



Temperature-driven nanoscale brittle-to-ductile transition of the C15 CaAl_2 Laves phase

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ABSTRACT

The influence of temperature on the deformation behaviour of the C15 CaAl_2 Laves phase, a key constituent for enhancing the mechanical properties of Mg alloys up to service temperatures of 200 °C, remains largely unexplored. This study presents, for the first time, the nanoscale brittle-to-ductile transition (BDT) of this intermetallic phase through *in situ* testing including nanoindentation and micropillar splitting conducted at elevated temperatures. By correlating observations from these techniques, changes in deformation of CaAl_2 were identified in relation to temperature. High-temperature nanoindentation quantitatively determined the BDT temperature range, and revealed that CaAl_2 undergoes a BDT at $\sim 0.55 T_m$, exhibiting an intermediate region of microplasticity. A noticeable decrease in nanoindentation hardness was observed at ~ 450 – 500 °C, while indentation cracking was not observed above 300 °C. Results from high-temperature micropillar splitting revealed cracking and brittle pillar splitting up to 300 °C, with an increase in apparent fracture toughness from $0.9 \pm 0.1 \text{ MPa}\cdot\sqrt{\text{m}}$ to $2.8 \pm 0.3 \text{ MPa}\cdot\sqrt{\text{m}}$, and subsequent crack-free plastic deformation from 400 °C. Transmission electron microscopy analysis of the deformed material from nanoindentation revealed that the BDT of CaAl_2 may be attributed to enhanced dislocation plasticity with increasing temperature.

1. Introduction

Laves phases constitute one of the largest class of intermetallic compounds and are usually present as fine precipitates in various engineering alloys such as Mg alloys, steels, Ni-based superalloys, etc. [1–3]. They have been found to be important for improving the strength and high-temperature creep resistance of structural materials [1]. Laves phases are categorised into three polytypes depending on their crystal structure – cubic C15, hexagonal C14, and dihexagonal C36 type [1,4]. These crystals have topologically close packed structures with very high space filling, and therefore possess a high barrier to plastic deformation by dislocation motion at room temperature [1,5–7]. Hence, Laves phases are generally brittle under ambient conditions [1,5]. Additionally, and similar to other intermetallics [8,9], Laves phases can undergo a brittle-to-ductile transition (BDT) accompanied by a decrease in strength as the temperature increases [4]. A precise knowledge of the BDT temperature (BDTT) is important for Laves phase-strengthened alloys, in order to

predict their high-temperature mechanical response for design purposes.

A common intermetallic precipitate present in binary Mg–Al alloys is $\text{Mg}_{17}\text{Al}_{12}$ ($T_m = 458$ °C [10], where T_m is the melting temperature), which undergoes a marked decrease in hardness from ~ 3.5 GPa to ~ 0.7 GPa at 150 °C [11]; a much lower temperature than the desired service temperature of 175–200 °C for Mg alloys [12]. The C15 CaAl_2 Laves phase is commonly found in Mg-rich ternary alloys containing Al and Ca. It has garnered interest for its potential to withstand higher service temperatures compared to other intermetallics in Mg–Al alloys, such as $\text{Mg}_{17}\text{Al}_{12}$, attributed to its high melting point of 1079 °C [13,14]. Tuning the Al–Ca ratio in ternary Mg–Al–Ca alloys can therefore favour the formation of higher melting point intermetallics such as the C14 CaMg_2 and C15 CaAl_2 Laves phases [15–17], leading to improved high-temperature mechanical properties. Nevertheless, the CaMg_2 phase has been noted for its inadequate creep properties attributed to its hexagonal structure [14]. This underscores the need for a detailed investigation of the high-temperature deformation behaviour of the C15 CaAl_2 Laves phase.

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Recent nano- and micromechanical studies have shown that C15 CaAl_2 possesses high hardness and strength [18], but a low fracture toughness at room temperature [19], typical of Laves phases. *In situ* microcantilever fracture tests on single-phase cast specimens of C15 CaAl_2 revealed a fracture toughness of $\sim 2 \text{ MPa}\cdot\sqrt{\text{m}}$, with $\{110\}$ and $\{112\}$ as preferential cleavage planes [19]. Freund *et al.* performed nanoindentation and micropillar compression of the same cast CaAl_2 material, and reported a room temperature hardness of $\sim 4.8 \text{ GPa}$ and yield stress $\sim 2\text{--}3 \text{ GPa}$ [18]. In that study, it was possible to introduce plasticity in the brittle CaAl_2 during microcompression at room temperature due to the small length-scales involved, which favours dislocation plasticity over crack initiation as commonly observed for brittle materials [20–22]. While there is some understanding of the micromechanical properties of CaAl_2 at room temperature, knowledge regarding its elevated temperature deformation and fracture behaviour, and potential BDT is currently limited. In the sole study to the authors' knowledge investigating the high-temperature deformation of CaAl_2 , Rokhlin *et al.* reported from microhardness tests that CaAl_2 was the hardest among the intermetallics in the ternary Mg–Al–Ca system, where the microhardness was observed to decrease $\sim 20\%$ between 20 and 300°C [14]. However, detailed insights into temperature-induced deformation changes, such as cracking and slip activity, or a possible BDT, were not discussed. Furthermore, the microhardness measurements in Ref. [14] were conducted on CaAl_2 precipitates embedded within the Mg alloy, where the compliance of the surrounding matrix could also influence the obtained results.

High-temperature deformation and the BDT, however, have been extensively investigated in high melting-point transition metal Laves phases such as NbCo_2 , FeCo_2 , NbCr_2 , or TaCo_2 using hardness testing [23] or macroscale compression testing [4,24,25]. These studies revealed that while the intermetallics exhibited brittleness at room temperature, they experienced a decrease in hardness or significant reduction in yield strength (at 0.2% strain), accompanied by an increase in creep deformation above the BDTT of $\sim 0.65 T_m$. Additionally, the presence of pre-existing defects in the cast specimens, such as microcracks and pores, was found to limit ductility and adversely affect plasticity and fracture behaviour during macroscale testing, thereby impeding the accurate determination of the BDTT. Small-scale testing methods may offer a viable alternative to overcome this limitation for determining the BDTT of Laves phases.

Advances in nano- and micromechanical testing have opened up new possibilities to investigate small-scale mechanical properties across a wide range of temperatures. This allows for examination without the material being influenced by fabrication defects such as pre-existing flaws which affect fracture measurement [26]. Notched microcantilever bending and micropillar splitting techniques [27] have been used to determine the temperature-dependent fracture toughness of ceramic coatings [28,29] and BDT behaviour at small length-scales for Si [30,31] and W [32]. Nanoindentation has been widely used to study the elevated temperature mechanical properties for a variety of brittle materials and monitor plasticity changes with temperature [26]. Complementary to indentation testing, scratch testing has also been employed to probe the plasticity and cracking behaviour at small length-scales [33,34], and to determine orientation dependent changes in brittle and ductile deformation at room temperature due to changes in crack formation and scratch depth with crystal orientation [35,36]. In the context of Laves phases, indentation-based testing has been employed to examine the high-temperature mechanical properties of C14 CaMg_2 [37], where the indentation hardness decreased above $0.59 T_m$. High-temperature nanoindentation and micropillar compression were also used to determine the temperature-dependent hardness and critical resolved shear stress (CRSS) of the activated slip systems in C14 CaMg_2 between $25\text{--}250^\circ\text{C}$ ($0.53 T_m$) [38], where no change in the mechanical properties was observed within the temperature range. These studies suggest the versatility of small-scale testing methods to obtain meaningful fracture and plasticity properties of brittle materials over a wide range of

temperatures, without the limitation of premature fracture induced by pre-existing flaws in the material.

