Molten Salt Shielded Synthesis (MS^3) of oxidation prone materials in air

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Abstract:

In order to prevent spontaneous oxidation during the high-temperature synthesis of non-oxide ceramics, an inert atmosphere is conventionally required[1,2]; this, however, results in high energy demand and production costs. Here we present a process for the synthesis and consolidation of oxidation-prone materials, named Molten Salt Shielded Synthesis/Sintering process (MS^3), which uses molten salts as a reaction medium and additionally protecting the ceramic powders from oxidation during high-temperature processing in air. Synthesis temperatures are also reduced, and the final product is a highly pure, fine and loose powder that does not require additional milling steps. MS^3 has been used for the synthesis of different ternary transition metal compounds (MAX phases, such as Ti_3SiC_2[3], Ti_2AlN[4], MoAlB[5]), binary carbides (TiC) and for the sintering of titanium (Ti). The availability of high-quality powders, combined with energy and cost savings, may remove one of the bottlenecks for the industrial application of these materials.

Main body:

The high synthesis temperature (T > 1000°C) of non-oxide ceramics is due to the covalent nature of the atomic bonds and high melting points. Solid state synthesis from the primary reactants usually results in a dense or porous block of the reacted products, which needs to be ground and milled into fine powder for further processes. The milling process presents several complications for large scale powder production: the abrasion resistance and hardness of ceramic materials imply high wear and operating costs with long milling times and a potential contamination by impurities. This is particularly a problem for MAX phases due to the lack of easy synthesis methods. MAX phases are a large class of layered ternary carbides or nitrides ($M_{n+1}AX_n$) where M, A and X are early transition metal, group 13/14 elements and C/N atoms respectively[6]. These materials possess high stiffness resembling ceramics and are readily machinable like metals, bridging the gap between ceramics and metals[6]. This combination of properties has attracted considerable interest for high temperature applications on the account–of excellent oxidation/corrosion resistance, light weight with outstanding damage tolerance and machinability. In the present study, we have developed a process for synthesizing non-oxide ceramic powders in air at a relatively low temperature without further milling. The process is referred to as molten salt shielded synthesis/sintering with an acronym MS^3. Although the process works for the synthesis of a wide variety of non-oxide ceramics, we have focused on the synthesis of MAX phase ceramics as a particular successful example[6]. The lack of feasible bulk production methods of highly pure MAX phase powders has limited their industrial applications until now. Furthermore, as MS^3 inhibits oxidation, the process can also be used for the sintering of metals or non-oxide ceramics in a normal air environment; we have demonstrated this by sintering Ti using MS^3. Ti is used in a variety of applications from aerospace components[7] to scaffolds for bio-implants[8] and a cheaper consolidation step will result in low-cost powder metallurgical (PM) Ti parts. Since Ti has high affinity towards oxygen and nitrogen, the sintering is carried out in argon or vacuum. Although argon atmosphere has the problem of volatile impurity removal, it is preferred considering the initial investment for expensive vacuum furnace. At 1200ºC a sintered density of 95% was reported with starting particle size <40µm, whereas a higher density needs pressure assisted sintering techniques or the use of finer powder[9,10]. A similar density was obtained with the process of MS[3] which suggests that the sintering condition during MS[3] is like that in vacuum furnace with respect to the oxygen deficient ambience. Existing methods for the fabrication of porous Ti[11] includes sacrificial wax method along with rapid prototyping[12], selective laser melting[13], solid state foaming[14], space holder technique[15] or simply incomplete sintering[16]. Irrespective of the method, the sintering of porous titanium is carried out in vacuum or argon atmosphere. In certain methods, the polymer used in the process is burnt and is irrecoverable. In view of the initial investment for laser processing or rapid prototyping, MS[3] process is cheaper considering the usage of air furnace alone and the fact that the salt particles which are used as pore formers can be recycled. In summary, MS[3] provides the possibility to sinter Ti both in its dense and porous form in an air furnace.

Molten salt synthesis for ceramic powders is well known, but for non-oxide compounds the process has been so far always carried out in argon atmosphere to protect the material from oxidation [17,18]. These are efficient methods yet are expensive, limiting their use at the industrial scale. In the MS[3]-process, we have used potassium bromide (KBr) as the reaction medium. KBr has high ductility at room temperature and can be cold pressed to densities above 95 % relative density[19,20]. We exploit this property of KBr to have a gas tight encapsulation around the specimen before placing it in the KBr salt bed for further heating (**Fig.1a I**). The heating can be divided into two segments: i) salt pre-melting and ii) salt post-melting. The gas-tight salt encapsulation protects the specimen from oxidation during salt pre-melting segment, whereas the post melting oxidation protection is achieved because the specimen is submerged in molten salt, and a barrier is formed between the ambient air and the sample (**Fig.1a II**). After cooling, the sample is recovered by dissolving the salt with water (**Fig.1a III**). Free powder is obtained by boiling the samples in water followed by filtration (**Fig.1a IV**). **Fig.1a** shows the step-wise schematic of MS^3 process.

