al}_3(\text{Sc,Zr})$ precipitates

Chemistry of $\text{Al}_3(\text{Sc,Zr})$ precipitates was measured by APT on CR-med and calculated by Thermo-Calc for CR-hi, CR-med, and CR-lo. The Zr concentration predicted by Thermo-Calc was considerably higher (4.56–8.44 at.%) compared to the actual APT measurements (max. 1.15 at.%). The composition of L_{12} $\text{Al}_3(\text{Sc,Zr})$ can vary based on the alloys' composition: Harada et al. [66] reported Zr concentrations of 5.4 at.% ($\text{Al}_3(\text{Sc}_{0.75}\text{Zr}_{0.25})$) and 12.2 at.% ($\text{Al}_3(\text{Sc}_{0.5}\text{Zr}_{0.5})$). The Sc/Zr ratio in CR-med is comparable to this data and agrees with Thermo-Calc results. Interestingly, the APT Sc concentration is higher and the Zr concentration is lower in the presence of an $\text{Al}_{45}\text{Cr}_7$ dendrite (see Fig. 10c). The same phenomenon is described for the Al matrix in Section 4.1.1 and suggests a general enrichment with Sc and depletion of Zr at MPBs. Consequently, the available Zr for secondary $\text{Al}_3(\text{Sc,Zr})$ precipitates is limited at MPBs. In the case of primary $\text{Al}_3(\text{Sc,Zr})$, two reasons are

possible for the reduced Zr concentration: The competing solidification of $\text{Al}_{45}\text{Cr}_7$ (see Section 4.2.3) and trapping of Zr in those phases could be one reason. Another reason is the low diffusion rate of Zr, which is also known to create Zr-shells around $\text{Al}_3(\text{Sc,Zr})$ precipitates [5,9,67]. As APT measurements were only performed at MPBs, the lower Zr concentration of the MPB also affects the measured Zr concentration in $\text{Al}_3(\text{Sc,Zr})$ precipitates.

Another difference between APT and Thermo-Calc results on $\text{Al}_3(\text{Sc,Zr})$ precipitates is the Cr and Mo concentration. APT measurements did show small amounts of Cr (max. 0.99 at.%) and Mo (max. 1.46 at.%), especially in secondary precipitates, while Thermo-Calc did not consider that at all. Electron microprobe analysis of $\text{Al}_3(\text{Sc,Zr})$ precipitates in slowly cooled Al-Sc-Cr alloys did show only ≤ 0.2 at.% Cr [68] and the involvement of Cr has been reported in interlayers between $\text{Al}_3(\text{Zr,Ti})$ precipitates and the Al matrix in a rapidly solidified Al-Cr-Zr-Ti alloy [69]. The reason for the high Cr concentration in this study is currently unknown. Mo, however, has been reported with an amount of 0.95 at.% partitioning in the shell of L_{12} precipitates of an Al-Zr-Sc-Er-Si alloy and reducing the precipitates' coarsening rate [70]. The contribution of both Cr and Mo to $\text{Al}_3(\text{Sc,Zr})$ could be an explanation for the thermal stability of Al-Cr-Mo-Sc-Zr alloys [14,18].

4.2. Columnar to bimodal transition

Textures of MG, CR-hi and CR-lo were obtained by HEXRD measurements and are in agreement with the observed microstructures: MG is known for its bimodal microstructure and has a comparable maximum mrd to literature (1.3–3.4 [53,71,72]). Rather columnar additively manufactured Al alloys have a maximum mrd of 4.0–8.3 [53,73,74], close to CR-lo (8.7) which has a fully columnar grain structure. A rotation to the Z-axis has also been reported in one columnar case [53] and might be a result from the heat dissipation during the PBF-LB process depending on gas flow.