In this context, the present study aims to determine the elevated temperature deformation behaviour and BDT of a cast single-phase C15 CaAl_2 Laves phase intermetallic specimen using a nano- and micro-mechanical testing approach. For this, high-temperature testing using a commercial *in situ* nanoindenter is employed for precise quantitative determination of the BDTT from changes in hardness and fracture toughness using high-temperature nanoindentation and micropillar splitting, respectively. The mechanical properties measured at various temperatures are then correlated with their corresponding structural changes concerning crack formation and slip activity through subsequent examination of the deformed specimens using scanning and transmission electron microscopy (SEM and TEM, respectively).

2. Materials and methods

2.1. Sample fabrication and microstructural characterisation

Bulk single-phase specimens of the C15 CaAl_2 Laves phase were prepared by casting individual high purity elements of Al (99.999% purity, HVM Hauner GmbH & Co. KG, Germany) and Ca (98.8% purity, Alfa Aesar, Germany) in a cylindrical mould. The cast sample was then annealed at 600°C for 24 h in an Argon atmosphere to homogenise the microstructure and relieve any residual stresses from the casting process. Small pieces of the specimen were machined using electric discharge machining and metallographically polished from 4000 grit SiC paper down to 40 nm colloidal silica to obtain a good surface finish. Further details of the sample preparation procedure can be found in Ref. [39]. Composition analysis of the same CaAl_2 Laves phase material was performed using electron probe microanalysis in Ref. [19]. Fig. S1 in the Supplementary Information shows the representative microstructure of the annealed C15 CaAl_2 Laves phase where the grains had the CaAl_2 phase with the desired target composition of 67 at.% Al and 33 at.% Ca, with a skeleton network of CaAl_4 phase formed along the grain boundaries (chemical analysis of the respective phases from electron probe microanalysis is detailed in Ref. [19]). The grain orientation was characterised using electron backscattered diffraction (EBSD) performed with an EDAX system equipped with Hikari CCD camera mounted inside Zeiss Auriga dual beam focused ion beam/scanning electron microscope (FIB/SEM) and data collection was done using TSL OIM v7 software.

2.2. High-temperature mechanical testing

The effect of temperature on the deformation of CaAl_2 Laves phase was investigated using *in situ* high-temperature nano- and micro-mechanical testing. Measurements of BDT and high-temperature fracture behaviour of CaAl_2 was obtained from *in situ* nanoindentation and micropillar splitting. All *in situ* mechanical tests were performed inside a Zeiss Gemini 500 SEM under high vacuum conditions ($<5 \times 10^{-6}$ mbar) using a Hysitron PI-88 (Bruker, USA) testing system equipped with high-temperature module. Active heating of both the indenter tip and sample was used to ensure temperature matching and minimise thermal drift. The tip holder was affixed to a small ceramic sleeve to minimise heat loss and improve thermal insulation. For each type of test, the CaAl_2 specimen was positioned on the sample heating stage and fixed using three Mo pins. The sample and indenter tip temperatures were measured independently using two separate thermocouples, in close contact with the tip and sample heater for all tests.

2.2.1. High-temperature nanoindentation

High-temperature nanoindentation was performed within a single grain of the CaAl_2 intermetallic with $\sim(536)$ surface plane, determined *a priori* using EBSD. Grain orientations close to $\sim(111)$ in CaAl_2 have shown a propensity for indentation cracking at room temperature [38], and were thus chosen to monitor changes in cracking behaviour with

temperature. A high temperature diamond cube corner tip (Synton-MDP AG, Switzerland) was used in order to facilitate investigation into crack formation as a function of temperature. Prior to testing, the tip area function calibration was carried out on fused quartz. The nanoindentation tests were performed at eight different temperatures from 25 to 580 °C, with an average of 7 to 8 indents at each temperature. This was followed by another set of indentations made at 25 °C after cooling the sample down from the maximum temperature to check for repeatability before and after the heating excursion. Both the sample and indenter were heated during the indentation experiments. Care was taken to ensure that the indents were made inside the grain, away from grain boundaries, and the spacing between the indents was maintained at greater than three times the lateral dimension of the indents to avoid the influence of overlapping plastic zones between adjacent indents [40]. The tests were performed in load-controlled mode, wherein the load was ramped up to a maximum value of $P_{\max} = 9$ mN followed by holding at the peak load for 10 s (and 30 s at temperatures higher than 450 °C to minimise transient plasticity effects during initial unloading). A drift correction segment of 30 s was introduced during unloading at 10 % of $P_{\max}$. The drift correction load was sufficiently low to ensure linear drift without time-dependent plasticity. The thermal drift rate was calculated from the drift correction segment for every indentation test at each temperature and the drift corrected load–displacement curves were subsequently obtained. The indentation hardness H was calculated for each case as [41]:

$$H = \frac{P_{\max}}{A} \quad (1)$$

where the contact area A depends on the contact depth of penetration according to the calibrated area function of the cube corner indenter tip. Post-nanoindentation, the residual indent impressions were observed in the SEM in secondary electron mode to visualise changes in the indent size and microstructural features such as cracks and slip lines around indents at different temperatures.

2.2.2. High-temperature micropillar splitting

Micropillar splitting was performed to determine the effect of temperature on the fracture toughness of CaAl_2 Laves phase. In total, 17 cylindrical micropillars were fabricated by FIB milling in a Zeiss FIB-SEM. It is to be noted that as a sufficiently large grain with (111) orientation to accommodate a full set of pillars was not found, the micropillars were fabricated in a grain with surface orientation $\sim(5\ 3\ 13)$. The final milling was performed at 30 kV, 3 nA Ga^+ ion beam current down to a final pillar diameter of 10 μm and aspect ratio ~ 1.4 . The dimensions of the pillars (i.e. the pillar diameter and height) were measured after FIB milling. An overview image of the micropillar and the surface orientation of the grain are given later in Section 3.3. Recently, Lauener *et al.* [30] reported that for pillars with diameter greater than 10 μm , ion beam damage has limited influence on the pillar splitting fracture toughness [28,29]. The effect of ion beam and pillar size on the room temperature fracture toughness of CaAl_2 has also been investigated by the authors [19], where no observable differences between the apparent fracture toughness of 10 μm diameter pillars milled with either Ga^+ or Xe^+ ions were observed. Furthermore, in the same study, CaAl_2 micropillars of 5 and 10 μm diameter fabricated by Ga^+ FIB were found to have similar toughness values [19]. Hence, the pillar size and fabrication procedure used in this study will not lead to ion beam induced damage effects on toughness measurement. To facilitate fracture of the micropillars and also maintain consistency with the nanoindentation tests, the pillar splitting tests were also performed using a high temperature diamond cube corner indenter (Synton-MDP AG, Switzerland) at 25, 150, 300, 400 and 500 °C. Pillar splitting tests were conducted in pseudo-displacement-controlled mode at 20 nm/s. The tests were terminated once either a load drop occurred or pillar splitting was visually observed during testing. The load–displacement behaviour

was recorded and the maximum load at which splitting occurred was identified to calculate the pillar splitting fracture toughness. Since drift correction cannot be conducted during the pillar splitting tests, separate nanoindentation tests with a drift hold segment were performed immediately before and after the pillar splitting tests at each temperature to ensure temperature matching between the tip and sample and to minimize thermal drift rates. However, it is also important to note that for displacement-controlled testing thermal drift will mainly cause error in displacement measurements and not the load values [30]. During pillar splitting it is the critical load which is required for fracture toughness calculation, and hence thermal drift is not a critical factor here unlike in nanoindentation. *Post-mortem* microscopic examination was performed in a Zeiss Gemini500 SEM to observe the fractured pillars.

2.3. TEM investigation

To characterise the deformation structure underneath the indents using TEM, cross-sectional specimens were prepared from the nanoindents using a Thermo Fisher Scientific Scios 2 FIB equipped with a Ga^+ ion source. To understand the effect of temperature on deformation, TEM specimens were extracted from an indent made at room temperature (after cooling down from 580 °C) and an indent made at 450 °C, for which the indentation testing was stopped at this temperature without exposing the deformed microstructure to higher temperatures. TEM imaging and selected area electron diffraction (SAED) were performed on a JEOL JEM 2100+ operated at 200 kV and a Cs_s image-corrected Thermo Fisher Scientific Titan Themis 60-300 equipped with the Ceta CMOS camera operated at 300 kV. To identify Burgers vectors of dislocations, TEM imaging was carried out in JEOL JEM F200 at 200 kV under different two-beam conditions followed by $g\cdot b$ extinction analysis (where g is the diffraction vector and b the Burgers vector).

