8. APPENDICES

8 APPENDIX A

A1 Optimisation of conditions for Rietveld calculations

For the calculations in the 22-125^o range, there was inconsistency between the predicted and calculated quantities of SiC polytypes for the powder mixtures which contained UF15 SiC (which is primarily α- SiC) and B20SiC (which is mainly β-SiC). i.e. with the 50UF15:50B20, the 30UF15:70B20 and the 70UF15:30B20 mixtures, the Rietveld analysis of the mixtures consistently gave higher values for the α- SiC polytypes and lower values for the β-SiC polytype (3C) (shown in Table A2).

A strong texture effect of the 6H polytype was observed in the Rietveld calculations of these powders (see Table A3). However, the silicon carbide powder used in this research work (UF15SiC) did not contain a high fraction of β-SiC and therefore the conditions used produced consistent results.

Note that in Appendix A1: A16= A16 Al_2O_3 powder, UF15 = UF15SiC powder and B20 = B20 SiC powder.

Table A1 Summary of the Rietveld calculations conducted on different unsintered powders

Sample	Conditions (Calculation)			Phase content (%)						Rwp (%)
	Xrddat file name	2 theta range (°)	Step size (°)	6H	4H	15R	3C	2H	Al_2O_3	
UF15 (177)	a0921I00	10 – 120.00	0.05	66.00 ± 2.37	5.44 ± 1.65	23.26 ± 2.19	4.34 ± 1.23	0.96 ± 1.17	-------	11.74
UF15	a0920I00	10 – 90.00	0.02	64.30 ± 2.07	6.19 ± 1.23	21.64 ± 1.38	7.76 ± 1.32	0.11 ± 0.81	-------	10.59
UF15detail	a0927I00	10 – 125.00	0.02	65.81 ± 1.20	3.17 ± 0.75	29.15 ± 1.23	1.87 ± 0.63	-------	-------	9.40
UF15detail	a0927I00	10 – 125.00	0.02	67.34± 1.11	2.80 ± 0.78	29.86 ± 1.23	-------	-------	-------	9.46
UF15detail	a0927I00	10 – 125.00	0.02	64.85 ± 1.38	2.52 ± 0.66	29.82 ± 1.17	1.76 ± 0.66	1.05 ± 0.51	-------	9.38
UF15detail	a0927I00	25 – 95.00	0.02	69.59 ± 1.38	2.10 ± 0.66	24.10 ± 1.26	4.21 ± 0.75	-------	-------	10.17
UF15detail	a0927I00	15 – 125	0.02	64.64 ± 1.38	2.54 ± 1.38	30.06 ± 1.71	1.71 ± 0.66	1.04 ± 0.51	-------	9.21
UF15detail	a0927I00	22 – 125.00	0.02	63.87 ± 1.47	2.61 ± 1.29	30.11 ± 1.80	2.22 ± 0.90	1.19 ± 0.51	-------	9.22
UF15detail	a0927I00	25 – 125.00	0.02	63.91 ± 1.38	2.69 ± 0.63	29.69 ± 1.08	2.48 ± 0.90	1.22 ± 0.51	-------	9.23
F500	a0927I01	10 – 125.00	0.02	74.80 ± 0.75	12.10 ± 0.57	12.78 ± 0.78	0.00 ± 0.00	0.32 ± 0.33	-------	11.02
F500	a0927I01	10 – 125.00	0.02	74.72 ± 0.69	12.41 ± 0.54	12.87 ± 0.69	-------	-------	-------	11.05
F500	a0927I01	25 – 125.00	0.02	75.28 ± 0.78	12.33 ± 0.57	12.38 ± 0.84	-------	-------	-------	10.92
F1200 (189)	a0927I02	10 – 125.00	0.02	89.51 ± 0.69	0.60 ± 0.26	9.68 ± 0.69	0.00 ± 0.00	0.22 ± 0.33	-------	12.87
F1200	a0927I02	10 – 125.00	0.02	89.30 ± 0.66	0.59 ± 0.26	10.10 ± 0.69	-------	-------	-------	12.85
F1200	a0927I02	25 – 125.00	0.02	89.54 ± 0.66	1.50 ± 0.90	8.96 ± 1.11	-------	-------	-------	12.62
B20	a0920I01	10 – 90.00	0.02	4.78 ± 1.38	0.94 ± 0.78	9.11 ± 1.35	85.17 ± 1.17	0.00 ± 0.00	-------	17.45
B20	a1013I01	22 – 125.00	0.02	4.75 ± 0.78	0.43 ± 0.63	6.90 ± 0.96	87.91 ± 0.78	0.00 ± 0.00	-------	12.76
B20	a1013I01	25 – 125.00	0.02	4.41 ± 0.78	0.46 ± 0.63	6.34 ± 0.96	88.79 ± 0.81	0.00 ± 0.00	-------	12.64

Table A2 Investigating the reliability of the Rietveld calculations on unsintered powder mixtures

Note that the results in black with "*" denotes the results from calculations of masses of powders mixed, and red text with "**", indicates the results of the Rietveld calculations of the % of the phases present.