Fig.1b-e gives an overview of the possibility of synthesizing and sintering a wide range of materials in air. The process was used to synthesize binary carbides like TiC (**Fig.1b**), ternary carbides (Ti_3SiC_2, **Fig.1c**), nitrides (Ti_2AlN, **Fig.1d**) and borides (MoAlB, **Fig.1e**). The process was also used to sinter metal parts to high density or with controlled porosity. Respective XRD (**Fig.1b-e**) shows that highly pure phases were obtained.

TiC (predominantly single phase XRD) ceramic powders were synthesized. The synthesized Ti_3SiC_2 was 96 wt. % (Rietveld refinement of XRD data) pure and did not have any oxide second phase, only traces of TiC were detected by XRD (see **Fig.S1,S2** and **Table S1** for details of phase evolution of sintered Ti_3SiC_2 from synthesized powder). All the steps of the MS^3 process are similar irrespective of the batch size. The powder was free flowing after washing the salt content and did not need any extra milling (**Fig.S3**). However, an optional milling step can be adopted to further tailor the particle size. Highly pure (XRD) Ti_2AlN was also synthesized by MS^3 process. Nitrogen containing compounds normally need a N_2 partial pressure to prevent the outgassing of nitrogen from the material. MoAlB, was synthesized with MoB_2 as the second phase for the proof of concept. The powder morphology and the characteristic layered structure of damage tolerant phases are shown in **Fig.1c-e**. It is noteworthy that none of the material has oxides as the secondary phases as detected by XRD.

As MS^3 impedes oxidation of non-oxide materials; the sintering of Ti was also carried out using this process. MS^3 sintered Ti was polished and the characteristic luster of metal is shown in **Fig.1f**. The density of the sintered titanium was measured to be 4.27 g/cm^3 (94% relative density). It was also possible to produce Ti with 70% porosity using KBr as water soluble space holder particles. **Fig.1f,g** shows the microstructure of the sintered dense and porous titanium respectively, revealing no second phase apart from pores. The sintering of titanium both in dense and porous forms has been achieved in an air furnace.

The fact that the encapsulation of KBr acts as a barrier between the atmosphere and the sample in the pre-salt melting stage is demonstrated by measuring density and gas permeability of a 4 mm thick KBr disk cold pressed at room temperature. The KBr disk was pressed uni-axially at 200 MPa and then iso-statically at 300 MPa. The geometrical density was 98% of the theoretical value. The permeability values of helium and air through the KBr disk were found to be 1.4E-7 hPa.dm^3.s^{-1} at room temperature, which suggests that the encapsulation of the sample by KBr is gas tight. Hence, a cladding thickness of 4mm is enough to isolate the sample material from ambient oxygen. Differential scanning calorimetry (DSC, **Fig.2a,c**) and thermo-gravimetric (TG, **Fig.2b,d**) analysis were performed in air on specimens with and without encapsulation of KBr (**Fig.2**) to corroborate the absence of oxidation by MS^3. Since the elemental precursors (Ti, Si, and C) will have their respective oxidation peaks and it would make the analysis cumbersome, pre-synthesized Ti_3SiC_2 powder was used for thermal analysis to demonstrate the possibility of MS^3 process in air. The specimens without encapsulation showed severe oxidation and an obvious increase in mass, whereas the encapsulated specimen showed a slight oxidation. The exothermic peak in **Fig.2a,c** below 740^{o}C denotes the oxidation of Ti_3SiC_2 and Ti respectively (red curve). An initial oxidation is observed in case of encapsulated Ti_3SiC_2 and Ti (blue curve). The oxidation ceased after the melting point of KBr which is denoted by an endothermic peak at 740^{o}C (black curve). **Fig.2.b,d** show only initial mass gain of encapsulated samples due to oxidation (blue curve). Further heating results in mass loss in case of encapsulated samples due to the evaporation of salt. The mass loss trend is similar when only KBr is heated (black curve), whereas samples of Ti_3SiC_2 or Ti (**Fig.2b,d**) heated without an encapsulation suffer only mass gain due to oxidation (red curve). A chemical analysis for the estimation of oxygen was performed on Ti_3SiC_2 powder after washing it with hot distilled water for five times. The oxygen content was found to be 1.53 wt. % as compared to the initial oxygen content of 0.36 wt. %. The oxygen content is comparable to commercially available Ti_3SiC_2 MAX phase (1.25 wt. % O) whereas the phase purity is higher in case of the presently synthesized Ti_3SiC_2. The initial oxidation, results in a minute oxygen uptake as shown by the moderate increase in oxygen content of the sintered Ti (0.49 wt. % O) as compared to the starting Ti powder (0.32 wt. % O). The oxygen content of the initial powder and the salt used for the sintering is decisive to the final oxygen content of the component. A low temperature melting salt composition for MS^3 can result in even lower oxygen uptake. The oxygen uptake of Ti after heat treating (1000^{o}C/4hrs) already dense Ti plate in LiCl, and $CaCl_2$ was measured to be 0.48 and 0.47 wt. % respectively. Hence the process

(MS^3) is also flexible in terms of the selection of the salt system (see **Table S2** for details of oxygen content).