3. Results

3.1. Effect of temperature on nanoindentation hardness

Hardness variation with temperature was determined through nanoindentation tests to enhance understanding of how deformation behaviour changes with temperature in the C15 CaAl_2 phase. Fig. 1a shows the EBSD IPF map of the region where nanoindentation was performed, and the surface orientation of the tested grain has been marked. Fig. 1b shows the representative thermal drift-corrected load–displacement curves at temperatures from 25 to 580 °C. The load–displacement behaviour at 25 and 300 °C is also shown separately in the inset of Fig. 1b. With increasing temperature, clear differences are observed in the load–displacement behaviour in terms of: (i) progressive increase in indentation depth at the beginning of load-hold segment at the peak load from 500 °C; (ii) higher time-dependent displacement and maximum depth of indentation at the peak load from 450 °C. Both effects suggest that plastic deformability of CaAl_2 increases from ~ 450 °C, and is in broad agreement with the deformation changes observed from our preliminary scratch testing analysis of CaAl_2 (refer to the [Supplementary Information](#)). This implies that nanoindentation hardness of the material varies with temperature, as observed in Fig. 2. The hardness at room temperature was ~ 4.5 GPa, similar to that recently reported for CaAl_2 [18]. The hardness remained constant at ~ 4.5 GPa up to 400 °C, and dropped by 22 % at 450 °C to 3.5 GPa. This was followed by a more pronounced decrease at 500 °C to ~ 1 GPa. Subsequently, the hardness further reduced and was nearly constant at ~ 0.6 GPa between 550 to 580 °C. Thus, the temperature range between 450 to 500 °C marks the region where a significant enhancement in plastic deformation of CaAl_2 occurs in the cube corner nanoindentation tests. The elastic modulus (determined from the unloading segment of the load–displacement curves) was constant between 25 and 400 °C with an average value $\sim 140 \pm 6$ GPa, while at higher temperatures the modulus values were

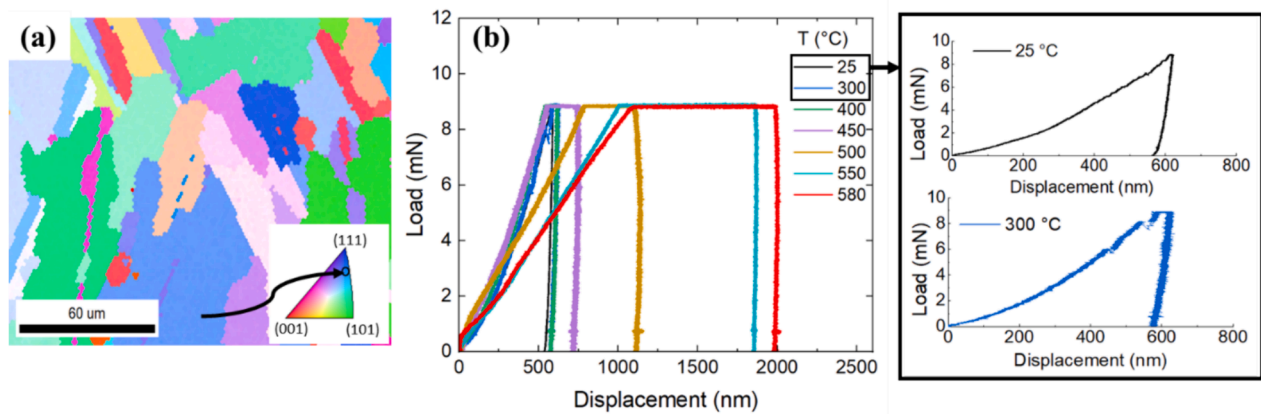


Fig. 1. High-temperature nanoindentation of CaAl₂. (a) Orientation map of CaAl₂ obtained from EBSD showing the grain orientation where nanoindentation tests were conducted. (b) Representative load–displacement curves at different temperatures obtained from nanoindentation; the inset in (b) shows separately the zoomed in version of load–displacement curves at 25 and 300 °C. In (b) the data for 25 to 500 °C correspond to 10 s hold at P_{max} , while those at 550 and 580 °C correspond to 30 s hold at P_{max} .

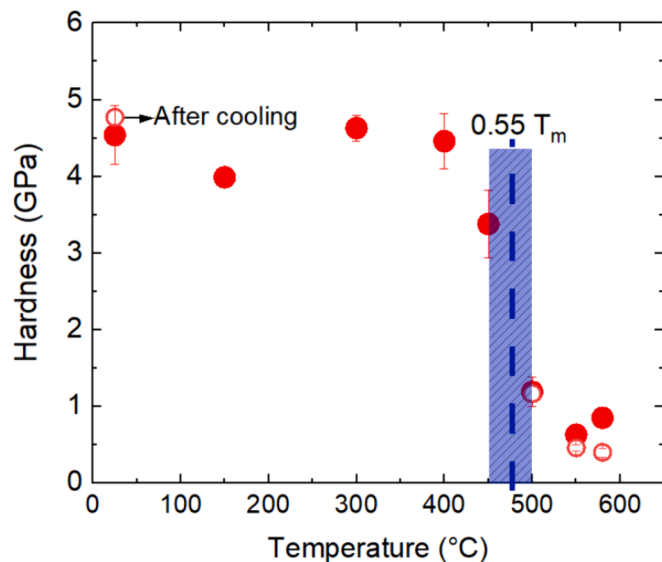


Fig. 2. Variation of nanoindentation hardness with temperature for the C15 CaAl₂ Laves phase. The filled circles denote the data for 10 s hold time and open circles are for 30 s hold time at peak load. Error bars indicate the standard deviation of hardness values at each temperature and for cases where it is invisible the error bar was smaller than the symbol size. The blue shaded region represents the transition temperature range where the hardness values decrease significantly from the upper plateau region before saturating to lower values.

affected by increasing transient deformation and could not be reliably interpreted. The observed time-dependent displacement during the hold segment (Fig. 1b) is attributed to creep deformation, influenced by high temperature and pressure in the centre of the plastic zone, as well as stress gradients from the cube corner geometry. This is distinguished from thermal drift, where displacement would vary linearly with time (discussed in Section 4.2). Comparison of hardness at different hold times (Fig. 2) reveals no significant difference at 500 °C. Longer hold times in the high-temperature regime slightly reduce hardness without altering the overall trend of saturation to lower values. A slight but consistent drop in hardness of ~12 % is observed at 150 °C with enhanced pile-up around the residual indent (Fig. 3b), although the reason for this is unclear.

Increased plastic deformation with temperature was also observed from the *post-mortem* SEM analysis of the residual indents. Fig. 3 shows representative secondary electron images of the indents performed at

various temperatures. The size of the residual indent impression is similar below 450 °C and then increases from 450 °C and above. A larger size of indent impression for fixed maximum load is consistent with the lower hardness at higher temperatures shown in Fig. 2. Notable changes in deformation features around the indent can also be observed with temperature. Slip steps and material pile-up are visible in the low temperature indents, along with cracks (indicated by white arrows) extending from the corners of the indents. No slip lines or cracks are visible in the transition and high temperature regime above 300 °C. Pile-up diminishes noticeably at 450 °C and is not observed at ~500 °C. Surface features appear less defined in post-cooling images due to surface oxidation at elevated temperatures. It must be emphasised that even with high vacuum level (5×10^{-6} mbar) in the SEM, surface oxidation of CaAl₂ cannot be avoided (see presumed oxide scale of ~60 nm thickness observed from the TEM cross-section of an indent made at RT after exposure to 580 °C in Fig. 7a). These changes in deformation features with temperature, in conjunction with the significant decrease in hardness, suggests that the deformation behaviour of the CaAl₂ Laves phase changes at ~450 °C and is facilitated by higher plastic deformability with the absence of cracking. To further correlate the changes in hardness with changes in fracture behaviour across this transition zone, high-temperature micropillar splitting tests were conducted.