Sample (including powders used and mass ratios used)	Conditions (calculation)			Phase content						Rwp (%)
	% Ratio of mass of powders in column 1	Xrddat file name	2 theta range (^{o})	Alumina	6H	4H	15R	3C	2H	
UF15SiC*	**100**	**a0927l00.njc**	**22- 125**	**-------**	**63.87±1.47**	**2.61±1.29**	**30.11±1.80**	**2.22±0.90**	**1.19±0.51**	**9.22**
B20SiC*	**100**	**a1013l01.njc**	**22-125**	**-------**	**4.75±0.78**	**0.43±0.63**	**6.90±0.96**	**87.91±0.78**	**0.00±0.00**	**12.76**
30UF15/70B20 (*)	30.08/69.92		22-125	-------	22.49±0.99	1.08±0.83	13.86±1.21	62.20±0.82	0.36±0.15	(11.70)
Rietveld calc.(**)	30.08/69.92	a1024l02.njc	22-125	-------	39.30±1.83	1.30±0.30	6.42±1.20	52.97±1.32	0.00±0.00	11.17
50UF15/50B20*	49.98/50.02		22-125	-------	34.31±1.13	1.52±0.96	18.51±1.38	45.07±0.84	0.60±0.26	10.99
50UF15/50B20**	49.98/50.02	a1013l00.njc	22-125	-------	48.77±1.71	1.46±0.30	13.76±1.11	36.00±1.23	0.00±0.00	10.60
70UF15/30B20*	69.96/30.04		22-125	-------	46.13±1.26	1.96±1.09	23.15±1.55	27.93±0.86	0.83±0.36	10.28
70UF15/30B20**	69.96/30.04	a1024l01.njc	22-125	-------	62.71±1.83	1.60±1.33	18.04±1.11	17.65±1.35	0.00±0.00	10.26
50UF15/50A16*	49.99/50.01		22-125	50.00	31.94±0.74	1.31±0.65	15.06±0.90	1.11±0.45	0.60±0.26	
50UF15/50A16**	49.99/50.01	a1013l04.njc	22-125	48.21±0.48	32.26±0.81	0.97±0.22	17.87±0.81	0.69±0.36	0.00±0.00	7.76
80UF15/20A16*	79.94/20.06		22-125	20.00	51.10±1.18	2.09±1.03	24.09±1.44	1.78±0.72	0.95±0.41	
80UF15/20A16**	79.94/20.06	a1024l00.njc	22-125	19.04±0.51	51.17±1.17	1.44±0.27	25.99±1.11	1.99±0.63	0.37±0.51	8.15
80B20/20A16*	79.91/20.09		22-125	20.00	3.80±0.62	0.34±0.50	5.52±0.77	70.33±0.62	0.00±0.00	
80B20/20A16**	79.91/20.09	a1013l05.njc	22-125	19.32±0.54	3.06±1.05	2.71±0.66	8.02±1.11	66.89±0.87	0.00±0.00	12.52
UF15SiC*	**100**	**a0927l00.njc**	**25 –125**	**-------**	**63.91 ± 1.38**	**2.69 ± 0.63**	**29.69 ± 1.08**	**2.48 ± 0.90**	**1.22 ± 0.51**	**9.23**
B20SiC*	**100**	**a1013l01.njc**	**25 -125**	**-------**	**4.41 ± 0.78**	**0.46 ± 0.63**	**6.34 ± 0.96**	**88.79 ± 0.81**	**0.00 ± 0.00**	**12.64**
30UF15/70B20*	30.08/69.92		25 - 125	-------	22.26±0.96	1.08±0.63	5.25±1.00	62.90±0.84	0.37±0.15	11.62
30UF15/70B20**	30.08/69.92	a1024l02.njc	25 - 125	-------	38.19 ± 1.80	1.41 ± 0.30	6.59 ± 1.20	53.81 ± 1.29	0.00 ± 0.00	11.10
50UF15/50B20*	49.98/50.02		25 - 125	-------	34.16±1.08	1.58±0.63	18.02±1.02	45.64±0.86	0.61±0.26	10.94
50UF15/50B20**	49.98/50.02	a1013l00.njc	25 - 125	-------	48.77 ± 1.68	1.49 ± 0.30	13.57 ± 1.11	36.18 ± 1.20	0.00 ± 0.00	10.56
70UF15/30B20*	69.96/30.04		25 - 125	-------	46.06±1.20	2.02±0.63	22.69±1.04	28.37±0.87	0.85±0.36	10.25
70UF15/30B20**	69.96/30.04	a1024l01.njc	25 - 125	-------	63.25 ± 1.83	1.64 ± 0.33	17.74 ± 1.14	17.37 ± 1.32	0.00 ± 0.00	10.23
50UF15/50A16*	49.99/50.01		25 - 125	50.00	31.96±0.69	1.35±0.32	14.85±0.54	1.24±0.45	0.61±0.26	
50UF15/50A16**	49.99/50.01	a1013l04.njc	25 - 125	48.30 ± 0.48	32.79 ± 0.69	0.91 ± 0.22	18.00 ± 0.81	0.00 ± 0.00	0.00 ± 0.00	7.76
80UF15/20A16*	79.94/20.06		25 - 125	20.00	51.13±1.10	2.15±.0.50	23.75±0.86	1.98±0.72	0.98±0.41	
80UF15/20A16**	79.94/20.06	a1024l00.njc	25 - 125	19.01 ± 0.54	51.61 ± 1.20	1.48 ± 0.28	25.62 ± 1.11	1.92 ± 0.63	0.36 ± 0.51	8.13
80B20/20A16*	79.91/20.09		25 - 125	20.00	3.53±0.63	0.37±0.50	5.07±0.77	71.03±0.65	0.00±0.00	
80B20/20A16**	79.91/20.09	a1013l05.njc	25 - 125	19.01 ± 0.54	51.61 ± 1.20	1.48 ± 0.28	25.62 ± 1.11	1.92 ± 0.63	0.36 ± 0.51	8.13

Table A3 Summary of texture observed in the powder mixture Rietveld studies

Sample (including powders used and mass ratio used)	Anisotropy factor 6H SiC		Anisotropy factor Al_2O_3	
	00l	**110**	**00l**	**110**
UF15 SiC	1.25	1.02	---	---
B20SiC	0.02	2.42	---	---
30UF15/70B20SiC	1.90	1.43	---	---
50UF15/50B20SiC	1.77	1.26	---	---
70UF15/30B20SiC	1.77	1.19	---	---
50UF15/50A16Al_2O_3	1.22	1.01	1.19	1.06
80UF15/20A16Al_2O_3	1.18	1.02	1.62	1.16
80B20SiC/20A16Al_2O_3	1.00	1.00	1.20	0.79

A2 Polishing procedure

The following polishing procedure was used to polish large surface area (about 40 mm^2) samples. Note that the polishing time on each cloth/ grit size was reduced when smaller surface areas were polished.

<u>Grinding:</u>

- Petrodisc M – (Iron- Copper- plate)
- Diamond suspension
  - 9 μm till planar (ca. 1 hour)
    - Ultrasonic cleaning
  - 6 μm (ca. 30 minutes)
    - Ultrasonic cleaning
  - 3 μm (ca. 40 minutes)
    - Ultrasonic cleaning (long)

Force: ca. 90 N, complimentary

<u>Polishing:</u>

- Diamond paste
  - 6μm (16 hours)
  - Ceramant cloth (from company Sommer)
  - OPS (chemical) polish (Struers) (1hour)
  - 6μm (3hours)
  - OPS (chem.) polish (Struers) (2hours)
  - 3μm (13 hours)
  - OPS (chem.) polish (Struers) (2hours)
  - 3 μm (4hours)
  - 1 μm (2hours)

Force applied for 6 μm, 3 μm, 1μm 30 N, complimentary (sample holder)

For some samples, individually (held by hand): 20 N, complimentary

OPS (chemical polish): Force applied:

Sample holder: 30 N, contra.

Single samples (hand): 5 N, contra.