Most of the Scancromal[®] alloys for PBF-LB exhibit a fully columnar grain structure even when up to 1 wt.% Sc + Zr is added [18]. There is only one example of a more pronounced bimodal Scancromal[®] alloy (Al-Cr4-Mo1.36-Sc0.78-Zr0.52) [20] and another example of a fully bimodal Al-Cr4-Zr1.5 alloy [21]. Zicromal[®] is also fully bimodal with a high alloying content (Al-Cr5.03-Mn1.56-Zr1.26) but becomes columnar when mixed with 33% Al (Al-Cr3.8-Mn1-Zr1) [18]. In the case of Al-Mg alloys, 0.6 wt.% of Sc + Zr is already sufficient to achieve a bimodal grain structure [75]. The authors assume that Cr influences precipitation formation and the effectiveness of Sc and Zr on grain refinement, which will be discussed through the following three hypotheses on the columnar to bimodal transition in Al-Cr alloys.

Please note that the hypotheses represent initial concepts regarding the origins of the different grain structures. Each of these can be considered individually or in combination. They are intended to be used as guidelines for future research.

4.2.1. Kinetic hypothesis

The first hypothesis for the columnar to bimodal transition is based on kinetics. The diffraction peak distance between α -Al and $\text{Al}_3(\text{Sc,Zr})$ in Fig. 8(c) is larger for Al-Cr and smaller for Al-Mg. This is consistent with the reported lattice parameters depending on Cr or Mg content [30,76]. Fig. 11 visualizes the lattice parameters of Al-Cr, Al-Mg, $\text{Al}_3(\text{Sc,Zr})$, and includes (i) the calculated lattice parameters by HEXRD peak positions of as built CR-lo, CR-hi, and MG as coloured data points (see Table 6), and (ii) the measured Cr concentrations by APT of α -Al in CR-med as brown data points (see Table 5). Both HEXRD and APT measurements result in similar concentrations and a smaller lattice parameter than pure Al. The lattice mismatch between α -Al and $\text{Al}_3(\text{Sc,Zr})$ is decreased in Al-Mg alloys, leading to easier heterogeneous nucleation of the former on the latter. The opposite occurs in Al-Cr alloys, which

¹ Unless otherwise specified, alloy compositions are given in wt.%.

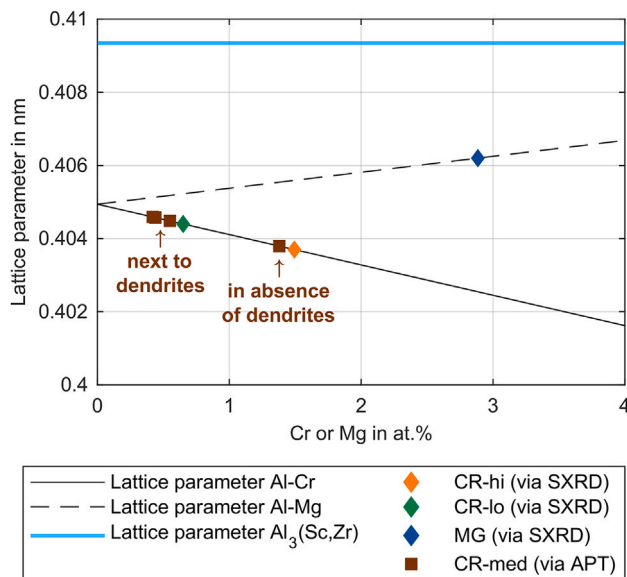


Fig. 11. Lattice parameter of L_{12} $Al_3(Sc,Zr)$ precipitates and α -Al in dependence on Cr or Mg concentration [30,66,76] including HEXRD and APT results. Annotations belong to CR-med.