3.2. Effect of temperature on the pillar splitting fracture toughness

Fig. 4a shows an overview of micropillars fabricated on a single CaAl₂ grain, whose surface orientation is marked in the inset IPF. A representative high-magnification image of a micropillar is also shown in the inset in Fig. 4a. Fig. 4b shows a micrograph of the *in situ* configuration with cube corner indenter prior to testing, while Fig. 4c shows the representative load–displacement response of the pillar splitting tests at various temperatures. The load–displacement curves maintain a consistent shape up to 300 °C, showing minimal variation in slope and indicating negligible effects from indenter positioning and thermal drift. The maximum load at which pillar splitting occurs (identified by a sharp load drop) increases only slightly from 25 to 150 °C, and then increases significantly at 300 °C. A transition is observed at 400 °C, wherein the peak load increases slightly, but pillar splitting does not occur. Above 400 °C, the peak load at the pre-set maximum indentation depth decreased, signifying that the CaAl₂ intermetallic becomes more plastically deformable. Due to lack of pillar splitting at 400 and 500 °C, a load drop was not observed up to the maximum set displacement value of 2.5 μm, where the tests were terminated. Hence, the apparent fracture toughness was determined only up to 300 °C. The critical stress intensity factor for splitting was evaluated using Eq. (2) [27]:

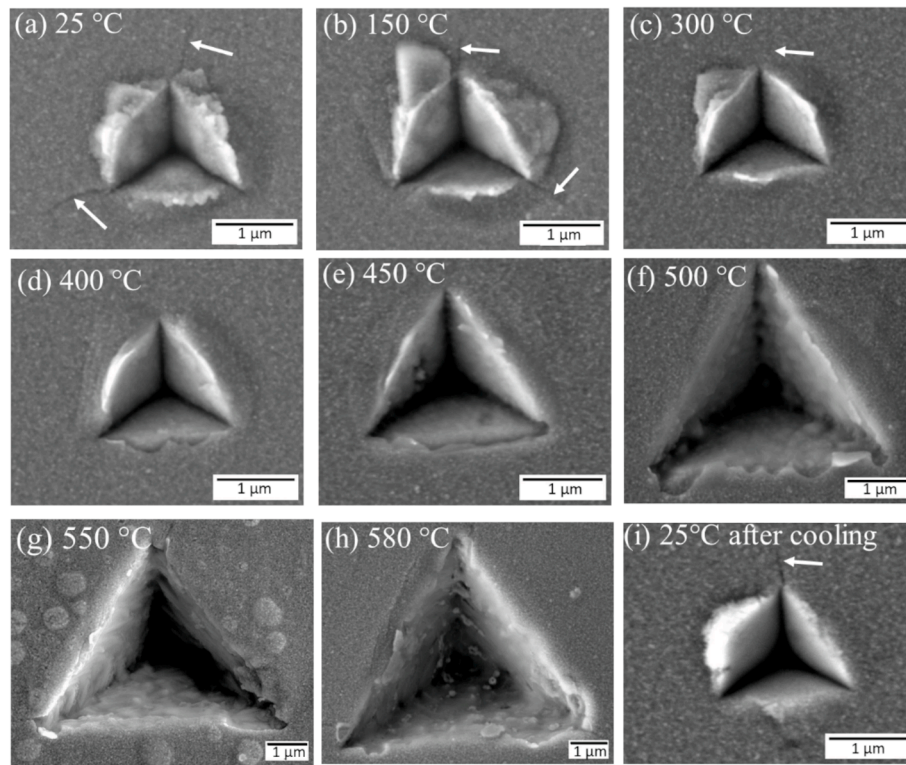


Fig. 3. Secondary electron *post-mortem* images of nanoindents made at various temperatures showing changes in slip lines and crack formation (marked with white arrows) around indents. From 25 to 450 °C all images were taken at the same magnification, whereas from 500 to 580 °C a lower magnification was used to capture the larger indents.

$$K_c = \gamma \frac{P_c}{R^{1.5}} \quad (2)$$

which assumes an isotropic material volume. K_c is the apparent fracture toughness, P_c is the critical load at which pillars split, R is the radius of the pillar, and γ is a factor which depends on the geometry of the indenter and E/H ratio of the material. A constant elastic modulus E of 140 ± 6 GPa was used between 25 and 400 °C, based on modulus values obtained from unloading segment of the nanoindentation experiments. It is to be noted that no positive displacement due to creep occurred during unloading up to 400 °C. Using the hardness values at each temperature obtained from nanoindentation measurements in Section 3.1, the E/H ratio was obtained within the constant γ range for a cube corner indenter geometry reported from Ref. [42] (i.e. ~ 31), and therefore $\gamma \approx 0.85$ was applied over the studied temperature range of 25 to 300 °C. Fig. 4d shows the variation of apparent fracture toughness from pillar splitting as a function of temperature along with the maximum load $P_{\max}$ for all temperatures. $P_{\max}$ corresponds to P_c for the case where pillar splitting occurred from 25 to 300 °C, whereas at 400 and 500 °C it was the maximum load till the displacement set-point was reached. The K_c calculated from Eq. (2) was 0.94 ± 0.05 MPa $\cdot\sqrt{m}$ at 25 °C, and increased slightly to 1.2 MPa $\cdot\sqrt{m}$ at 150 °C, whereas at 300 °C it increased significantly to 2.76 ± 0.26 MPa $\cdot\sqrt{m}$ with a commensurate increase in the critical load for splitting. Pillar splitting was observed again after cooling back to 25 °C with $K_c \sim 0.9 \pm 0.1$ MPa $\cdot\sqrt{m}$, implying that exposure to high temperature did not induce any major structural changes in the material to influence the toughness, and that surface oxidation did not severely impact the toughness measurement, similar to the nanoindentation results in Section 3.1.

Fig. 5 shows *post-mortem* images of the pillars after the splitting tests at different temperatures. From 25 to 300 °C straight cracks predominately extend from the corner of the indents, leading to 3-way splitting of the pillars. In few cases, due to inaccuracy in indenter positioning, an ideal 3-way splitting did not occur wherein two of the cracks extending

from the indenter corner reached the edge of the pillar while the third did not. At 400 and 500 °C no critical crack initiation for pillar splitting was observed, although some isolated tortuous cracks are present on the surface of the deformed pillars. Such surface cracks could be due to stresses arising from accommodation of the larger plastic zone below the indent, or cracking of the surface oxide layer. However, these surface cracks do not lead to pillar splitting. Crack formation was not observed during nanoindentation at similar temperatures due to the hydrostatic constraint from the surrounding material, which is reduced in the case of a micropillar volume. For the lower temperatures where pillar splitting did occur, the crack planes were indexed using the method used for surface trace analysis discussed in Ref. [18]. Some of the crack planes have been marked in Fig. 5 and belong to low index planes. However, it is not possible to discern any possible change in crack plane with temperature in this case, as cracking would primarily be driven by the cleavage planes which are aligned with the sharp corners of the indenter. In our earlier study [19], the fracture toughness values of different low index cleavage planes in C15 CaAl₂ were found to be similar. Hence the grain orientation and alignment of the cleavage planes with indenter diagonal will likely not significantly impact the pillar splitting fracture toughness value of C15 CaAl₂.