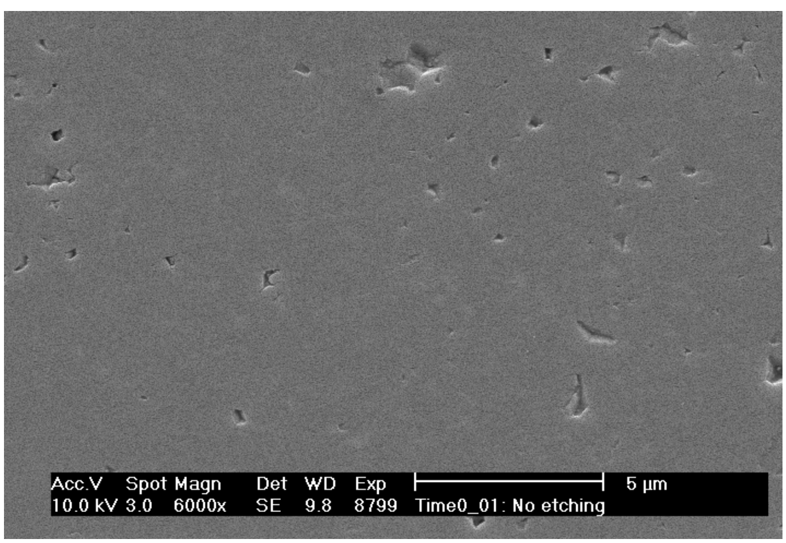
A3 Chemical etching experiments

Etching is a process in which either the main phase (in this case SiC) or the secondary phase (the grain boundary phase) is "dissolved" allowing for the separation between the grains to be clearer. There are different methods for etching materials like the liquid-phase sintered silicon carbide ceramics.

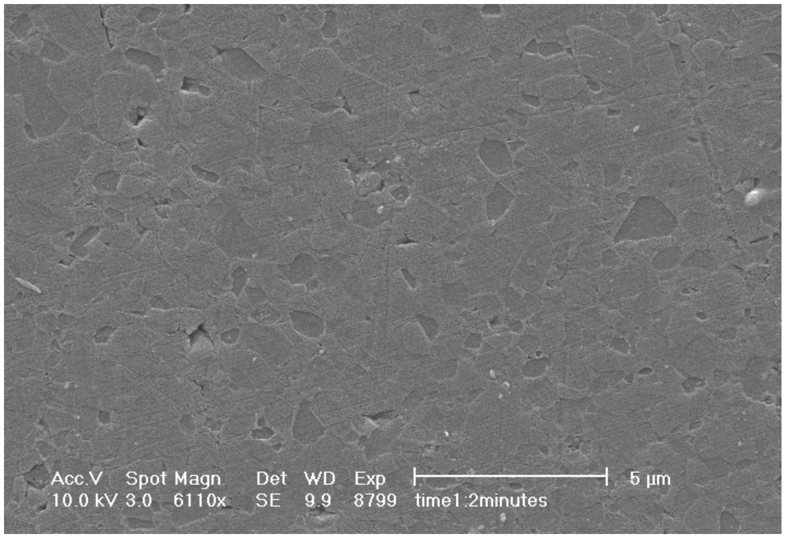
Plasma chemical etching with CF_4 or a mixture of O_2 and Ar gas are commonly used in liquid-phase sintered silicon nitride and silicon carbide ceramics. The equipment for plasma etching was, however, not available for use in this project.

Chemical etching was then experimented with. Firstly a sample was placed in 1 mol HF acid for 1 hour. When viewed under SEM, this sample did not appear to be etched to any significant extent.

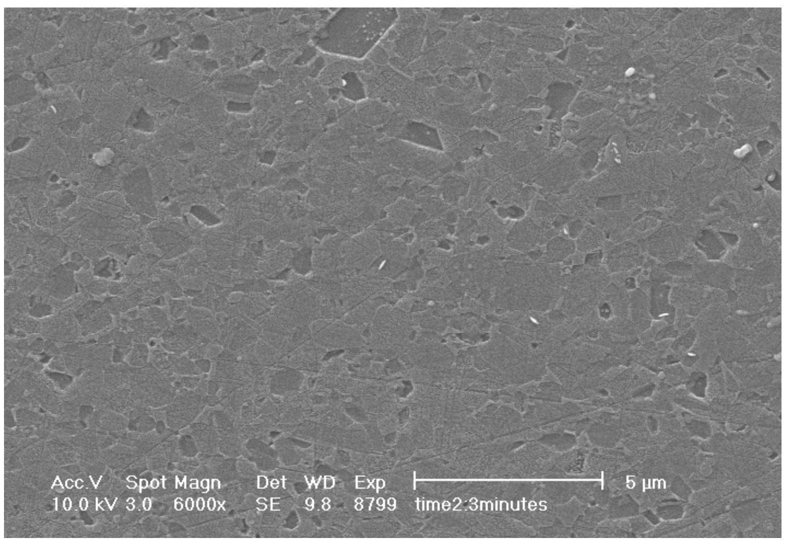
A mixture of potassium nitrate and potassium thiocyanate and water was brought to boil and from the point of boiling samples were etched for 3 minutes, 4 minutes, 5 minutes and 6 minutes.