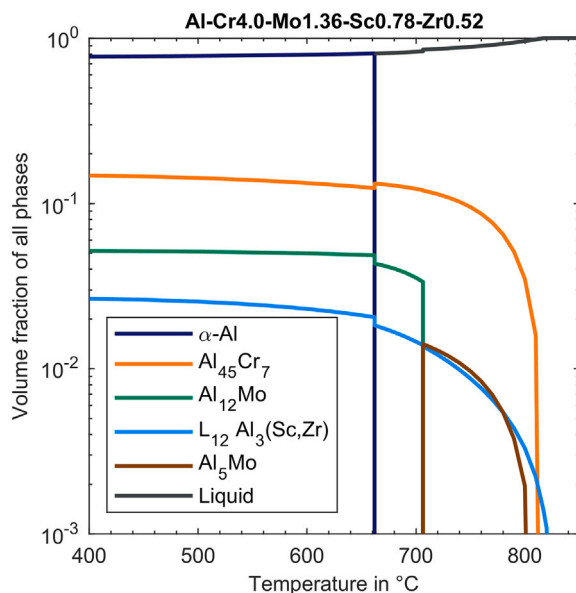


Fig. 12. Thermo-Calc one-axis equilibrium diagram using the composition of the more pronounced bimodal Scancromal[®] alloy by Gómez et al. [20]. Tetragonal DO_{23} Al_3Zr and monoclinic Al_5Cr were excluded (see Section 2.2).

could be one reason for the less potent grain refining characteristics of Sc and Zr in Al-Cr alloys.

4.2.2. Thermodynamic hypothesis

The second hypothesis for the columnar to bimodal transition is based on thermodynamics, more precisely the solidification sequence. Thermo-Calc calculations indicated that for all three of the presented Al-Cr alloys in this study, the $Al_{45}Cr_7$ phase forms before the grain refining $Al_3(Sc,Zr)$ precipitates (see Table 4). However, the solidification maps in Fig. 2 did show that CR-hi is close to a composition where $Al_3(Sc,Zr)$ solidifies first and could explain the weakly bimodal grain structure of

CR-hi. Al_3Zr also solidifies first in the earlier mentioned bimodal Al-Cr4-Zr1.5 example by Kimura et al. [21]. Additionally, another Thermo-Calc one-axis diagram of the more pronounced bimodal Scancromal[®] alloy reported by Gómez et al. [20] was performed in Fig. 12 and it confirms that $Al_3(Sc,Zr)$ forms first from liquid in this case as well. From this correlation it seems reasonable that a certain amount of Sc + Zr has to be added to enable grain refinement. In these examples $Al_3(Sc,Zr)$ only acts as a grain refiner when it is formed first from liquid and, therefore, the solidification sequence affects whether a columnar or bimodal microstructure develops. Nonetheless, it raises the question of why $Al_3(Sc,Zr)$ cannot act as a grain refiner despite solidifying before α -Al. A possible reason for this question is answered by the following third hypothesis.

4.2.3. Grain growth hypothesis

The third hypothesis for the columnar to bimodal transition is based on the assumed grain growth as follows: From the observed concentrations of APT measurements (Section 3.3) and solidification calculations by Thermo-Calc (Section 3.1), the authors suppose that the larger equiaxed dendrites (poor in Sc and Zr) solidify first in the liquid close to MPBs because of thermal undercooling, the locally increased G , and decreased V . While the liquids' temperature is still high, the dendrites have enough time to grow into their pronounced snowflake-like shape and cause a reduction of Cr in the surrounding liquid. Following the solidification maps in Fig. 2, the lower Cr content in the remaining liquid could trigger the solidification of $Al_3(Sc,Zr)$ and lead to the precipitates' clusters next to large dendrites. The solidification of $Al_3(Sc,Zr)$ could also act as nuclei [4–8] for smaller $Al_{45}Cr_7$ dendrites (rich in Sc and Zr), which then cover the surface of $Al_3(Sc,Zr)$. Meanwhile, the liquids' temperature has dropped and the smaller dendrites do not have the time to grow into their pronounced shape before they get enclosed by the solidifying α -Al matrix. α -Al starts to grow from the MPB, follows the crystallographic orientation of the previous layers, and creates the epitaxial columnar grain growth. The columnar grains are not hindered by equiaxed dendrites at MPBs because there is free space between each of them to grow beyond the MPB region. The $Al_{45}Cr_7$ dendrites do not act as nuclei for α -Al because of their different crystal lattice (monoclinic vs. fcc). Lastly, small amounts of excess Cr and Mo remain between the growing columnar grains as $Al_{45}Cr_7$ GBPs.