4. Discussion

4.1. BDTT of C15 CaAl₂ Laves phase: Comparison of test methods

The results presented in Section 3 highlight a clear change in the deformation behaviour of C15 CaAl₂ Laves phase with increasing temperature, and is supported by three distinct changes: (i) significant drop in nanoindentation hardness at 450–500 °C; (ii) absence of cracking at the corners of indents at 300 °C and above; (iii) brittle pillar splitting between 25 to 300 °C, followed by no splitting from 400 °C. These changes imply an overall transition from brittle to a more ductile

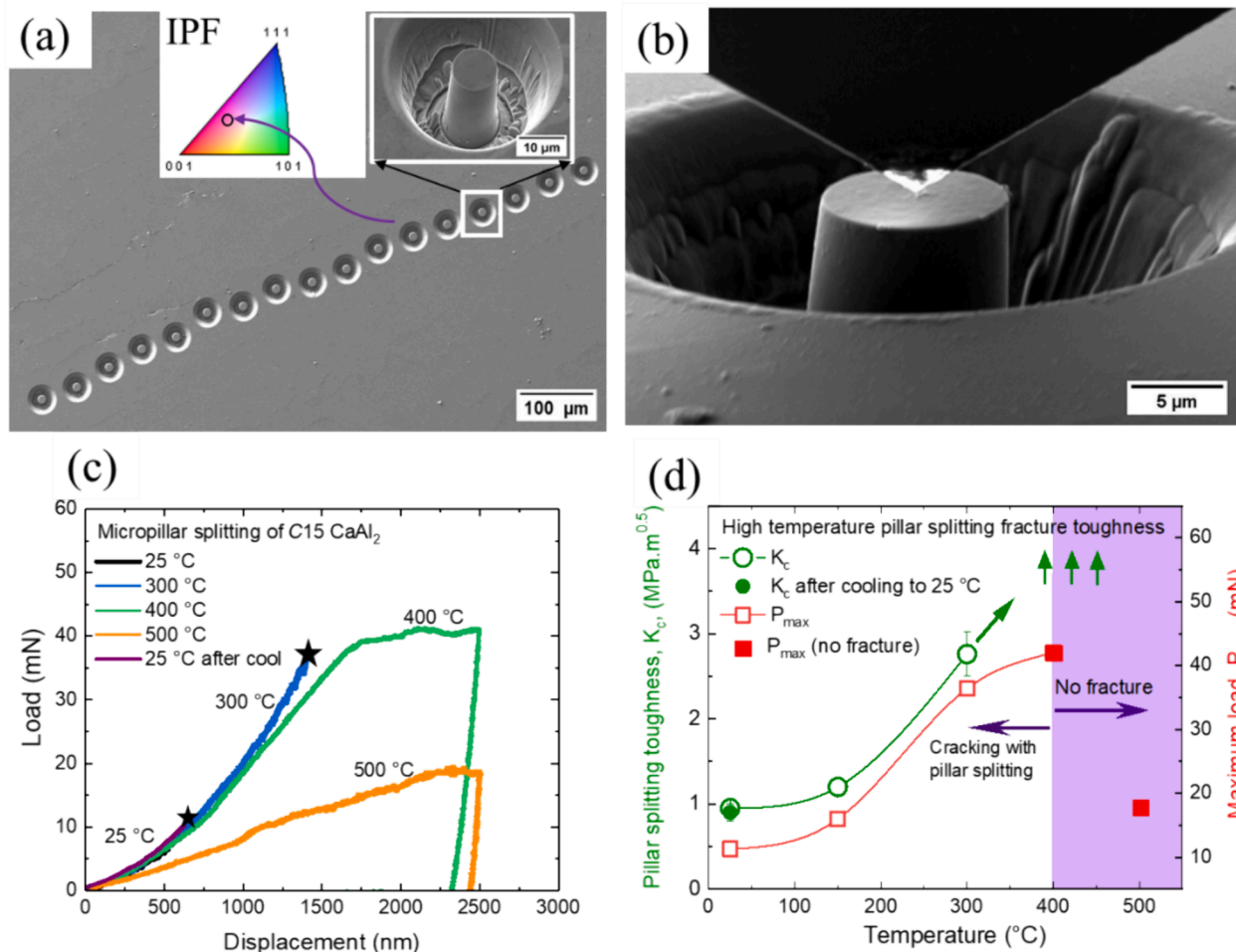


Fig. 4. (a) Secondary electron overview image of micropillars fabricated in a single grain whose surface orientation is indicated in the IPF (inset) together with a high magnification tilt-corrected image of a single micropillar at 45° tilt angle; (b) Micropillar loaded with a cube corner indenter prior to testing at 300 °C; (c) Representative load–displacement curves for pillar-splitting at various temperatures; (d) Variation of pillar-splitting fracture toughness and maximum load P_{max} with temperature. The filled red squares in (d) indicate the maximum load for the cases where no splitting occurred. The green arrows in (d) indicate that apparent fracture toughness would increase with temperature above 300 °C.

behaviour of CaAl₂, accompanied by a higher contribution of plasticity to fracture. Disappearance of cracks at ~300 °C during cube corner nanoindentation suggest that crack tip shielding due to local dislocation activity is already operative at these lower temperatures, which together with the hydrostatic constraint from the surrounding material may limit crack extension. This is consistent with the increase in pillar splitting fracture toughness at 300 °C. During micropillar splitting, unstable crack initiation and extension occurs at the critical load for instability. Enhanced dislocation activity under the indenter tip at higher temperatures can better accommodate local stress thereby affecting the critical load for crack initiation during the splitting process. However, brittle splitting fracture of the micropillars is still observed at 300 °C, implying that CaAl₂ remains brittle at this temperature.

The influence of local plasticity is more evident as temperature increases to 400 °C, where the maximum load reaches a peak value (see Fig. 4), however no splitting occurs, indicating that CaAl₂ becomes less brittle at this temperature. Ast *et al.* [43] reported that for crack nucleation and pillar splitting to occur within a micropillar volume size which can be typically achieved by FIB milling, the K_c/H ratio should be less than 0.8 for a cube corner indenter. For our system at 300 °C the ratio is 0.61, whereas at 400 °C it would increase to 0.88 if one assumes that the K_c increases with temperature following a linear extrapolation beyond 300 °C (see green arrow in Fig. 4d). Since pillar splitting is limited to materials which fail in a brittle manner, it is unsuitable for

obtaining a high-temperature toughness for which alternate elastic–plastic fracture mechanics approaches are required. Interestingly, while local dislocation activity can blunt the crack tip, increase fracture toughness and even prevent pillar splitting at 400 °C, no decrease in indentation hardness or increase of the residual indent size was observed (see Figs. 2, 3). Only at and above ~450 °C does the hardness drop and dislocation plasticity becomes more dominant (see TEM analysis discussed in Section 4.2). The transition zones between brittle and ductile behaviour of CaAl₂ are shown in Fig. 6, where both the temperature-dependent variation of hardness and pillar splitting toughness have been compared. Up to 300 °C, CaAl₂ exhibits brittle behaviour with constant hardness and brittle failure due to cracking. Between 300 and 400 °C a microplasticity zone is present where although the hardness does not change, cracks at indenter edges are not observed during nanoindentation, while significant local dislocation activity at the indenter apex and possible crack tip shielding effects increase the toughness to an extent that a critical fracture initiation could not be determined from micropillar splitting tests. The microplastic region above 300 °C compares well with the morphological changes in wear tracks from high-temperature nano-scratch testing of CaAl₂ (refer to Supplementary Information). At approximately 450 °C and above, CaAl₂ exhibits enhanced plasticity due to dislocation activity, as evident from the significant drop in hardness together with absence of pillar splitting, thereby transitioning into a more ductile behaviour. The close