Potassium halide salts (KCl, KBr) are ductile at room temperature, hence they can be used to obtain a gas tight encapsulation for protection against oxidation. Nevertheless, the maximal processing temperature of a material is limited by the boiling points of the salt used (KCl or KBr). The evaporation of the salt above its boiling point may lead to the exposure of the underneath materials to ambient oxygen, resulting in severe oxidation. The eutectic temperature of a 2 or 3 component salt system offers the possibility to have a very low melting point as in case of KCl-LiCl-NaCl. The synthesis of Ti_3SiC_2 was carried out with KCl-LiCl-NaCl and $CaCl_2$ under the same conditions as with KBr (**Fig.S4**). The prime criteria of selecting a salt system are to be cost effective, easily available and water-soluble. Further consideration of vapor pressure, diffusivity of the reactants in the molten salt and reactivity of the salt with the material also needs to be taken into account.

MS^3 is a molten salt based process, hence inter-diffusion of the atomic species occurs forming the targeted reaction product by dissolution-precipitation[21]. The molten salt provides a medium for the transport of metals in the form of ions. An oxidant has a major role to play for the diffusion of metal ions into the molten salt[22]. Since no oxidant was added to KBr melt, it is believed that small amounts of dissolved oxygen in the forms of superoxide and peroxide may have assisted the transfer of both metal ion and electron by hoping mechanism[23]. **Fig.3a,b** shows the interaction zone of the material with salt in the cross-section of alumina crucible. A diffusion sphere is observed around the Ti plate in the solidified salt whereas there is none in case of Ti_3SiC_2, suggesting negligible mass loss from the sample in that case. **Fig.3c** shows the presence of second-phase precipitates in the KBr solidified matrix.[24] EDS scans (**Fig.3e,f,g**) near the interface (**Fig.3d**) confirm that the globular dark grey inclusions (**Fig.3c**) are Ti metal. This difference is probably because in the case of pure metals, no reaction partners are locally available for producing a new phase and dissolved metal ions can thus diffuse across longer distances through the molten salt. As a result, the synthesis temperature is reduced; Ti_3SiC_2 is typically formed by solid state reaction above 1350°C whereas by MS^3 the required temperature is 1250°C. It also depends on the precursors used for the synthesis. The synthesis temperature is lowered by 100°C in case of MS^3, and this decrease was observed for other MAX phases as well. **Fig.4** shows the purity of all MAX phases synthesized by MS^3 and other processing routes along with the attributes (lower synthesis temperature and higher purity) of MS^3 as compared to conventional processing routes.

MS^3 process cuts down the milling step required to pulverize dense blocks into micron-sized powder for further fabrication of complex shapes by slip casting[25], tape casting[26], injection moulding[27], additive manufacturing[28] or any other powder metallurgical operations. MS^3 process opens up an avenue for cheap synthesis of high purity MAX phases/non-oxide ceramics and the sintering of metals in air. The process developed herein does not need any expensive equipment like vacuum furnace, hot isostatic pressing, spark plasma sintering furnace or atmosphere-controlled furnace which requires an uninterrupted flow of argon or any inert gas to prevent oxidation [4,29–34]. MS^3 enables us to obtain free powder by just dissolving the heat-treated samples in water. The solubility of KBr in water is 1020 g/L at 100°C [35]. Hence production of 1 kg of MAX phase would need approximately 1 L of boiling water to dissolve the salt content. Further washing to ensure the complete removal of the salt which requires an extra 2 L of water. An average estimate of 3 L of water is required to produce 1 kg of MAX phase. The salt recovered from the saline water can be reused in MS^3 process.

The use of molten salt further reduces the synthesis temperature resulting in additional cost reduction. The milling of MAX phase imposes safety threats because of the energy intensive communition process which might result in the self-ignition of MAX phase. The sintering of titanium in air is a demonstration of the fact that metals can be sintered in air without oxidation. The cost of powder metallurgical component is mainly due to the heat treatment. MS^3 makes the high temperature processing step cheaper and provides a possibility for the fabrication of more economical components.

MS^3 process can be industrially scaled-up by simply increasing the batch size or making the process continuous. Successful trials have been made with a batch size of 500 g for the powder production of Ti_3SiC_2 MAX phase. The sintering of metals via powder metallurgy is also industrially scalable by modifying the process. MS^3 can be regarded as an environmentally friendly process because the salts when used in the proper temperature window are not volatile and harmful. Moreover, recycling of the salt is also possible, further making the process sustainable. MS^3 opens therefore a new direction for the synthesis of non-oxide ceramic powders and the sintering of metals in air.

