albedo regions that suggest surface materials may be similar to shergottite meteorites³. Analysis of depressions ("ghost craters") in the lowlands indicate that the basement there is of Noachian age¹⁹, like the southern highlands, so it is plausible that the entire planet had an ancient basaltic crust that was altered where water ponded. This hypothesis may also explain the absence of andesite among martian meteorites, because either this material might exist only as weathering rinds or more thoroughly weathered rocks might not survive impact ejection. McSween and Keil²⁰ compared compositions of martian soils and concluded that the global dust formed by weathering of basalts rather than andesites. Although the existence of andesite on Mars remains a viable hypothesis, linear deconvolution of martian thermal infrared spectra, spectral matching with terrestrial volcanic rocks, and the geographic distribution of the Surface Type 2 spectrum suggest that martian northern lowland plains materials are basalts weathered under submarine conditions and/or sediments derived from weathered basalt and deposited in this basin. □

Methods

Linear deconvolutions using three spectral end-member sets¹² (refs 1, 6 and this study) were run for each martian surface spectrum. Algorithm outputs include a best-fit model spectrum for each martian surface spectrum, percentage of each mineral end-member used, and an r.m.s. error value (average error over the entire spectrum). The r.m.s. value indicates goodness of fit for a particular model iteration for the same martian spectrum, rather than a comparison between fits of the two martian spectra. Spectral fitting for both methods was constrained to 1,280–400 cm⁻¹, although TES data cover the wavenumber range of 1650–200 cm⁻¹. The atmospheric correction used to derive the TES surface spectra used in this study did not include the high wavenumber range of TES data owing to numerous water vapour and minor CO₂ features. Furthermore, there are no fundamental silicate features in the 1,650–1,400 cm⁻¹ region. Similar to ref. 1 the deconvolution algorithm also did not use the 400–200 cm⁻¹ spectral range. Residual atmospheric water vapour rotational bands are apparent in both the martian surface spectra as well as in the Arizona State University (ASU) mineral library end-member spectra. This restricted wavenumber range prevents the deconvolution algorithm from attempting to fit water vapour features instead of surface mineralogy.

Accurate deconvolution is largely dependent on spectral end-member sets representing an appropriate range of compositions in the mixture. The high-silica glass phase (77.9% SiO₂, 12.6% Al₂O₃, 3.90% Na₂O, 5.67% K₂O) not included in the end-member set used in this study has been interpreted^{15,6} as representing a primary volcanic glass. High-silica volcanic glasses are often not present in high abundances in unweathered basalts, compared to andesites, and typically alter to clays in a weathering environment. For these reasons, we have excluded this volcanic glass phase in our end-member set that is designed to represent basalts and low-temperature aqueously altered basalts. K-feldspar is not included in the Hamilton *et al.*⁶ spectral end-member set as it is not typically found in unweathered basalt and andesite. K-feldspar is however included by Bandfield *et al.*¹ to represent possible mineralogies in a larger suite of igneous, metamorphic and sedimentary rock types and in this study as a possible alteration product¹³.

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Formation of tough interlocking microstructures in silicon nitride ceramics by dynamic ripening

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Ceramics based on Si₃N₄ have been comprehensively studied and are widely used in structural applications^{1,2}. The development of an interlocking microstructure of elongated grains is vital to ensure that this family of ceramics have good damage tolerance^{3,4}. Until now this has been accomplished by heating the appropriate powder compacts to temperatures above 1,700 °C for extended periods. This procedure involves a necessary step of controlling the size and population of seeds—added *ex situ* or formed *in situ*—to ensure selective grain growth^{5,6}. Here we report the very fast (within minutes) *in situ* formation of a tough interlocking microstructure in Si₃N₄-based ceramics. The microstructures are obtained by a dynamic ripening mechanism, an anisotropic Ostwald ripening process that results from the rapid heating rate. The resulting microstructures are uniform and reproducible in terms of grain size distribution and mechanical properties, and are easily tailored by manipulating the kinetics. This process is very efficient and opens up new possibilities to optimize mechanical properties and cost-effectively manufacture ceramics.

Sintering Si₃N₄-based ceramics is a complex process, during which densification, phase transformation and grain growth take place simultaneously. Therefore, it is not an easy task to clarify the mechanisms determining the rate of grain growth, for example. Research carried out during recent years indicates that the grain growth is dominated by an Ostwald ripening mechanism driven by the reduction of interface energy, that is, the smallest grains deriving from the precursor powder and early precipitates dissolve in the

liquid formed at high temperatures, and the appropriate constituents (ionic species and/or clusters) are transported in the liquid to larger grains where they re-precipitate. Efforts have thus been made to use this mechanism to form a tough interlocking microstructure of elongated grains by means of: (1) seeding; (2) varying the amount and composition of co-existing liquid; (3) stimulating the dissolution process by using fine-grained precursor powders; (4) controlling nucleation through phase transformation^{5,7,8}. Although it has been observed that under high nitrogen pressure a few grains grow extremely fast above 1,900 °C (refs 9, 10), and that the growth of anisotropic grains is directly related to the difference in solubility between small and large grains¹¹, it is generally accepted that growth of elongated grains is predominantly diffusion-controlled¹². This implies that extended holding at high temperature is a necessary requirement to develop a tough interlocking microstructure in any process that is based on such a principle of selective grain growth.