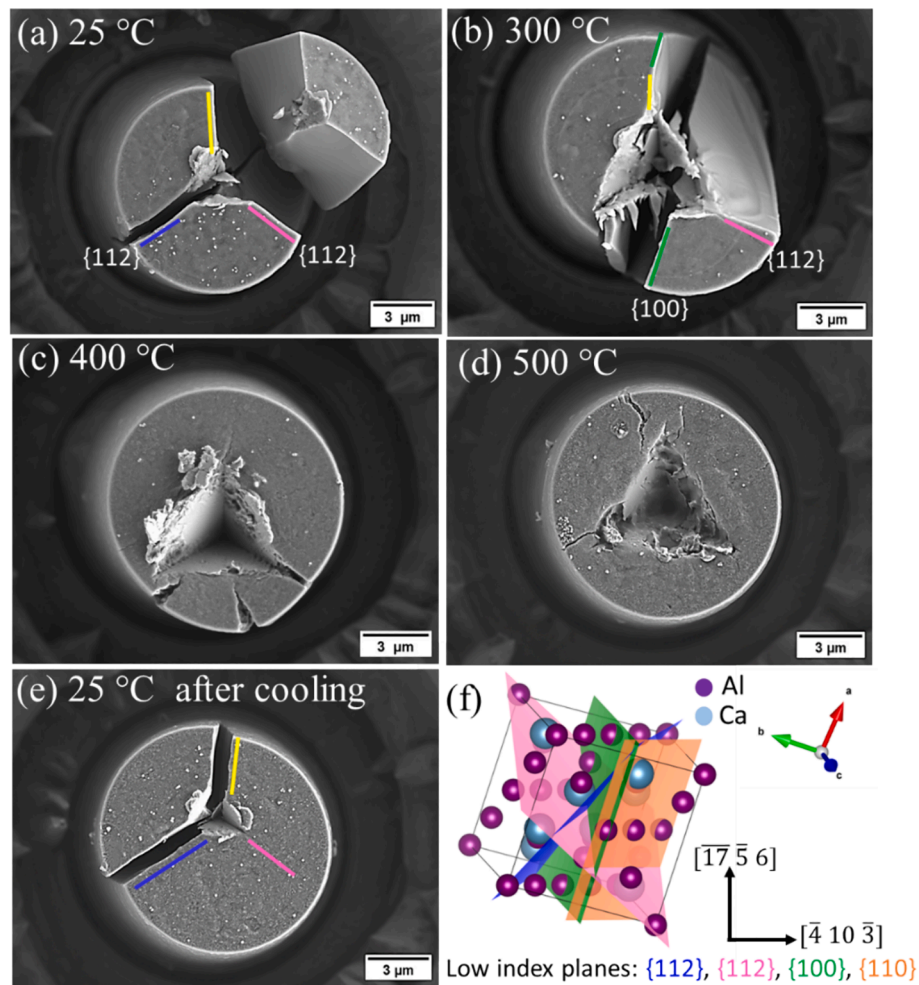


Fig. 5. Post-mortem secondary electron micrographs, showing the top view after pillar splitting tests at (a) 25 °C, (b) 300 °C, (c) 400 °C, (d) 500 °C and (e) after cooling back to 25 °C. (f) Crystal orientation of the grain showing potential low-index planes for cracking; the in-plane orientations of pillars in (a-e) are indicated in (f). The yellow lines in (a), (b) and (e) indicate crack planes for which two possible solutions were obtained and hence could not be assigned unambiguously.

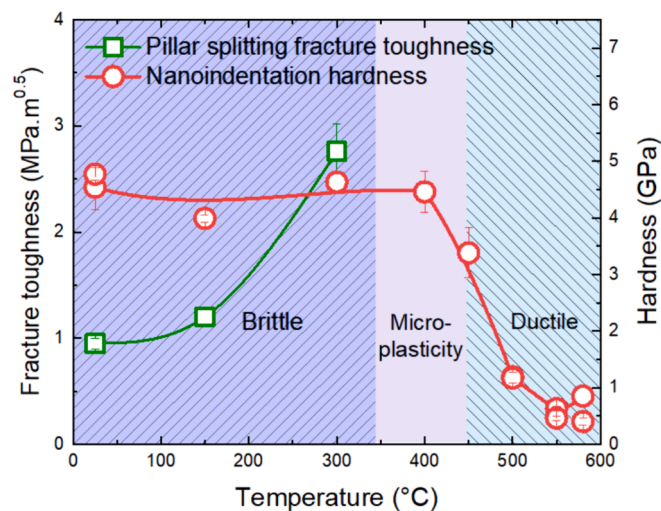


Fig. 6. Comparison of nanoindentation hardness and pillar splitting fracture toughness with temperature, highlighting brittle and ductile deformation zones.

correspondence in the temperatures where plasticity prevents the brittle failure of pillars (~400 °C) and decreases nanoindentation hardness (~450 °C) suggests that a prominent change over into the ductile regime

will occur from 450 °C (~0.55 T_m).

The nanoscale BDTT (~0.55 T_m) of C15 CaAl_2 determined here is lower than the macroscale BDTT of ~0.65 T_m typically reported for other C15 Laves phases via macro-compression testing [4], where BDTT was defined as the temperature at which a compressive strain of 1–2 % could be achieved without specimen fracture. However, from Vickers indentation of C15 NbCr_2 a BDTT of ~0.55 T_m was obtained [44], equal to that obtained for C15 CaAl_2 in this study. Further, to contextualise the BDTT behaviour of CaAl_2 determined here using small-scale testing methods in relation to macroscale testing, the microplasticity zone at small length-scales suggests a wider temperature range for complete transition into the ductile regime. In comparison, during macroscale tests a more abrupt BDTT could occur for intermetallic compounds [9,45,46].

Method and length-scale-dependent BDTT differences are evident in other literature examples, where various testing methods were employed. The toughness reported from Si micropillar splitting increased at ~175 °C due to local crack tip shielding possibly facilitated by dissociation of dislocations into partials [30,47], whereas the microhardness decreased at higher temperatures of 500 °C due to enhanced dislocation activity [48]. Additionally, high-temperature microcantilever fracture tests on Si demonstrated a progressive increase in mode I fracture toughness from ~300 °C to 600 °C [31]. On the other hand, macroscale testing using pre-cleaved Si single crystals revealed a sharp increase in fracture toughness at 705 °C [49]. This supports our observation that small-scale toughness increases at lower

temperatures when compared to the indentation hardness. Similar length-scale effects have been observed for tungsten [32], where the BDTT obtained from macroscale testing of three- and four-point bending specimen geometries was ~ 150 to 200 °C [50,51], while microcantilever fracture tests revealed a BDTT of ~ 0 to 75 °C [32], with a gradual increase in fracture toughness and change from brittle-cleavage to micro-cleavage fracture due to increasing dislocation activity. These studies suggest that the onset of BDTT, facilitated by dislocation activity enhancing fracture toughness and promoting ductile behaviour, may occur at lower temperatures on small length scales. Differences based on the testing method, evident in case of CaAl_2 , can also arise.

Regarding surface oxidation challenges for CaAl_2 at high temperatures, if small-scale techniques sensitive to surface deformation are used, as for nano-scratching, the formation of an oxide scale can obscure slip trace observation near the wear track and quantitative insights into elastic and plastic wear depth or friction coefficient with temperature may become unreliable [36]. Additionally, it must be noted that due to the observed oxidation, BDTT determination using notched microcantilever tests is not possible due to the changing stress/chemistry at the notch root, which can strongly affect the measured fracture toughness [52]. Moreover, the plastic zone size r_p ahead of the crack tip of notched microcantilevers can increase with temperature and exceed the cantilever dimensions, leading to size effects on cantilever fracture toughness. As such, microcantilever fracture tests were not performed here, and our nano-scratch tests (in the Supplementary Information) were interpreted with a degree of caution.