Methods:

Synthesis of Ti_3SiC_2

Elemental powders of Ti, Si, Al (>99.5%, Alfa Aesar, -325 mesh), graphite (Alfa Aesar, 2 µm) were mixed in the stoichiometric molar ratio of 3:1:0.2:2. KBr (Alfa Aesar) in 1:1 weight ratio was added to the resulting mix. The mixture was milled in a slurry form with ethanol and zirconia milling balls (Φ 5mm) for 24 hours in a multidirectional mixer (Turbula, WAB, Switzerland). The resulting slurry was dried in a vertical column rotary evaporator at 60°C. The dried powder was sieved in 300 µm sieve to homogenize the agglomerate size. The dried powder was uniaxially pressed in a steel die under a pressure of 200 MPa followed by isostatic pressing at 300 MPa. The consolidated specimen was further encapsulated with KBr (Fig.1a I) and placed in a KBr salt bed inside a cylindrical alumina crucible covered with an alumina lid without any sealant. The KBr salt bed supplied with enough salt after melting to completely submerge the specimen with molten salt for protection against ambient oxidizing atmosphere. The chemical composition of the protective encapsulation and the salt bed should always be the same to avoid the formation of inhomogeneous eutectic at the interface of salt bed and the encapsulated material. The encapsulation of KBr was achieved by re-pressing the already consolidated green sample in a larger steel die with KBr on all sides of the green sample. The samples were heated in a resistance furnace (Nabertherm, Germany) to a temperature of 800°C at a rate of 20°C/min and further heated to 1250°C at a rate of 5°C/min with a soaking time of 1 hour at 1250°C (Fig.1a II). The MAX phase powders were obtained after washing with distilled water repeatedly to dissolve the salt (Fig.1a III) followed by filtration (Fig.1a IV). The phase purity was identified by X-ray diffraction (XRD, D4 Bruker, Germany). Rietveld refinement (Topas) was performed to obtain the purity of the synthesized powder. The addition of 0.2 mol. of Al resulted in highly pure grade of Ti_3SiC_2. The washed

Ti_3SiC_2 powder was milled with ethanol and zirconia milling balls (Φ 2mm) on a roller bench at a rotation speed of 100 rpm for 24 hours. Roller bench milling was used to break down the soft agglomerates formed during the MS^3 process and not reduce the primary size. The morphology of free powder was observed using a scanning electron microscope (SEM, Crossbeam 540, Carl Zeiss AG, Oberkochen, Germany). Similarly, other MAX phase powders were also synthesized, and the phases were identified by XRD, as shown in Fig. 2. The analysis of the salt-material interface was done from cross sections of the alumina crucible after MS^3 process. Epoxy resin was poured to secure the solidified salt and prevent chipping off salt particles during dry cutting of the crucible with a diamond cutting wire. The cross section was ground successively with finer SiC paper. Since salt is soluble in water, polishing with diamond suspension was not possible. Localized areas near salt-sample interface were polished by ion beam (IM400, Hitachi) for further investigation by SEM.

Synthesis of Ti_2AlN

Elemental powders of Ti, Al (Alfa Aesar, -325 mesh) and TiN (d_{50} 10µm, H.C. Stark) were mixed in the stoichiometric molar ratio of 1:1:1. The same procedure for synthesis and characterization was followed as for Ti_3SiC_2.

Synthesis of MoAlB

Elemental powders of Mo, Al (Alfa Aesar, -325 mesh) and AlB_2 (Rboschco, China, d_{50} 10 µm) were mixed in the stoichiometric molar ratio of 2:1:1. The same procedure for synthesis and characterization was followed as for Ti_3SiC_2.

Ti_3SiC_2, Ti_2AlN and MoAlB were synthesized at 1250°C as a proof of concept to demonstrate the possibility of the synthesis of ternary carbides, nitride and borides in air by the proposed MS^3 process. Further optimization of temperature and composition of starting precursors needs to be done to obtain a pure phase material at a temperature as low as possible.

Sintering of dense Ti

Ti powder (purity: 99.95 %; powder size: below 45 μm, Alfa Aesar) was uniaxially pressed in die (Ø 13 mm) at a pressure of 200 MPa. The green cylindrical Ti sample was re-pressed at a pressure of 200 MPa in a die (Ø 20 mm) with KBr on top and bottom of the green Ti cylinder to have a gas-tight encapsulation of KBr around the green Ti. The encapsulated titanium specimen with KBr was placed in a KBr salt bed. The heating was done at a rate of 5°C/min till 1200°C, with a holding time of 1 hour at 1200°C. The sintered titanium was recovered by washing in water. The sintered pellet was ground on all sides and polished with diamond slurry for microscopy. The microstructure of the polished surface was observed using a polarized light microscope (MeF4, Leica).

Fabrication of porous Ti

Porous titanium samples were sintered by PM process. Commercially available titanium powder (purity: 99.95 %; powder size: below 45 μm, Alfa Aesar) was an initial material in PM process. Ti powder was mixed with KBr powder. KBr powder was used as space holder because it doesn’t react with Ti and it is water soluble. Moreover, KBr was used for protecting the sample from oxidation during the sintering process. 70 vol. % of KBr was mixed with Ti powder in ethanol and then dried at 60°C. The dried powder was consolidated uni-axially at 200 MPa. The pressed pellet was repressed in a steel die with a larger diameter to encapsulate with KBr. The sintering was carried out in air in a resistance heated furnace with a heating rate of 20°C/min up to 1200°C with a dwell time of 1hr followed by rapid cooling. The porous titanium was recovered by washing the salt with water and boiling the sample in water to dissolve all the space holder (KBr) particles. The porous sample was ground on all sides and further polished using diamond slurry. The microstructure of the polished surface was observed using scanning electron microscope (SEM, TM3000, Hitachi, Japan)

Thermal analysis

Differential scanning calorimetry and thermo-gravimetric analysis (DSC-TG, Netzsch) were performed on synthesized MAX phase (Ti_3SiC_2) and Ti powder with and without encapsulation of KBr in an alumina crucible. The furnace was heated at a rate of 20°C/min to a temperature of 1300°C followed by rapid cooling.