We have used a rapid consolidation technique, spark plasma sintering (SPS), to densify a variety of ceramic and powdered-metal materials. For Si₃N₄-based ceramics we have observed the densification and appropriate phase transformation during this process to occur within a narrow temperature interval and to be completed very rapidly, typically between 1,350 and 1,550 °C and within 1 to 2 min. The use of fast heating rates implies that: (1) formation of

unwanted crystalline intermediate phases can be avoided; (2) the grain growth in the low temperature region is suppressed; (3) the locally formed liquid is rapidly homogenized via the large capillary forces present between submicrometre and/or nano-sized grains. We obtained fully-dense compacts consisting of submicrometre-sized, nearly equiaxed, grains; this provided us with the opportunity to follow the grain growth taking place during subsequent heating and annealing at temperatures ranging from 1,600 to 1,800 °C.

The width and length of randomly selected equiaxed and elongated (when present) grains in a sample of β -sialon, a solid solution based on β -Si₃N₄, heated to temperatures ranging from 1,500 to 1,800 °C are given in Fig. 1a. These samples, which have an overall composition of Y_{0.096}Si_{1.663}Al_{0.222}O_{0.509}N_{2.196} and contain approximately 20 vol.% of an extra liquid/glassy phase, were heated at a rate of 200 °C min⁻¹ with no holding at final sintering temperature under an uniaxial pressure of 50 MPa. Corresponding data for isothermal grain growth at 1,600 °C are given in Fig. 1b. The insets show that the fracture toughness, as expected, increases with the formation of elongated grains. The microstructures of the samples sintered at 1,600 °C without and with 1 and 10 min holding times are shown in Fig. 2. It is very surprising that the anisotropic grain growth progresses so rapidly that the nearly equiaxed submicrometre-sized grains grow to well-developed elongated grains within 1 min. A tough interlocking microstructure was developed and every grain shows a clear tendency to develop elongated morphology. The grain growth process appears to be thermally activated, and for this particular composition the observed critical temperature is ~1,600 °C, because the samples prepared at 1,550 °C did not contain any elongated grains even after prolonged heat treatment at this temperature.

Similar fast grain growth has been observed in compacts of α -sialon, a solid solution based on α -Si₃N₄, both with stoichiometric compositions and with extra liquid phase added. For example, using α -Si₃N₄ as precursor powder, the stoichiometric ytterbium-stabilized α -sialon Yb_{0.35}Si_{9.75}Al_{2.25}O_{1.2}N_{14.8} was densified, without holding, at 1,700 and 1,750 °C under a pressure of 50 MPa by applying a heating rate of 200 °C min⁻¹. X-ray diffraction and SEM structural analyses revealed complete phase transformation in both cases, with the former preparation consisting of equiaxed submicrometre grains and the latter of elongated grains up to 10 μ m in length. The two materials showed similar hardness (22 GPa), but the latter is tougher than the former, with fracture toughness values of 3.5 and 5.5 MPa m^{1/2}, respectively. Using the same composition and otherwise identical experimental conditions but with a heating rate of 40 °C min⁻¹ yielded, at 1,750 °C, compacts containing equiaxed grains; see Fig. 3.

It is well known that the elongated growth takes place along the *c* direction of the unit cell of the α - and β -phases. It is commonly assumed that this is due to anisotropic interfacial energies. We ascribe the rapid grain growth described above to an anisotropic Ostwald ripening process that takes place dynamically—abbreviated as ‘dynamic ripening’. The difference between dynamic and steady-state Ostwald ripening is as follows. In the former case, owing to the fast heating rate applied, the chemical composition of the co-existing liquid phase deviates from that set by thermodynamic equilibrium. During the short time span when the liquid approaches equilibrium state, the dissolution of small grains is promoted so as to produce a momentarily supersaturated liquid, that is, the liquid is supplied with the appropriate constituents in a very fast and efficient way. The supersaturated liquid immediately responds by preferentially depositing these constituents onto the crystallographic surfaces that will most easily accommodate them. After this first stage of very fast dissolution of small grains the growth rate will decrease and finally the steady-state Ostwald ripening mechanism will govern the growth. The evolution of the microstructures shown in Fig. 2 with time is thus interpreted in

Figure 1 Width and length of randomly selected equiaxed and elongated (when present) β -sialon grains. **a**, Samples heated to temperatures ranging from 1,500 to 1,800 °C using a heating rate of 200 °C min⁻¹. **b**, Samples isothermally heated at 1,600 °C. The insets show the variation of the fracture toughness (K_{IC}) with the sintering temperature and holding time, respectively. We note the extremely fast formation of elongated grains and the evolution of the fracture toughness with the formation of elongated grains.