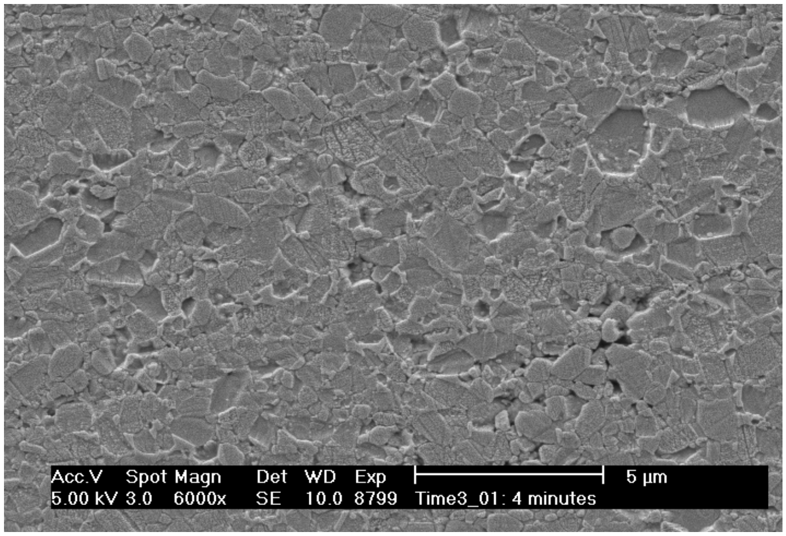
(a) No etching



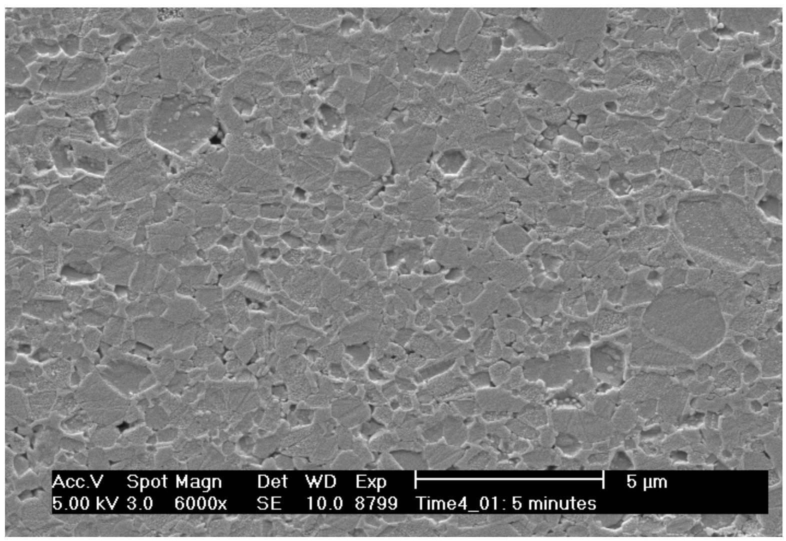
(b) Chemically etched for 2 minutes



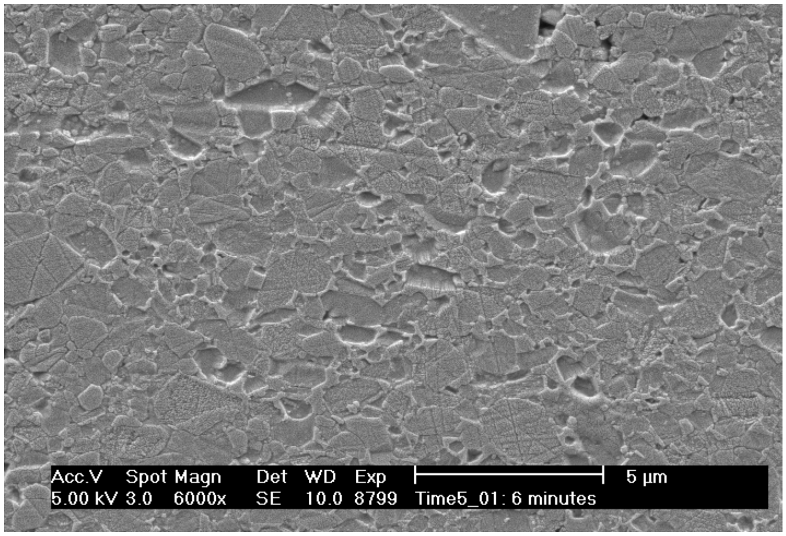
(c) Chemically etched for 3 minutes



(d) Chemically etched for 4 minutes



(e) Chemically etched for 5 minutes



(f) Chemically etched for 6 minutes

Figure A1 SEM micrographs (secondary electron mode) of chemically etched materials

From the micrographs above it is evident that the optimum time for chemical etching in this solution is between 4 and 5 minutes.

A4 Example of crack paths studied to determine crack roughness and primary mode of fracture

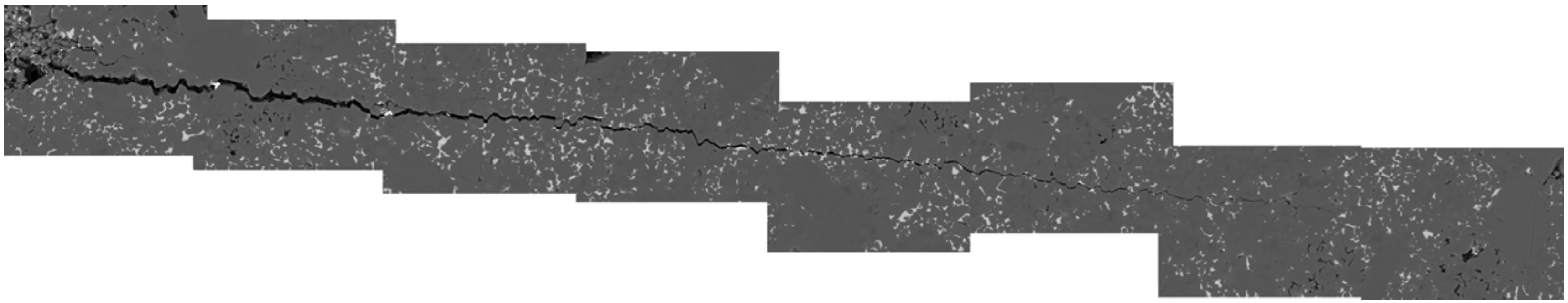


Figure A2 Crack path in the HT3GP1Y4Al material

8 APPENDIX B

Table B1 Results for HP-W materials

As- sintered (molar ratios given)			
Sample	HPW-1Y1Al	HPW- 3Y5Al	HPW- 4Y2Al
Density (g/cm^3)	3.2652 ± 0.0015 (3.259625)$^{\delta}$	3.2666 ± 0.00015 (3.25365)$^{\delta}$	3.2872 ± 0.0018 (3.267626)$^{\delta}$
HV10 (GPa)	21.171 ± 0.827	21.797 ± 1.283	21.677 ± 0.726
K_{1c} – surface ($MPa.m^{1/2}$.)	3.348 ± 0.275	3.639 ± 0.202	3.905 ± 0.287
K_{1c} – cross-section - perpendicular ($MPa.m^{1/2}$.)	3.084 ± 0.335	4.047 ± 0.537	3.603 ± 0.196
K_{1c} – cross-section - parallel ($MPa.m^{1/2}$.)	3.677 ± 0.199	4.540 ± 0.324	4.250 ± 0.417
Crack resistance – perpendicular (kg/ μm)	0.043	0.044	0.040
Crack resistance - parallel (kg/μm)	0.052	0.049	0.051
Characteristic frequency of 1st arc (300°C) (Hz)	184 520	123 890	3435
low frequency conductivity of 1st arc (300°C) $(\Omega cm)^{-1}$	8.96×10^{-5}	3.37×10^{-5}	0.249×10^{-5}
low frequency conductivity of 2nd arc (300°C) $(\Omega cm)^{-1}$	4.09×10^{-6}	2.47×10^{-6}	0.575×10^{-6}