4.2. Mechanistic insights into the thermally-activated deformation

The deformed microstructure beneath the indents made at RT, and at the BDTT, were analysed to examine the effect of temperature on dislocation structure. Site-specific lamellae were extracted from below two representative indents made at 25 °C after cooling, and 450 °C, and

examined by TEM. Both indents were not exposed to higher temperatures than the temperature of indentation. A schematic representation of the orientation in which the TEM lamella was extracted from indents has been given in Fig. S3 of the Supplementary Information. Fig. 7a,b show the bright-field TEM (BF-TEM) and BF-scanning TEM (BF-STEM) images of the deformed region underneath the indent at 25 °C, respectively. Straight parallel slip bands are visible, as indicated by the solid red arrows, along with dislocation entanglement in the plastic zone of the indent at 25 °C (refer to Fig. S4 for TEM images obtained from weak beam imaging by tilting to different two beam conditions). Similar slip bands in the deformed microstructure below nanoindents in the same C15 CaAl_2 sample were observed by Freund *et al.* [18] for Berkovich indents at RT. Furthermore, a crack is visible at the bottom of the indent (indicated by a dashed yellow arrow), which is consistent with SEM observation of surface cracks around the RT indent shown in Fig. 3. Fig. 7c shows the BF-TEM image of the plastic zone below a nanoindent at 450 °C. In contrast to the RT indent, no straight slip lines or cracks are observed. Rather, a high density of homogeneously distributed dislocations, forming a network of curved dislocation lines, is present in the vicinity of the indent, with some isolated dislocations extending to farther regions. The absence of slip lines and cracks supports the SEM observations of homogeneous deformation without formation of slip traces on the indent surface at 450 °C in Fig. 3d, and the lower hardness due to more uniform dislocation activity. It is noted that due to the load-controlled nanoindentation tests performed here, the deformation zone of the indents at 25 and 450 °C were not of equivalent maximum depth. It is reported for the same C15 CaAl_2 sample used in this study that $a/2\langle 110 \rangle$ (where a is the crystal lattice parameter) type perfect dislocations, as well as stacking faults on $\{111\}$ planes are present within the slip bands at RT [18]. The latter were thought to stem from the motion of $a/6\langle 112 \rangle$ dislocations. The TEM images of Fig. 8 show that in case of the high temperature (i.e. 450 °C) indent lamella (of Fig. 7c), tilting to different zone axes and two-beam conditions also revealed similar $a/$

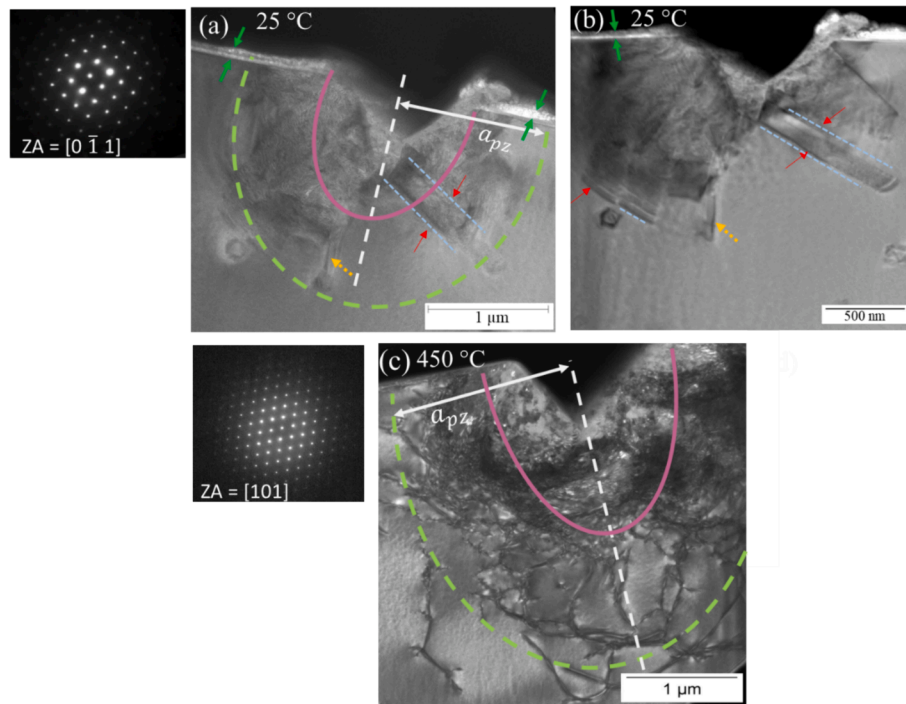


Fig. 7. TEM images showing the cross-section of the deformed region under nanoindents performed at different temperatures. (a) BF-TEM and (b) BF-STEM images of indent at 25 °C taken in the $[0\ \bar{1}\ 1]$ zone axis. The orientation of the specimen is seen by the SAED pattern shown. The red arrows in (a) and (b) show the activated slip planes and the yellow arrows mark the crack observed at 25 °C; the green arrows in (a) and (b) indicate presumed oxide layer formed on the surface of indent after exposure to 580 °C. (c) The BF-TEM image of indent at 450 °C shows no slip plane activation or crack formation and the SAED pattern shows that the BF-TEM image was acquired at the $[101]$ zone axis. In (a) and (c) the theoretically computed plastic zone has been shown by the solid magenta curve for $f = 1$ and green dashed curve for $f = 2.4$ (see main text for more details). The dark region above the indented surface in (a-c) is the Pt layer.

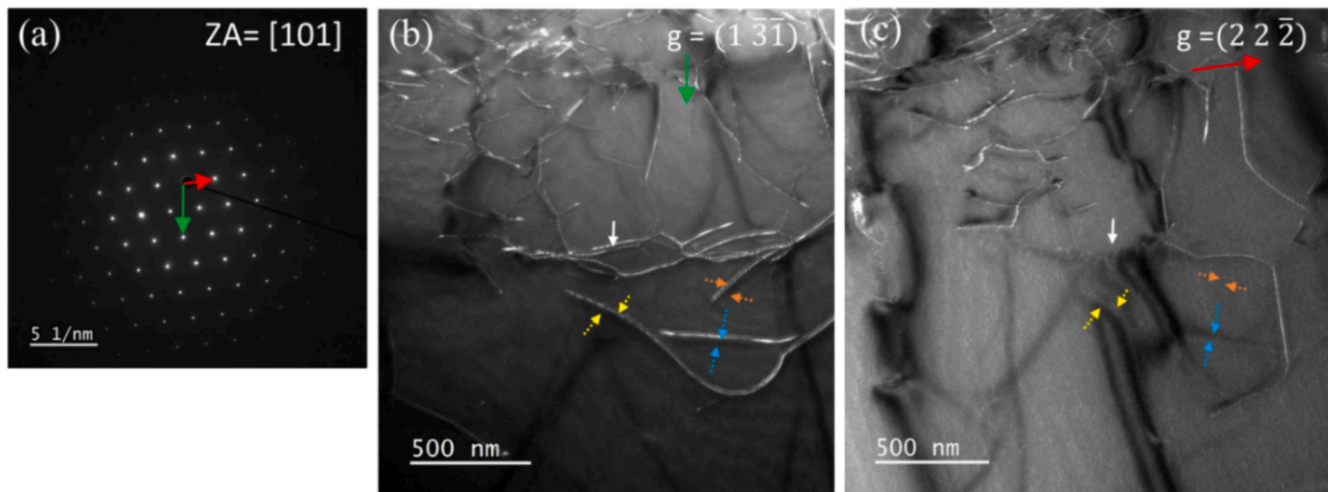


Fig. 8. Dislocation structure under different two-beam conditions underneath the nanoindent at 450 °C. (a) Diffraction pattern of [101] zone axis, and weak-beam dark field images under (b) $g = (1\bar{3}1)$ where the dislocations are visible and (c) $g = (22\bar{2})$ where the dislocations are invisible. Solid white arrows indicate perfect dislocation whereas dashed arrows of same colours denote partial dislocations identified from the $g\cdot b$ analysis.

$2\langle 110 \rangle$ perfect dislocations (indicated with solid white arrows) and partial dislocations of $a/6\langle 112 \rangle$ type (indicated with dashed arrows). These dislocations were identified by performing a $g\cdot b$ analysis on visible/invisible dislocation sets obtained from different two-beam conditions. A set of visible dislocations for zone axis [101] (in Fig. 8a) and $g = (1\bar{3}1)$ are shown in Fig. 8b, while the dislocations become invisible with $g = (22\bar{2})$ as shown in Fig. 8c. Refer to Fig. S5 in the Supplementary Information for further TEM images of dislocation structure below this indent for other two beam conditions. Although resolving the partial dislocations in the RT sample may simply be impeded by the overlapping strain fields where they are concentrated in planes of high defect density, the observation of partial dislocations at elevated temperature is consistent with synchroshear requiring substantial thermal activation to operate [53] and previous TEM investigations on the structurally related Nb-Co μ -phase, which also exhibits a transition from full to partial dislocation slip [54] within the Laves phase building block of its larger unit cell, also associated with a change in slip plane that cannot be resolved by conventional TEM [55].