Figure 2 Scanning electron microscopy pictures of fully dense β -sialon ceramic sintered at 1,600 °C. **a**, Sample sintered without any holding time at 1,600 °C. **b**, Sample sintered with a holding of 1 min at 1,600 °C. **c**, Sample sintered with a holding of 10 min at 1,600 °C. It can also be noted that the grain size distribution formed in our experiments is

much more narrow than that obtained by the techniques based on the concept of selective grain growth. A more detailed description of the evolution of the microstructure with the holding time and sintering temperature is given in the Supplementary Information.

terms of the conditions allowing the dynamic ripening process to take place, that is, when the liquid and solids present are thermodynamically far from their equilibrium state, dynamic ripening occurs at the very beginning of the annealing time, whereas a prolonged annealing time implies that the process is transformed from dynamic ripening to steady-state ripening.

α -Sialon ceramics with similar composition have been prepared previously, following the traditional method of selective grain growth. It was concluded that it is difficult to obtain a tough interlocking microstructure of elongated grains without seeding by using α - Si_3N_4 as precursor^{5,6}. As shown above, however, anisotropic grain growth, and hence also tough interlocking microstructures of α -sialon ceramics, can be achieved by using fast heating rates without any seeding.

The use of fast heating rates is essential for obtaining the required elongated grains because slow heating ($40^\circ\text{C min}^{-1}$), a heating rate typically used in conventional hot-pressing of Si_3N_4 -based ceramics, did not yield any elongated grains, that is, the dynamic

dissolution and re-precipitation state described above is never established. We have also succeeded so far in producing such tough interlocking microstructures in β - Si_3N_4 and O-sialon ceramics, using a processing concept similar to that described above, which suggests that improved microstructures also can be achieved in other ceramic systems that are produced via a liquid-phase sintering mechanism. □

Methods

Preparation and characterization

See Supplementary Information.

Compacting

The samples were sintered in vacuum in an SPS apparatus, Dr. Sinter 2050 (Sumitomo Coal Mining). The powder precursors were loaded in cylindrical carbon dies with an inner diameter of 20 mm. The samples were heated via a pulsed d.c. current that passes through the pressure die, that is, the pressure die also acts as a heating source and this arrangement allows the use of very fast heating rates (up to $600^\circ\text{C min}^{-1}$). The temperature was automatically raised to 600 °C over a period of 3 min, and from this point and onwards it was monitored and regulated by an optical pyrometer focused on the surface of the die. A heating rate of $200^\circ\text{C min}^{-1}$ was used if not otherwise stated, and a uniaxial pressure of 50 MPa was applied from the start to the end of the sintering cycle. No holding time was applied, if not otherwise stated. The set-up allows a cooling rate of about $400^\circ\text{C min}^{-1}$ in the temperature range 1,800–1,000 °C.

An inherent property of the SPS process is that the sample is exposed to a higher temperature than the recorded one. The size of this temperature difference depends strongly on the shape of the die and also on the density, electrical and thermal conductivity of the die and sample, respectively, the pressure applied, the effectiveness of used heating shields, and so on. The temperature difference between the inner part of the sample and the surface of the die has in the present case been estimated from the melting behaviour of pieces of Pt-wires embedded in Si_3N_4 and BN powder compacts that were heated to temperatures ranging from 1,500 to 1,750 °C with no holding time at the final temperature and using a heating rate of 200 and $40^\circ\text{C min}^{-1}$, respectively. These experiments clearly suggest that in the present case the temperature difference between the surface of the die (recorded temperature) and the interior of the sample is not larger than 75 °C and that this difference is of the same order independently of the heating rate used. Further details concerning these experiments are in the Supplementary Information.

Determination of grain size

Sintered compacts of the β -sialon samples were polished down to a 1- μm finish and chemically etched in a molten mixture of KOH and KCl to expose grain boundaries. SEM pictures with fixed magnification of five randomly selected areas of each sample were recorded. From each picture ten grains with their elongated direction parallel or almost parallel to the polished surface were randomly selected and their width and length were measured. The average values of the widths and lengths of the measured grains are presented in Fig. 1.