8 APPENDIX C

C1 FESEM images of the as-sintered HP and GPS materials

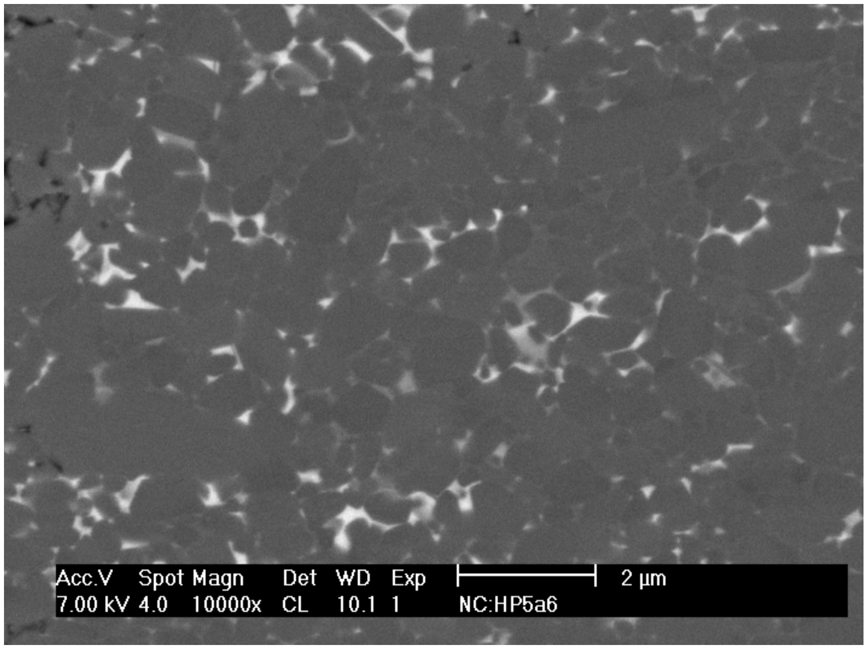


Figure C1 FESEM micrograph of HP1Y4Al material

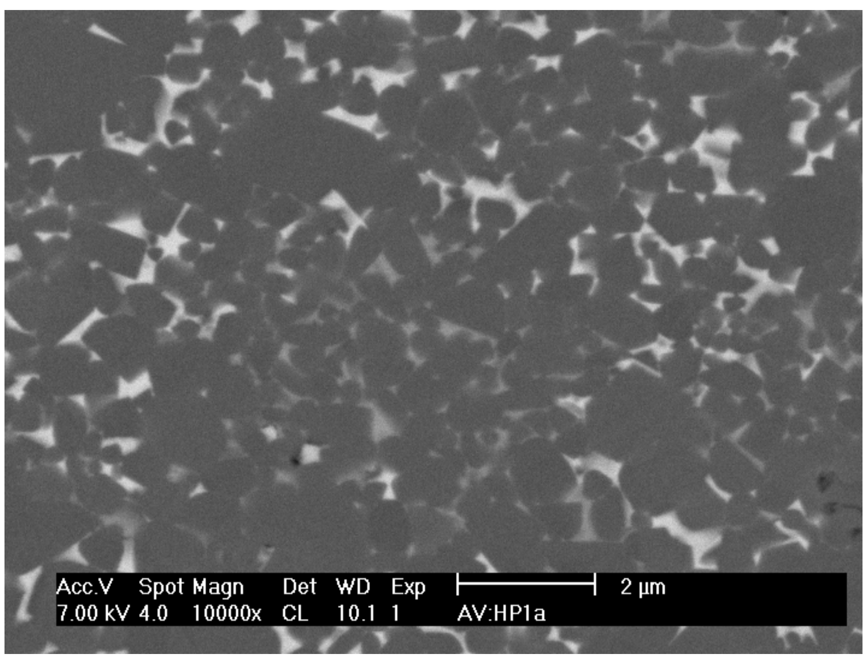


Figure C2 FESEM micrograph of HP3Y5Al material

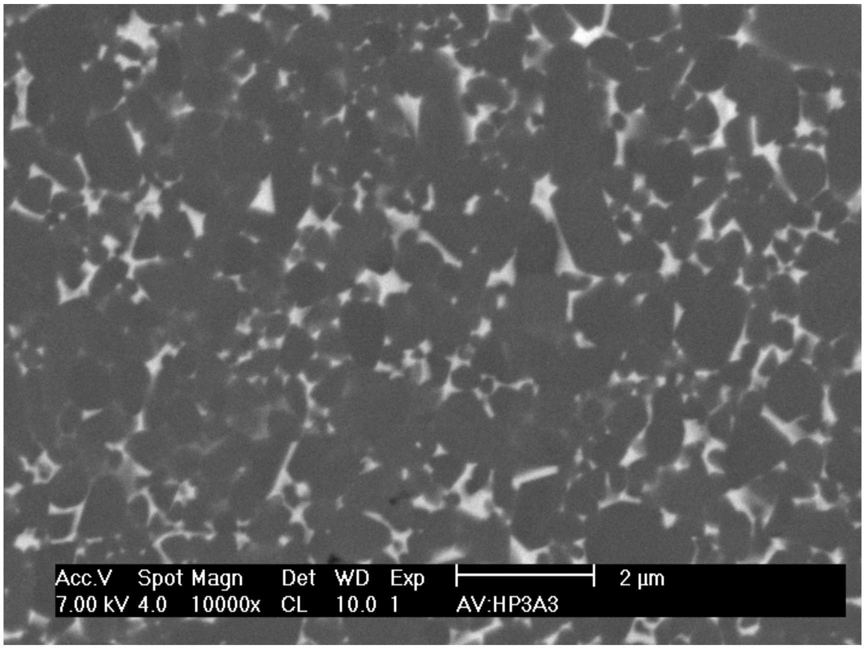


Figure C3 FESEM micrograph of HP1Y1Al material