Oxygen analysis

Since the process is carried out in air, oxygen uptakes were measured. Synthesized Ti_3SiC_2 powder and sintered Ti pellet were analyzed for the oxygen content. The oxygen was determined by hot gas extraction using a Leco TCH 600 instrument. Sample amounts of 30 to 250 mg were analyzed at least in triplicate. The sample was packed in tin capsules and nickel baskets prior to heating in a carbon crucible.

Data availability statement

The authors confirm that all the data generated and necessary to interpret the scientific findings are available within the paper. Extra data can be obtained from the corresponding authors on request.

Acknowledgement

This work has been funded by the Germany’s Federal Ministry of Education and Research (“Bundesministerium für Bildung und Forschung”) under the MAXCOM project (03SF0534).

Contributions

A.D. proposed the original idea and carried out the experiments, J.G. supervised A.D., all authors contributed to the discussion of the results and the writing of the manuscript.

Competing interest

The authors declare no competing interest.

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References

1. German, R. *Sintering: From Empirical Observations to Scientific Principles*. *Sintering: From Empirical Observations to Scientific Principles* (Elsevier, 2014). doi:10.1016/C2012-0-00717-X
2. Rahaman, M. *Sintering of Ceramics*. (CRC Press, 2007). doi:10.1201/b15869
3. Barsoum, M. W. & El-Raghy, T. Synthesis and characterization of a remarkable ceramic: Ti3SiC2. *J. Am. Ceram. Soc.* **79,** 1953–1956 (1996).

4. Barsoum, M. W., El-Raghy, T. & Ali, M. Processing and characterization of Ti2AlC, Ti2AlN, and Ti2AlC0.5N0.5. *Metall. Mater. Trans. A* **31,** 1857–1865 (2000).

5. Kota, S. *et al.* Synthesis and Characterization of an Alumina Forming Nanolaminated Boride: MoAlB. *Sci. Rep.* **6,** 26475 (2016).

6. Barsoum, M. W. *MAX Phases: Properties of Machinable Ternary Carbides and Nitrides*. (Wiley-VCH Verlag GmbH & Co. KGaA, 2013). doi:10.1002/9783527654581

7. Boyer, R. R. An overview on the use of titanium in the aerospace industry. *Mater. Sci. Eng. A* **213,** 103–114 (1996).

8. Singh, R., Lee, P. D., Dashwood, R. J. & Lindley, T. C. Titanium foams for biomedical applications: a review. *Mater. Technol.* **25,** 127–136 (2010).

9. Qian, M., Schaffer, G. B. & Bettles, C. J. in *Sintering of Advanced Materials* 324–355 (Elsevier, 2010). doi:10.1533/9781845699949.3.324

10. Froes, F. H., Eylon, D., Eichelman, G. E. & Burte, H. M. Developments in Titanium Powder Metallurgy. *JOM* **32,** 47–54 (1980).

11. Dunand, D. C. Processing of Titanium Foams. *Adv. Eng. Mater.* **6,** 369–376 (2004).

12. Ryan, G. E., Pandit, A. S. & Apatsidis, D. P. Porous titanium scaffolds fabricated using a rapid prototyping and powder metallurgy technique. *Biomaterials* **29,** 3625–3635 (2008).

13. Xue, W., Krishna, B. V., Bandyopadhyay, A. & Bose, S. Processing and biocompatibility evaluation of laser processed porous titanium. *Acta Biomater.* **3,** 1007–1018 (2007).

14. Davis, N. G., Teisen, J., Schuh, C. & Dunand, D. C. Solid-state foaming of titanium by superplastic expansion of argon-filled pores. *J. Mater. Res.* **16,** 1508–1519 (2001).

15. Torres, Y., Pavón, J. J. & Rodríguez, J. A. Processing and characterization of porous titanium for implants by using NaCl as space holder. *J. Mater. Process. Technol.* **212,** 1061–1069 (2012).

16. Oh, I.-H., Nomura, N., Masahashi, N. & Hanada, S. Mechanical properties of porous titanium compacts prepared by powder sintering. *Scr. Mater.* **49,** 1197–1202 (2003).

17. Kimura, T. in *Advances in Ceramics - Synthesis and Characterization, Processing and Specific Applications* (InTech, 2011). doi:10.5772/20472

18. Gogotsi, Y. *Materials Science of Carbides, Nitrides and Borides*. (Springer Netherlands, 1999). doi:10.1007/978-94-011-4562-6

19. Parker, E. R., Pask, J. A., Washburn, J., Gorum, A. E. & Luhman, W. Ductile ceramics — A high temperature possibility. *JOM* **10,** 351–353 (1958).

20. Gorum, A. E., Parker, E. R. & Pask, J. A. Effect of surface conditions on room temperature ductility of ionic crystals. *J. Amer. Ceram. Soc.* **41,** 161–164 (1958).