This theory, of a compound-phase consisting of $Al_{45}Cr_7$ with an $Al_3(Sc,Zr)$ nucleus, is supported by a study on the phase composition of slowly cooled Al-Cr-Sc alloys, where no Sc (≤ 0.13 at.%) was detected in $Al_{45}Cr_7$ phases [68]. This demonstrates that the measured concentration of Sc in smaller dendrites in this study (1.03 at.%) is not an equilibrium phenomenon, while the larger dendrites correspond to the measured values of the aforementioned study.

If primary $Al_3(Sc,Zr)$ precipitates act as nuclei for small $Al_{45}Cr_7$ dendrites as described above, this would explain the higher Sc + Zr concentration of smaller dendrites and could prevent parts of the added Sc + Zr from acting as grain refiners and precipitation hardeners. An estimation of the amount of trapped Sc and Zr in small $Al_{45}Cr_7$ dendrites was done using the mole fractions by Thermo-Calc and APT concentrations of CR-med (see Appendix A Supplementary data S4). According to this, approximately 11–19% of the added Sc and 25–71% of the added Zr are trapped in small $Al_{45}Cr_7$ dendrites, therefore, having a significant influence on grain refining and precipitation hardening. Note that this is an estimation based on APT results only from MPBs. Variations in mole fractions led to small deviations of a maximum of 4% for Sc and a maximum of 7% for Zr. Variations in element concentration led to deviations of a maximum of 6% in the case of Sc, but up to 41% in the case of Zr. This indicates that the Sc values of APT results are reliable at MPBs, but the Zr values vary significantly.

4.2.4. Columnar to bimodal map

The grain structure observations based on kinetic, thermodynamic and grain growth hypotheses are brought together in Fig. 13, where

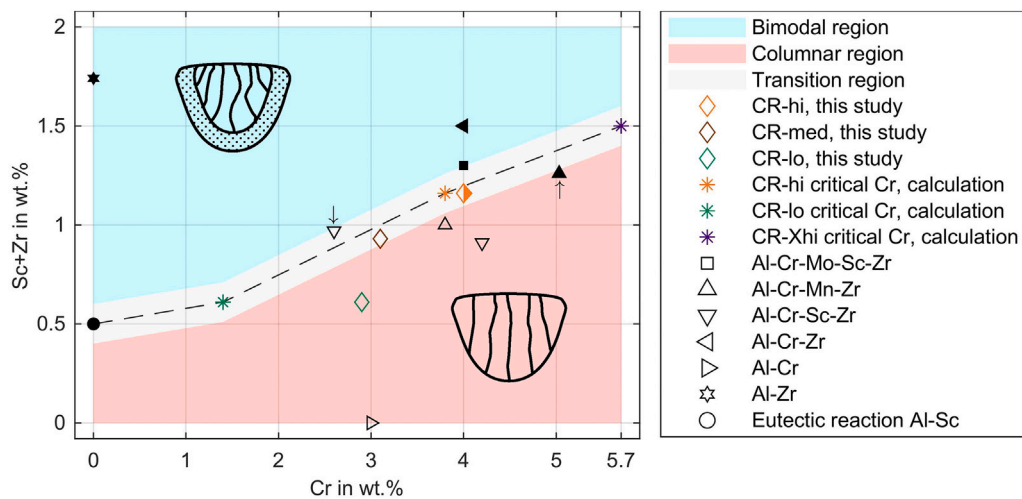


Fig. 13. Grain structure of relevant alloys from literature [18,20,21,23,78] and this study depending on Sc + Zr and Cr content. Filled markers indicate bimodal microstructure. The transition line is based on critical Cr concentrations by Thermo-Calc (see Fig. 2c,d) and the eutectic reaction of Al-Sc [77].