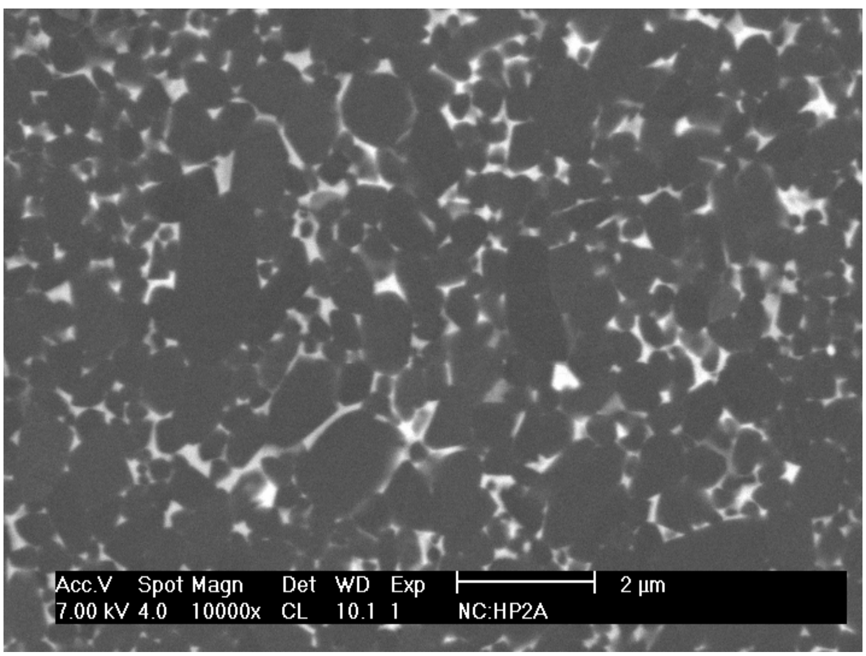


Figure C4 FESEM micrograph of HP4Y2Al material

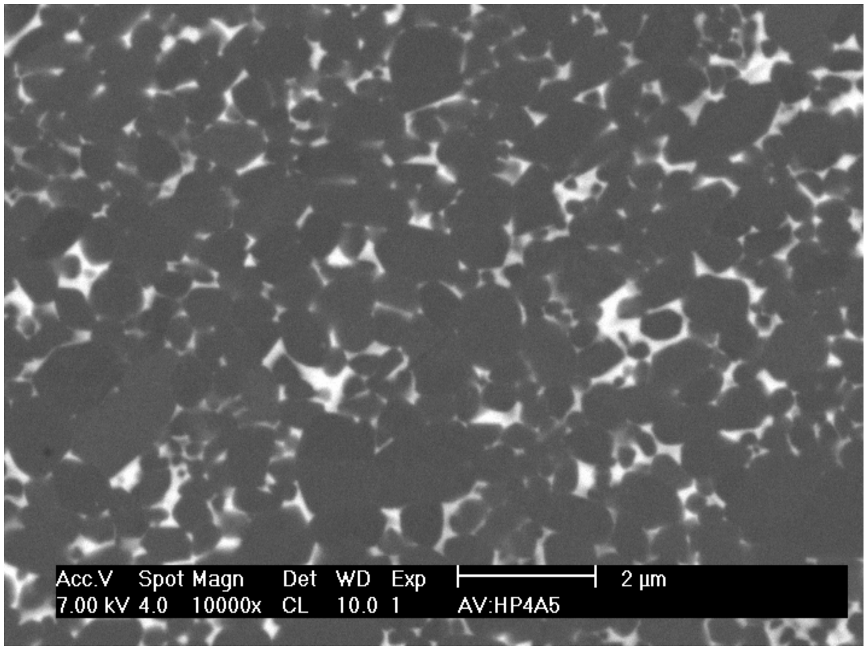


Figure C5 FESEM micrograph of HP4Y1Al material

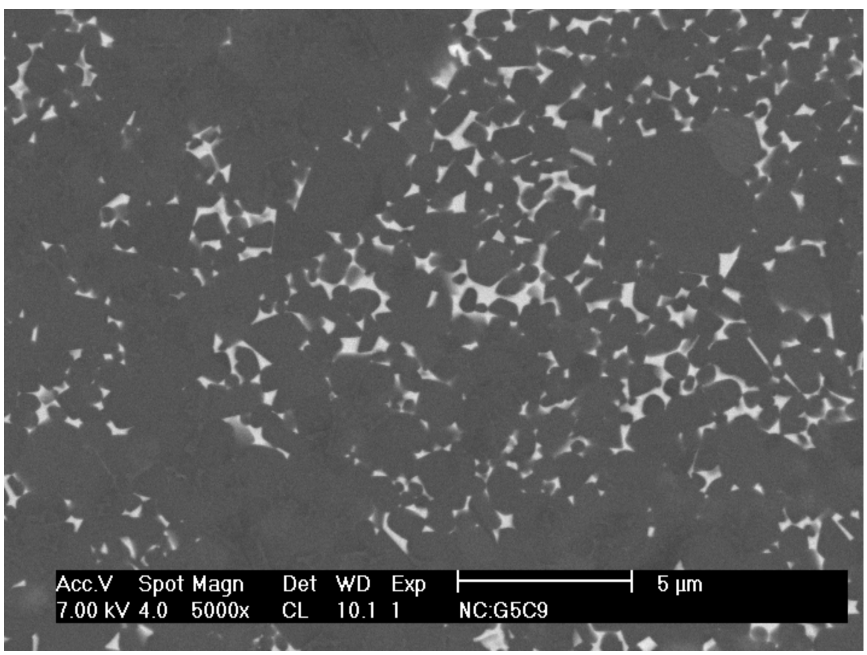


Figure C6 FESEM micrograph of GP1Y4Al material

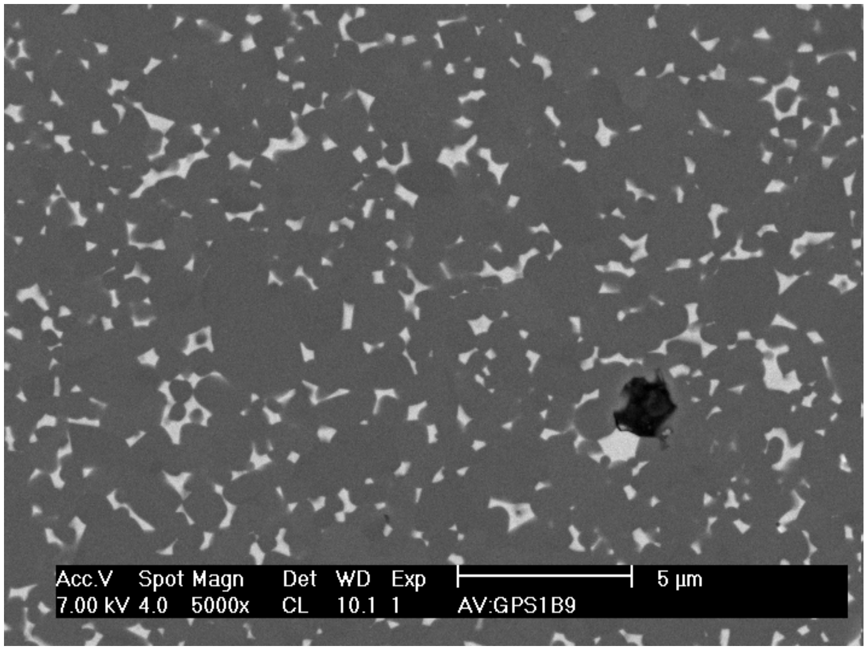


Figure C7 FESEM micrograph of GP3Y5Al material