21. Yoon, K. H., Cho, Y. S. & Kang, D. H. Molten salt synthesis of lead-based relaxors. *J. Mater. Sci.* **33,** 2977–2984 (1998).

22. Wang, Q. *et al.* The Equilibrium Between Titanium Ions and Titanium Metal in NaCl-KCl Equimolar Molten Salt. *Metall. Mater. Trans. B* **44,** 906–913 (2013).

23. Selloni, A., Carnevali, P., Car, R. & Parrinello, M. Localization, hopping, and diffusion of electrons in molten salts. *Phys. Rev. Lett.* **59,** 823–826 (1987).

24. Liu, X., Fechler, N. & Antonietti, M. Salt melt synthesis of ceramics, semiconductors and carbon nanostructures. *Chem. Soc. Rev.* **42,** 8237 (2013).

25. Hu, C., Sakka, Y., Tanaka, H., Nishimura, T. & Grasso, S. Fabrication of Textured Nb4AlC3 Ceramic by Slip Casting in a Strong Magnetic Field and Spark Plasma Sintering. *J. Am. Ceram. Soc.* **94,** 410–415 (2011).

26. Murugaiah, A. *et al.* Tape Casting, Pressureless Sintering, and Grain Growth in Ti $_3$ SiC $_2$ Compacts. *J. Am. Ceram. Soc.* **87,** 550–556 (2004).

27. Gonzalez-Julian, J., Classen, L., Bram, M., Vaßen, R. & Guillon, O. Near Net Shaping of Monolithic and Composite MAX Phases by Injection Molding. *J. Am. Ceram. Soc.* **99,** 3210–3213 (2016).

28. Nan, B., Yin, X., Zhang, L. & Cheng, L. Three-Dimensional Printing of Ti3SiC2-Based Ceramics. *J. Am. Ceram. Soc.* **94,** 969–972 (2011).

29. Tian, W. B., Wang, P. L., Kan, Y. M. & Zhang, G. J. Cr2AlC powders prepared by molten salt method. *J. Alloys Compd.* **461,** L5–L10 (2008).

30. Guo, X., Wang, J., Yang, S., Gao, L. & Qian, B. Preparation of Ti3SiC2 powders by the molten salt method. *Mater. Lett.* **111,** 211–213 (2013).

31. Tzenov, N. V & Barsoum, M. W. Synthesis and Characterization of Ti3AlC2. *J. Am. Ceram. Soc.* **83,** 825–832 (2004).

32. Gao, N. F., Li, J. T., Zhang, D. & Miyamoto, Y. Rapid synthesis of dense Ti3SiC2 by spark plasma sintering. *J. Eur. Ceram. Soc.* **22,** 2365–2370 (2002).

33. Zhang, Z. F., Sun, Z. M. & Hashimoto, H. Rapid synthesis of ternary carbide Ti3SiC2 through pulse-discharge sintering technique from Ti/Si/TiC powders. *Metall. Mater. Trans. A* **33,** 3321–3328 (2002).

34. Zhou, Y. & Sun, Z. Temperature fluctuation/hot pressing synthesis of Ti3SiC2. *J. Mater. Sci.* **35,** 4343–4346 (2000).

35. Pinho, S. . & Macedo, E. . Experimental measurement and modelling of KBr solubility in water, methanol, ethanol, and its binary mixed solvents at different temperatures. *J. Chem. Thermodyn.* **34,** 337–360 (2002).