Sc + Zr and Cr concentration define the grain structure. It includes other Al-Cr alloys from the literature and is divided into bimodal (blue region, filled data points) and columnar (red region, unfilled data points). The following data points, based on the thermodynamic hypothesis in Section 4.2.2, were used to separate these two regions (dashed line):

- The eutectic reaction of the Al-Sc system at 0.5 wt.% [77],
- the calculated critical Cr content for CR-hi and CR-lo that decides whether $\text{Al}_{45}\text{Cr}_7$ or $\text{Al}_3(\text{Sc,Zr})$ solidifies first (see Fig. 2c,d) and
- an additionally calculated critical Cr content for an extra-high alloyed variant CR-Xhi (Al-Cr6-Mo2.4-Sc1-Zr0.5).

The two regions in Fig. 13 can be used to decide on future compositions of Scancromal® or may be helpful to create other Al-Cr-based alloys for PBF-LB. Despite the commonly known fact that hot-cracking appears preferably on columnar grains, none of the Al-Cr alloys investigated so far show hot-cracks between columnar grains [18–21,23].

Literature data confirm the columnar and bimodal regions very well. Principally, when a higher amount of Cr is added, a higher amount of Sc + Zr is necessary to achieve a bimodal microstructure. There are only two data points (indicated by an arrow) with a grain structure different from that predicted by the two proposed regions. These two points and CR-hi are examples of an intermediate region. In this transition region (grey), bimodal, columnar, or intermediate grain structures can be observed. CR-hi is an ideal example of the transition region, because of its intermediate structure that exhibits small equiaxed grains at MPBs but there is no continuous fine-grained region. Additionally, epitaxial grain growth from one layer to another is still possible. Please note that Sc and Zr were treated equally in Fig. 13, despite the fact that Zr is a less potent grain refiner than Sc [4]. Variations in the Sc/Zr ratio will also affect the exact transition region, as this influences the solidification path (see Fig. 2a,b). Further experiments are necessary to verify the presented hypotheses and regions in Fig. 13.

The Mo content has been disregarded in Fig. 13 because of two reasons: First, none of the AlMo phases could be proven with certainty via HEXRD or EDS, and Al_{12}Mo was not observed in another study on rapidly solidified Al-Cr-Mo powder [31]. Second, even if small amounts of the AlMo phases are present, the volume fraction (by Thermo-Calc and on SEM images) of the equiaxed primary $\text{Al}_{45}\text{Cr}_7$ dendrites is much higher and their effect on capturing Sc and Zr must be much higher than a phase that is not clearly visible. Third, Thermo-Calc does not take the partitioning of Mo in $\text{Al}_{45}\text{Cr}_7$ into account and, therefore, it is not possible to specify the critical Mo concentration for $\text{Al}_{45}\text{Cr}_7$. To

take the possible influence of Mo on the columnar to bimodal map into account, an alternative map including Mo is printed in Appendix A Supplementary data S5.

4.2.5. Correlation between microstructure and mechanical properties

Based on the currently available literature data, it is not possible to make an appropriate comparison of the mechanical properties of bimodal and columnar Al-Cr alloys. In general, the bimodal alloys show slightly higher tensile strength and slightly lower ductility, but this can be attributed to the higher Sc + Zr content and, therefore, increased precipitation hardening and grain-boundary strengthening (Hall-Petch) effects [18,20,21,23]. When loaded longitudinally to the grains, columnar grains could be advantageous in creep tests [14]. The influence of grain structure and GBPs on high-temperature properties is currently under investigation. Further microstructural investigations of lower and higher alloyed Al-Cr alloys are required to verify the presented relationship between grain structure, composition and solidification sequence.