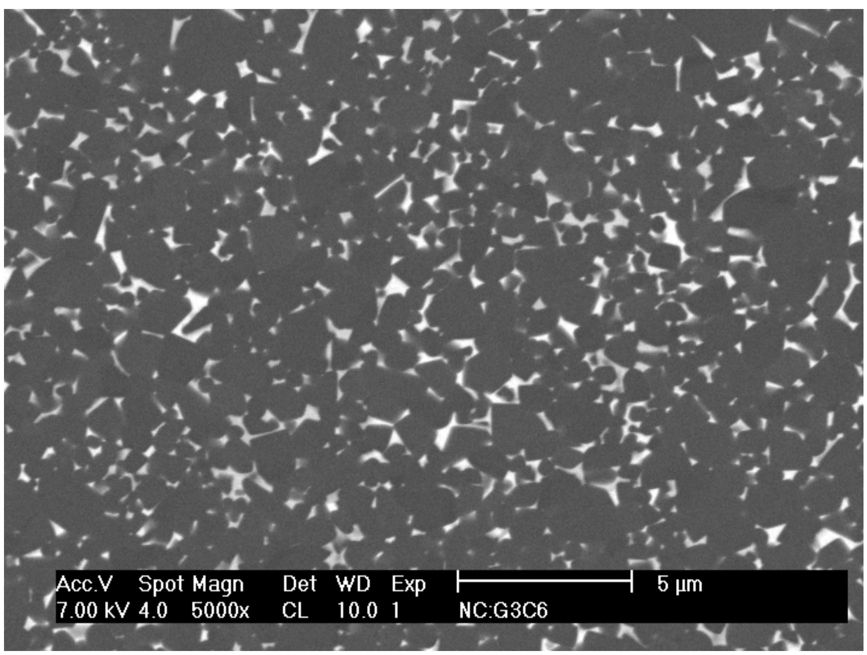


Figure C8 FESEM micrograph of GP1Y1Al material

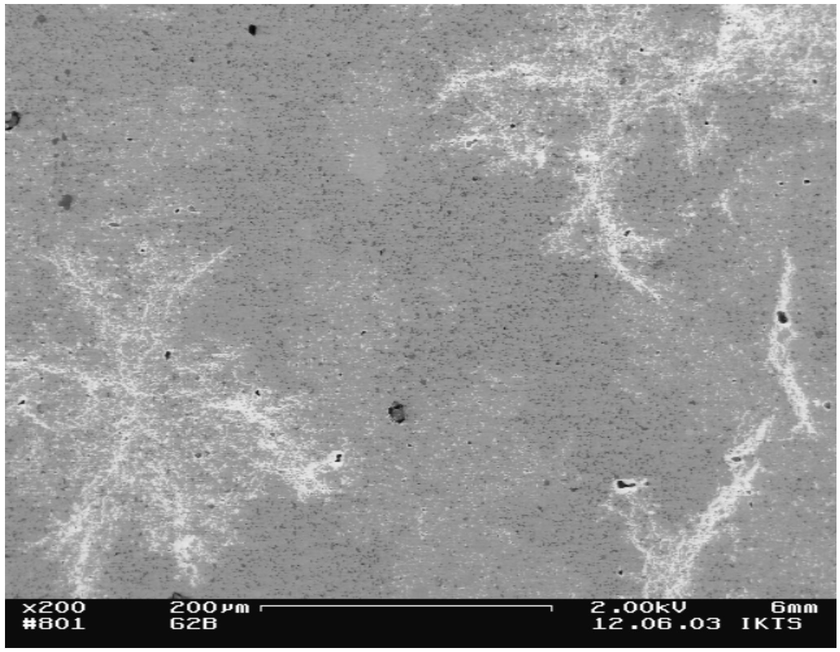


Figure C9 FESEM micrograph of GP4Y2Al material

C2 FESEM images of the heat treated HP and GPS materials

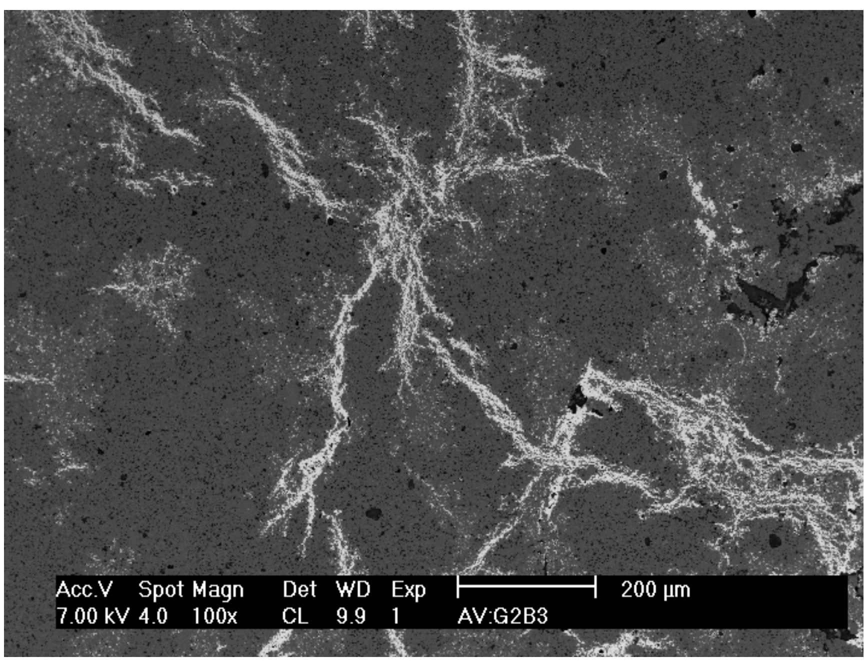


Figure C10 FESEM micrograph of HT2GP4Y2Al material

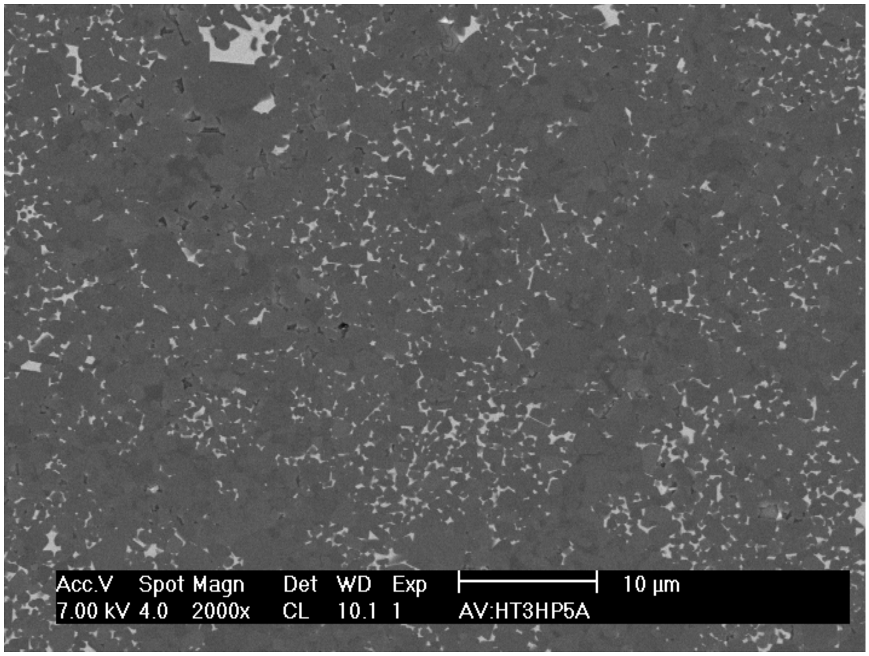