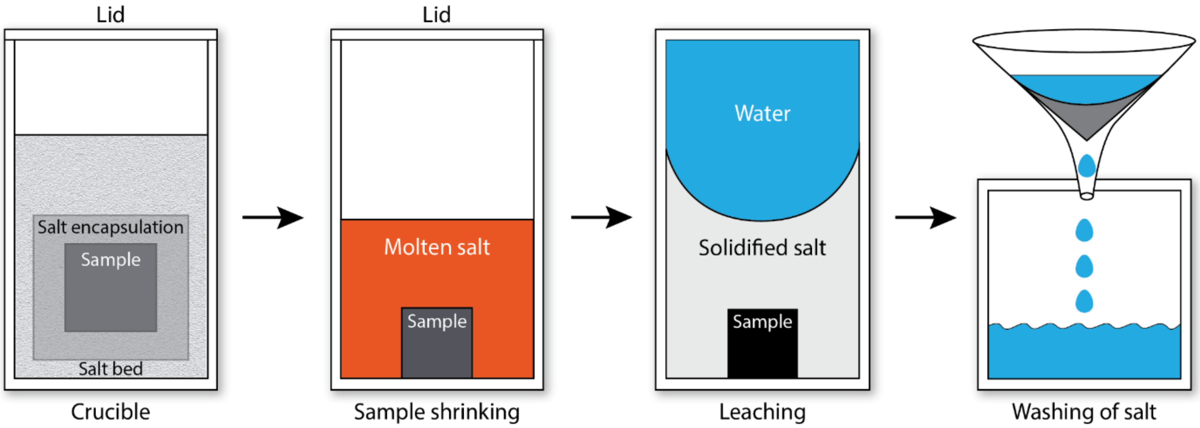

Figure 1. Schematic of molten salt shielded synthesis (MS^3*)*

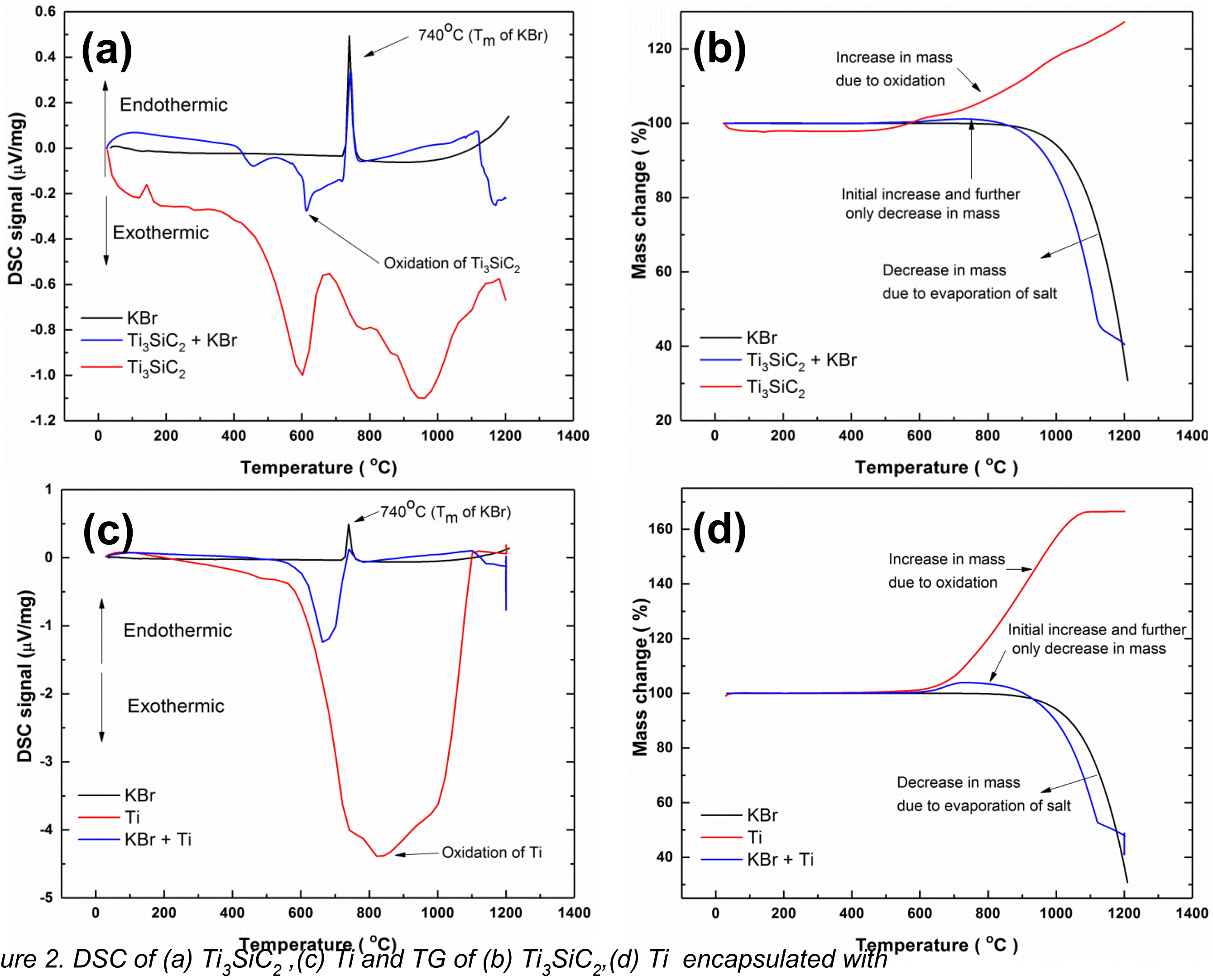

Figure 2. DSC of (a) Ti_3SiC_2 ,(c) Ti and TG of (b) Ti_3SiC_2,(d) Ti encapsulated with KBr conducted in air, oxygen uptake of (e) $Ti_3SiAl_{0.2}C_2$ during synthesis, (f) Ti during sintering, (g) dense Ti plate in different salt systems