4.2.6. Influence of process parameters

In addition to the alloy content, other process aspects can influence temperature gradients in the melt pool and, therefore, influence grain growth and texture. Higher build plate temperature and higher VED increased the volume fraction of equiaxed grains in an Al-Mg-Zr(Sc) alloy [37,51]. Due to the higher conductivity of nitrogen compared to argon, samples printed in a nitrogen atmosphere exhibit a slightly finer grain structure, which is, however, negligible overall [43,73,79,80]. A higher layer thickness has also been associated with smaller grains and a more bimodal grain structure in AlSi10Mg and Ni-Alloys [81,82]. Nevertheless, the earlier mentioned more pronounced bimodal examples (Al-Cr4-Mo1.36-Sc0.78-Zr0.52 [20] and Al-Cr4-Zr1.5 [21]) showed bimodal grain structures over a large range of VED from 50 to 107 J/mm³ with comparable process parameters and the same layer thickness as this study's CR-med. And yet, CR-med displays columnar grains. In order to understand the influence of process parameters on the microstructure of Al-Cr alloys, further studies should investigate the influences of individual factors such as process gas, scan pattern, layer thickness, and build plate temperature.

5. Conclusion

Al-Cr alloys for PBF-LB are still quite new and relationships between composition, phase formation and mechanical properties are

essential to decide on future developments and applications of these alloys. This study investigated the occurring phases in Al-Cr-Mo-Sc-Zr alloys using three different compositions to identify differences and similarities regarding solidification sequence, phase composition and grain structure. The following conclusions can be drawn:

- The presented Al-Cr-Mo-Sc-Zr alloys consist mainly of three phases, irrespective of the alloys' composition: α -Al, Al₄₅Cr₇, and Al₃(Sc,Zr).
- The alloys' composition determines whether Al₄₅Cr₇ or the grain refining Al₃(Sc,Zr) solidifies first from the liquid.
- Reasons for the columnar to bimodal transition have been proposed including kinetic, thermodynamic and grain growth hypotheses. All of these hypotheses can explain the alloys' different microstructures depending on their Cr, Sc, and Zr concentrations and should provide guidelines for further investigations on Al-Cr alloys.
- The composition of Al-Cr-Sc-Zr alloys should be chosen carefully to achieve the desired microstructural and mechanical properties without losing excess amounts of Sc in other primary phases. A (Sc + Zr)-Cr-map has been presented to decide on future compositions of Al-Cr alloys for PBF-LB.

The presented (Sc + Zr)-Cr-map should be verified in future studies by analysing Al-Cr-Mo-Sc-Zr alloys with lower and higher alloying contents. Simplified alloy compositions, such as Al-Cr-Sc/Zr or Al-Mo-Sc/Zr, would contribute to evaluating the interactions of Cr or Mo with Sc or Zr. Other aspects to consider are process parameters (build plate heating, layer thickness, and scan strategy). Further Transmission Electron Microscopy (TEM) investigations are necessary to verify the phases. Additionally, the possibility of a Cr and Mo enrichment at the shell of Al₃(Sc,Zr) precipitates and Al₃(Sc,Zr) serving as nuclei for Al₄₅Cr₇ should be examined via TEM. In-situ synchrotron experiments would also be interesting to prove the suggested solidification path that hinders the grain refining effect of Sc and Zr. The influence of GBPs on tensile and creep properties is currently under investigation.

CRedit authorship contribution statement

Barbara Agricola: Writing – original draft, Visualization, Validation, Project administration, Methodology, Investigation, Formal analysis, Data curation, Conceptualization. **Marko Bärtl:** Writing – review & editing, Visualization, Validation, Investigation, Formal analysis, Conceptualization. **Martin Landesberger:** Writing – review & editing, Visualization, Validation, Resources, Investigation, Formal analysis, Data curation. **Huan Zhao:** Writing – review & editing, Validation, Resources, Investigation, Formal analysis. **Frank Palm:** Writing – review & editing, Resources, Conceptualization. **Annegret Kerschenlohr:** Writing – review & editing, Supervision, Resources, Funding acquisition. **Eric A. Jäggle:** Writing – review & editing, Supervision, Resources.

Declaration of generative AI and AI-assisted technologies in the writing process

During the preparation of this work the first author used DeepL to improve the readability and language of the work. After using this tool, the author reviewed and edited the content as needed and takes full responsibility for the content of the publication.

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The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary data for this article can be found online at doi:[10.1016/j.matdes.2026.115770](https://doi.org/10.1016/j.matdes.2026.115770).

Data availability

Data will be made available on request.

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