Supplementary Information (SI) for Nanoscale.

Contactless health monitoring in autonomous self-reporting ceramic coatings

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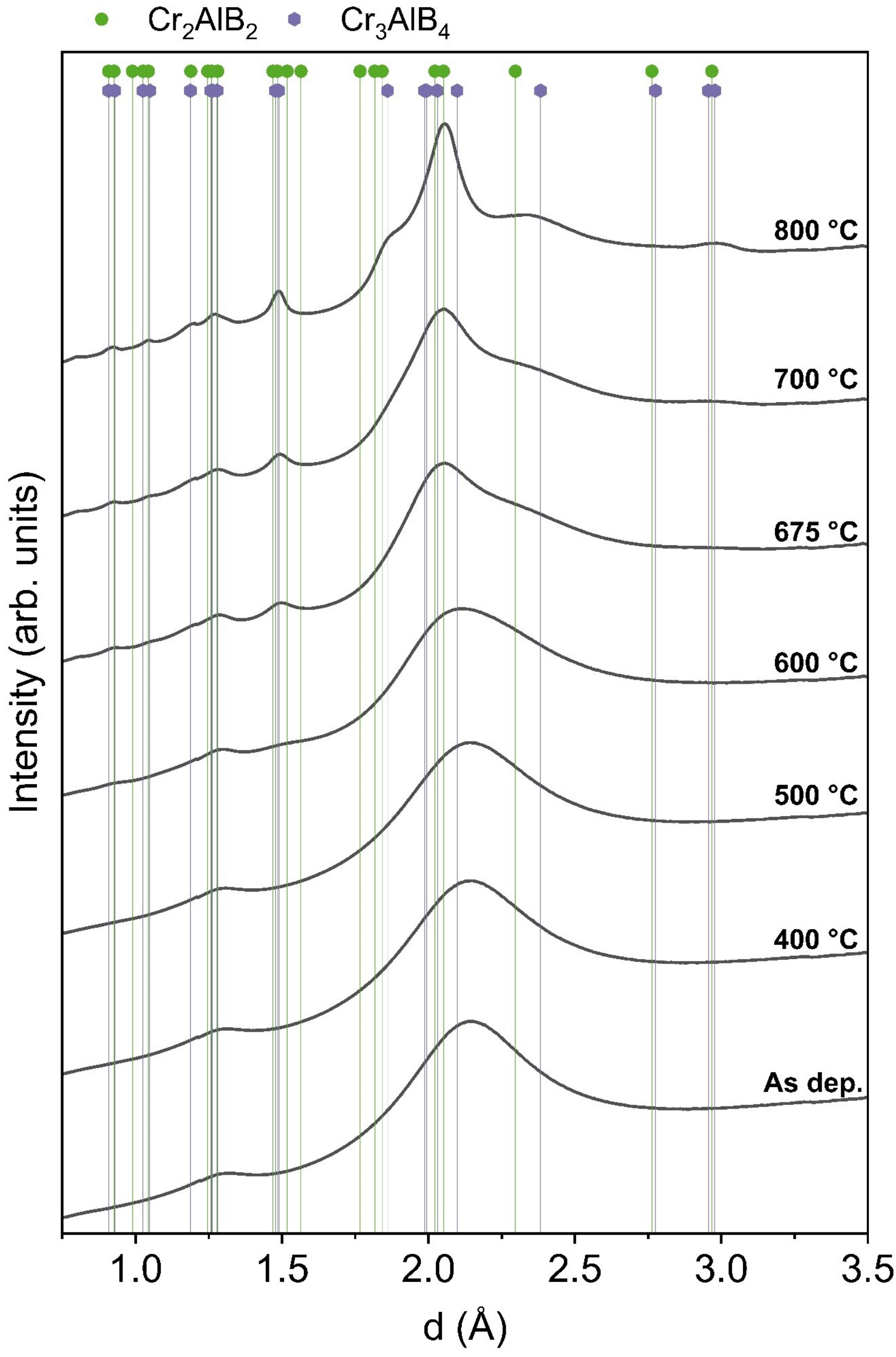
Supplementary Information

S 1: Results of resistance measurements for individual samples in as deposited and annealed state as well as thermal coefficient of resistance (TCR) obtained from cooling curves in the contact-based measurements.