Figure C11 FESEM micrograph of HT3HP1Y4Al material

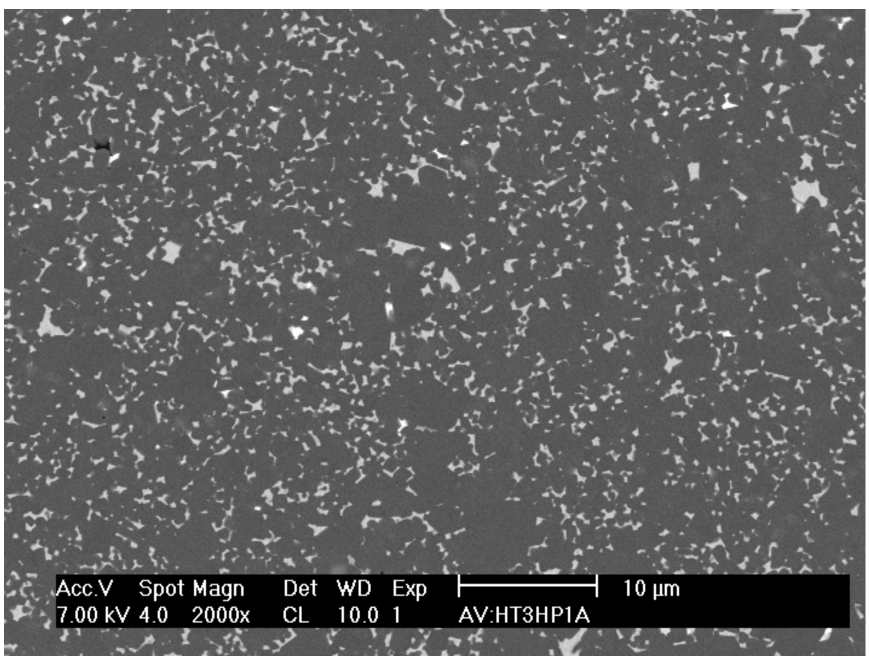


Figure C12 FESEM micrograph of HT3HP3Y5Al material

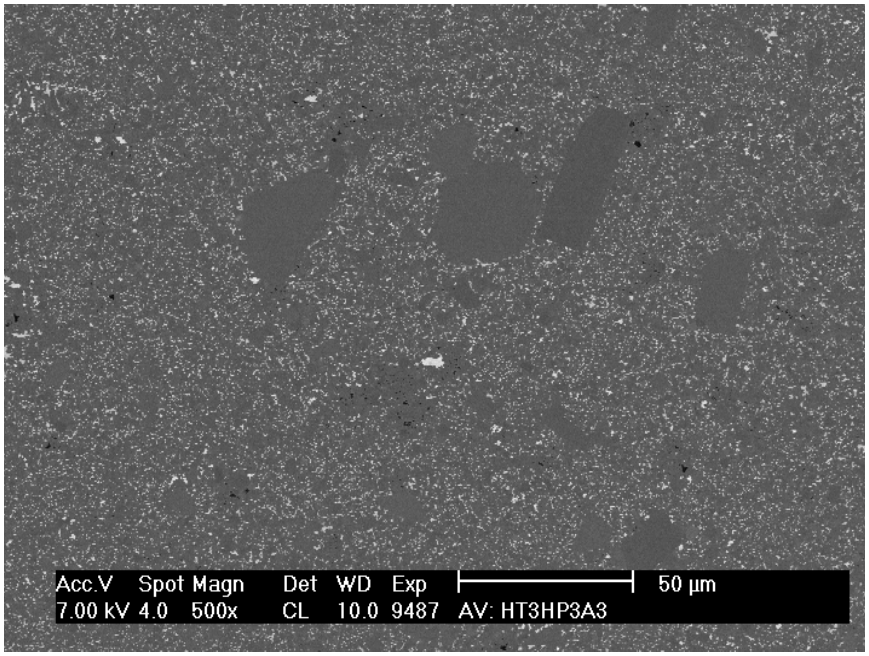


Figure C13 FESEM micrograph of HT3HP1Y1Al material

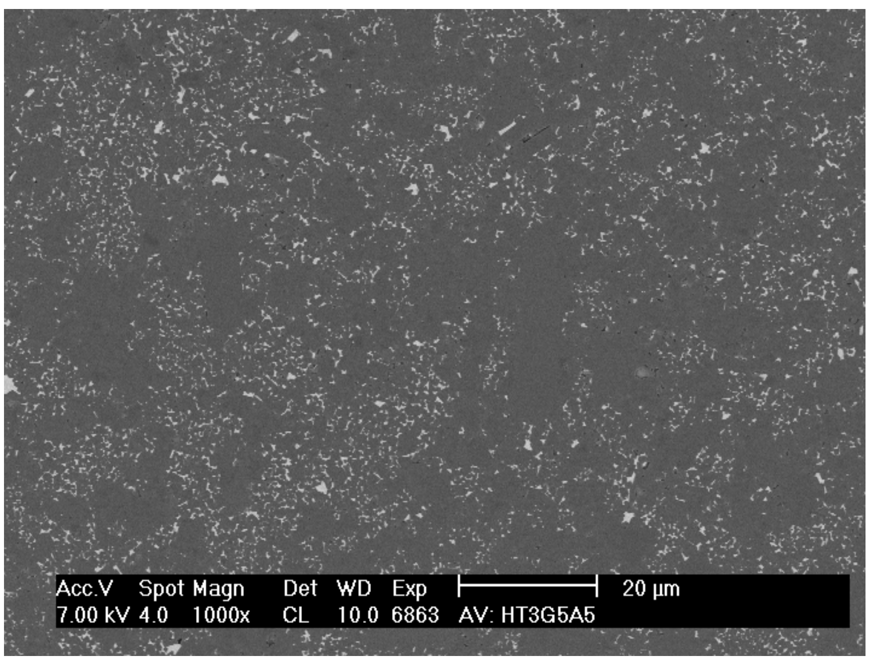


Figure C14 FESEM micrograph of HT3GP1Y4Al material