Fig. 7 highlights that the microstructural features within the deformed region changes with temperature, accompanied by an increase in plastic zone size. To compare between the observed plastically deformed region below the indents with the theoretical prediction, the plastic zone size a_{pz} was calculated according to the modified Nix-Gao model [56,57], where $a_{pz} = f \cdot a_c$, (where $a_c = h/\tan\theta$, and θ is the angle between surface and indenter and h is the indentation depth). The factor f (equal to 1 in the original Nix-Gao model [58], and greater than 1 in the modified one [56,57]), relates the contact radius to the plastic zone size, and depends on the material and its crystallographic orientation. From finite element simulations of cube corner indentation of *f.c.c.* Cu in Ref. [57], $f = 2.4$ was estimated. The theoretically predicted plastic zone regions, according to $a_{pz} = f \cdot a_c$, are indicated for both temperatures in Fig. 7a,c, for both $f = 1$ and $f = 2.4$ and with $\theta = 47.7^\circ$ for the cube corner indenter. It is observed that for $f = 2.4$ (where $a_{pz} = 1280$ nm at 25 °C and 1580 nm at 450 °C), the theoretically predicted plastic zone size matches reasonably with the deformed zones observed from TEM, although it appears slightly larger for the indent at 25 °C. It is to be noted that some differences can occur due to slight misalignment of the lamella with respect to the indent centre, the effect of stresses at the corner of the indent and also due to the tendency of the intermetallic phase to highly concentrate deformation onto individual planes at ambient temperature. This increase in the plastic zone size with depth of indentation of CaAl_2 Laves phase, equivalent to the behaviour of *f.c.c.* metals, confirms that the observed decrease in hardness and the BDT of

CaAl_2 intermetallic is controlled by enhanced dislocation mediated plasticity at elevated temperatures which can blunt the cracks and restrict brittle failure.

The limited plasticity of Laves phases below the BDTT is generally attributed to restricted dislocation activity within their complex close-packed structures. Initially, synchroshear was proposed as the sole dislocation mechanism [59–61]. A high lattice friction for dislocation glide has also been considered to hinder dislocation activity at RT for Laves phases [62,63]. From the room temperature activation volume of C15 CaAl_2 ($\sim 3.75b^3$, where b is the Burgers vector) [18], it was not possible to definitively determine if the deformation was governed by overcoming Peierls resistance. Here, the RT lattice friction stress of CaAl_2 intermetallic was estimated from the nanoindentation hardness data in Section 3.1 by following the method proposed by Qui *et al.* [64], as outlined in the Supplementary Information. Considering a perfect $a/2\langle 110 \rangle$ dislocation with $b = 0.5656$ nm for this analysis in CaAl_2 , the friction stress is estimated as 580 MPa, which lies in the range of values of friction stress (0.4 to 5.6 GPa) reported for other C15 Laves phases [65].

The enhancement of plasticity above the BDTT for many transition metal C15 Laves phases has been attributed to increased dislocation motion due to thermally activated processes such as creep deformation [4], while for some Laves phases it has been attributed to a Peierls mechanism due to high strain rate dependence and low activation volume [25,66]. The BDTT of the CaAl_2 Laves phase ($\sim 0.55 T_m$) in the present case as well as other transition metal C15 Laves phases [4], is above a homologous temperature of $0.5 T_m$ consistent with temperatures required for thermally-activated creep process. Noticeable creep deformation in CaAl_2 can be observed in Fig. 1b from the increased time-dependent displacement during the constant load hold segment in the nanoindentation tests at high temperatures (450 °C and above). The indentation creep behaviour of CaAl_2 was analysed for the highest temperatures (*i.e.* 550 °C and 580 °C with the longest holding times) from the corresponding indentation strain rate and hardness from nanoindentation results, and is presented in Fig. S6 of the Supplementary Information. The time-dependent increase in displacement and decrease in hardness during the constant load hold segment at 550 °C and 580 °C resembles typical creep behaviour (see Fig. S6a). The indentation strain rate was computed at these temperatures as the ratio of indentation velocity dh/dt to the indentation depth h [67]. After an initial rapid decrease, the strain rate varied almost linearly with hardness (see Fig. S6b), proportional to the contact stress. Interestingly, the indentation stress exponent (*i.e.* the slope of the indentation strain rate

versus hardness curve in Fig. S6b) obtained for CaAl_2 of ~ 3 to 3.2 is similar to the creep stress exponent of approximately 3.5 reported from compression creep tests of other C15 Laves phases [4], and is indicative of dislocation creep [68]. Decoupling additional effects of temperature-dependent critical resolved shear stress and effect on high temperature plasticity would require further studies using micropillar compression. Overall, the high BDTT of 450–500 °C obtained for CaAl_2 suggests that this intermetallic will not undergo a loss in its strength due to enhanced plasticity at the elevated temperatures of ~ 200 °C desired for Mg-rich alloys [12], thereby maintaining the overall alloy strength.

5. Conclusions

- Indentation-based testing using nanoindentation and micropillar splitting were used to estimate the nanoscale BDTT of the C15 CaAl_2 Laves phase and provide quantitative insights into the high-temperature deformation behaviour of this material.
- A significant decrease in nanoindentation hardness occurred at ~ 450 –500 °C, with distinct changes in the deformation features around the indents due to increase in size of the residual impression at and above 450 °C and disappearance of surface cracks around 300 °C. This implies a change in the deformation behaviour with temperature for the CaAl_2 Laves phase.
- Elevated temperature micropillar splitting revealed brittle pillar splitting up to 300 °C, with straight crack propagation from the centre to the edge of the pillar. The apparent fracture toughness remained nearly constant up to 150 °C, followed by a sharp increase at 300 °C. No pillar splitting occurred at 400 °C and above due to considerable plastic deformation.
- A comparison of the nanoindentation and micropillar splitting results indicate that CaAl_2 remains brittle up to 300 °C, followed by increasing microplasticity between 300–400 °C which can cause crack tip shielding but not affect the nanoindentation hardness. Finally, at ~ 450 °C and above a transition to a more ductile behaviour occurs with a pronounced decrease in hardness due to a more uniform dislocation activity and the absence of brittle pillar splitting.
- TEM examination of the deformed microstructure below the indents revealed slip bands and small cracks in the deformed zone under an indent made at 25 °C. At 450 °C, the deformation zone extends ~ 25 % further and reveals a more uniformly distributed entanglement of dislocations.
- Nanoindentation hold segments reveal creep above the BDTT with creep stress exponents indicative of dislocation creep at the highest test temperatures, suggesting that the BDT of CaAl_2 can be driven by thermally-activated effects on dislocation motion leading to creep.

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

During the preparation of this work the author(s) used ChatGPT (OpenAI) in order to improve the readability of some text sections. After using this tool/service, the author(s) reviewed and edited the content as needed and take(s) full responsibility for the content of the publication.

CRedit authorship contribution statement

Anwesha Kanjilal: Writing – review & editing, Writing – original draft, Visualization, Methodology, Investigation, Formal analysis, Data curation, Conceptualization. **Ali Ahmadian:** Writing – review & editing, Visualization, Methodology, Investigation. **Martina Freund:** Writing – review & editing, Methodology, Investigation. **Pei-Ling Sun:** Writing – review & editing, Methodology, Investigation. **Sandra Korte-Kerzel:** Writing – review & editing, Supervision, Funding acquisition. **Gerhard Dehm:** Writing – review & editing, Supervision, Project administration, Funding acquisition, Conceptualization. **James P. Best:** Writing –

review & editing, Supervision, Project administration, Methodology, Formal analysis, Conceptualization.

Declaration of competing interest

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.

Data availability

Underlying data for this publication is available at DOI: 10.5281/zenodo.13139961.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.matdes.2024.113206>.

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