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Figure 3 Scanning electron microscopy pictures of fractured surfaces of an α -sialon ceramic with a stoichiometric composition of $\text{Yb}_{0.35}\text{Si}_{9.75}\text{Al}_{2.25}\text{O}_{1.2}\text{N}_{14.8}$ heated to 1,750 °C. **a**, Sample heated using a heating rate of $200^\circ\text{C min}^{-1}$. **b**, Sample heated using a heating rate of $40^\circ\text{C min}^{-1}$. We note that the use of a high heating rate gives rise to the formation of elongated grains, whereas a slow heating rate yields equiaxed grains.

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Discrete stages in the solvation and ionization of hydrogen chloride adsorbed on ice particles

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Ionization and dissociation reactions play a fundamental role in aqueous chemistry. A basic and well-understood example is the reaction between hydrogen chloride (HCl) and water to form chloride ions (Cl^-) and hydrated protons (H_3O^+ or H_5O_2^+). This acid ionization process also occurs in small water clusters^{1–4} and on ice surfaces^{5–17}, and recent attention has focused on the mechanism of this reaction in confined-water media and the extent of solvation needed for it to proceed^{1–4,9,15–17}. In fact, the transformation of HCl adsorbed on ice surfaces from a predominantly molecular form to ionic species during heating from 50 to 140 K has been observed^{8,13,14}. But the molecular details of this process remain poorly understood. Here we report infrared transmission spectroscopic signatures of distinct stages in the solvation and ionization of HCl adsorbed on ice nanoparticles kept at progressively higher temperatures. By using Monte Carlo and *ab initio* simulations to interpret the spectra, we are able to identify slightly stretched HCl molecules, strongly stretched molecules on the verge of ionization, contact ion pairs comprising H_3O^+ and Cl^- , and an ionic surface phase rich in Zundel ions, H_5O_2^+ .

Our experiments focused on the Fourier-transform infrared (FTIR) transmission spectroscopy of HCl adsorbate on ice nanoparticles. Three-dimensional arrays of ice nanocrystals of a 12-nm

average diameter were deposited on the windows of the infrared cold-cluster cell¹⁸. Hydrogen chloride adsorbate was introduced by alternating the loading of ice particles with the loading of much smaller (~ 1 nm) clusters of HCl or DCl. These acid clusters vaporize in the range 50–65 K, giving HCl adsorbed on the surfaces of the ice nanocrystals within the array (with $\leq 30\%$ surface coverage). At least 4 samples each were prepared of HCl adsorbed on H_2O ice, DCl adsorbed on D_2O ice, and HCl adsorbed on D_2O ice. Consistent results were also obtained for HBr on H_2O . The main experimental results are the difference spectra obtained for acid-covered nanocrystals and bare nanocrystals prepared under similar conditions. This difference method eliminates the absorption bands associated with ice in the interior of the nanocrystal, and thus leaves the weaker bands due to adsorbed acids clearly visible.

The difference spectra of HCl adsorbed on H_2O and D_2O nanoparticles at 50 K reveal two distinct HCl bands with bandwidths of $\sim 150\text{ cm}^{-1}$ centred at 2,500 and $1,710\text{ cm}^{-1}$ (Fig. 1). The corresponding frequency shifts with respect to gaseous HCl are -385 and $-1,175\text{ cm}^{-1}$, suggesting that the bands correspond respectively to predominantly covalent, hydrogen-bonded molecules, and to strongly stretched molecules on the verge of ionization. Figure 2 shows analogous difference spectra for a fully deuterated system at 60, 80 and 90 K, with the changes in the spectrum with increasing temperature attributed to progressive ionization (see below). The spectra also exhibit a continuum absorption, which grows with temperature (Fig. 2, top panel)—this is a signature of the Zundel ion¹⁹.

To identify the surface adsorption sites available to HCl on ice and assign the spectra, a 50 K Monte Carlo simulation was first carried out for molecular HCl adsorbed on an ice particle, yielding molecular configurations adopted by the adsorbate on

Figure 1 FTIR difference spectra of HCl on ice particles at 50 K and $\sim 15\%$ coverage. The top spectrum (trace **a**) is for HCl on H_2O ice particles, and exhibits two molecular adsorbate bands, HCl(1) and HCl(2), and the residual acid nanoparticle band, HCl-solid. Traces **b** and **c** are spectra for HCl on D_2O ice and give a clearer view of the HCl(1) band because the interfering bending motion of surface water is downshifted, away from the HCl(2) band. The use of D_2O ice also eliminates possible contamination of this band by protonated-water absorption. Traces **b** and **c** are spectra of the same HCl-ice array but referenced to different bare D_2O ice samples; trace **b** has been smoothed. Trace **d**, a difference spectrum comparing two pure D_2O ice samples, illustrates the instrumental noise.