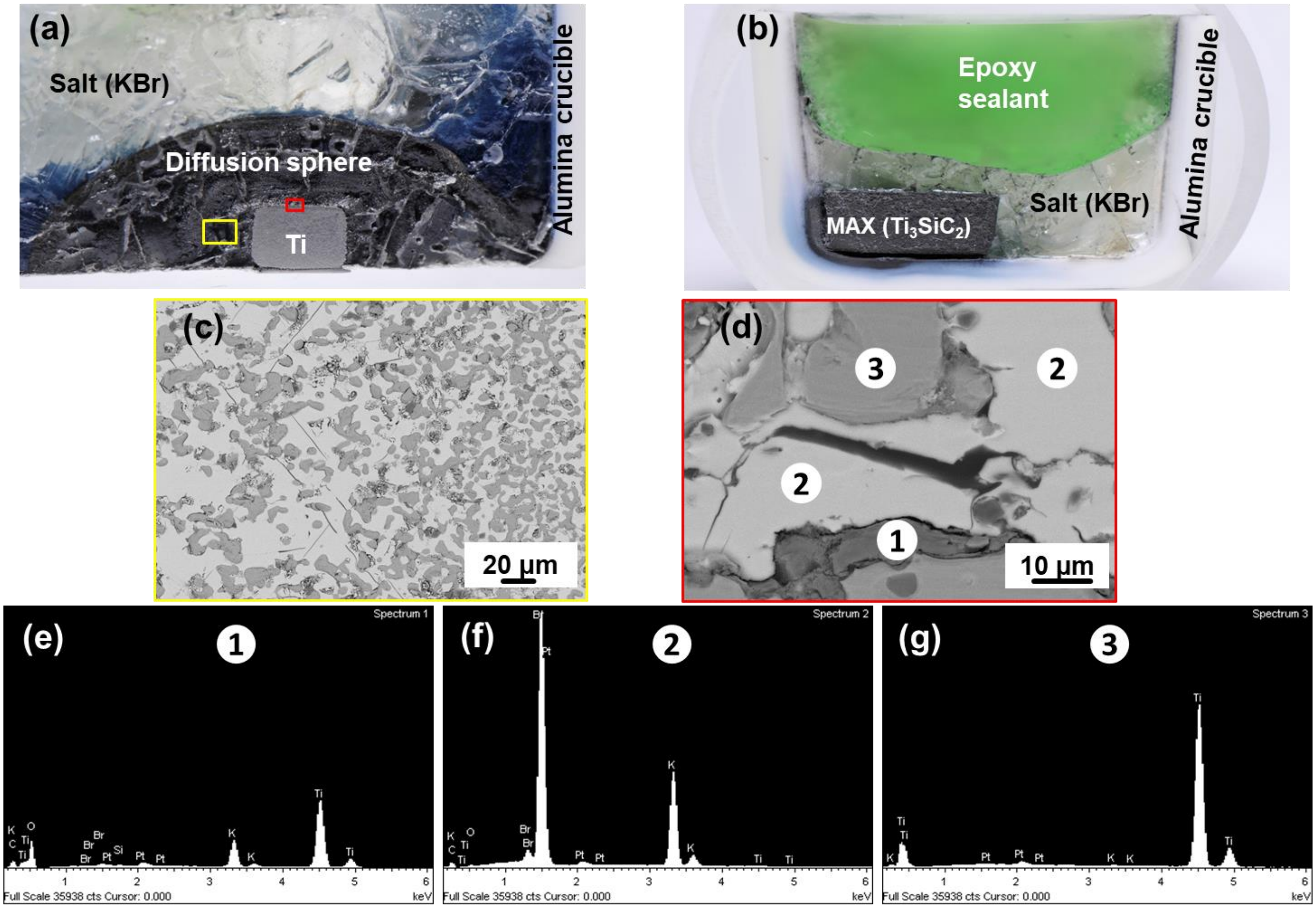

Figure 3. Cross-section of alumina crucible with (a) Ti metal and (b) Ti_3SiC_2 embedded in salt (KBr), (c) back-scattered image of the area corresponding to yellow rectangle in (a), (d) back-scattered image of the area corresponding with red rectangle in (a), (e,f,g) EDS scans of corresponding points in (d)

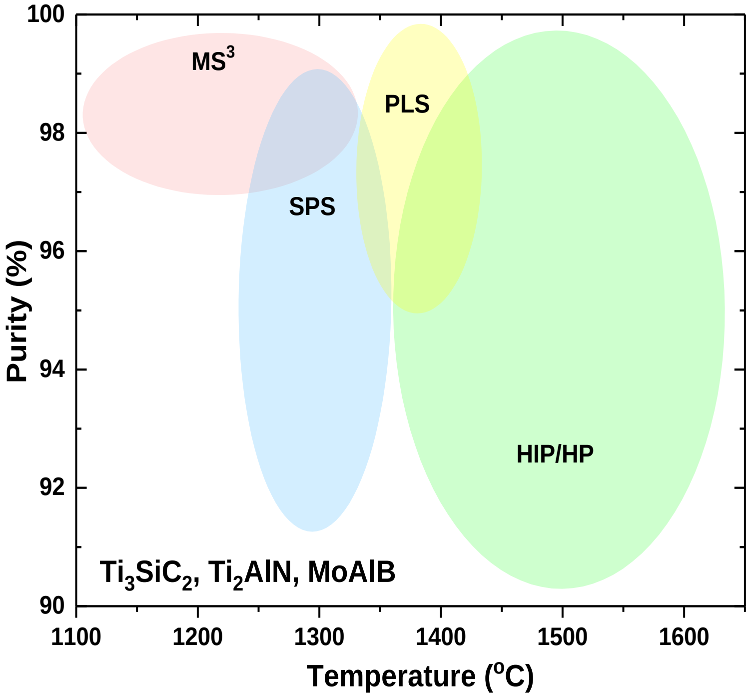

Figure 4. Purity vs. synthesis temperature of various MAX phases by different processing routes: Spark Plasma Sintering (SPS), pressure-less sintering (PLS) , Hot Isostatic Pressing/Hot Pressing (HIP/HP)