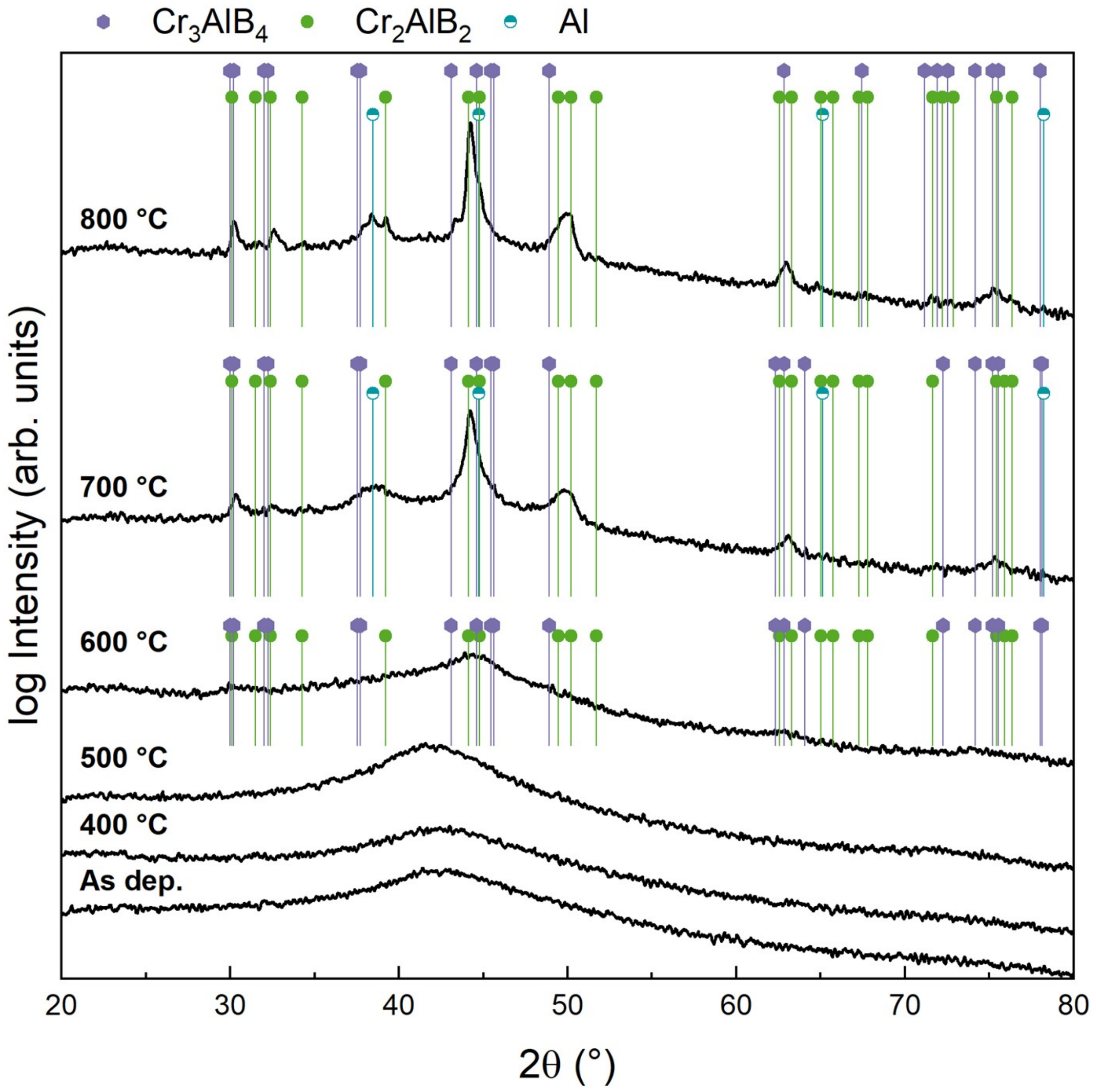
Annealing temperature [°C]	Resistance contact-based as dep. [Ohm/sq]	Resistance contact-based annealed [Ohm/sq]	Resistance contactless as dep. [Ohm/sq]	Resistance contactless annealed [Ohm/sq]	TCR [1/°C]
400	3.5	3.6	4.7	4.9	-5.3E-05
500	3.4	3.4	4.9	4.8	-1.2E-04
600	3.5	2.9	4.8	4.0	-1.5E-05
700	3.5	1.1	4.8	1.6	3.1E-04
800	3.5	0.8	4.8	1.2	3.6E-04

S 2: Chemical composition determined *ex situ* by ERDA measurements for samples annealed to the indicated temperatures.

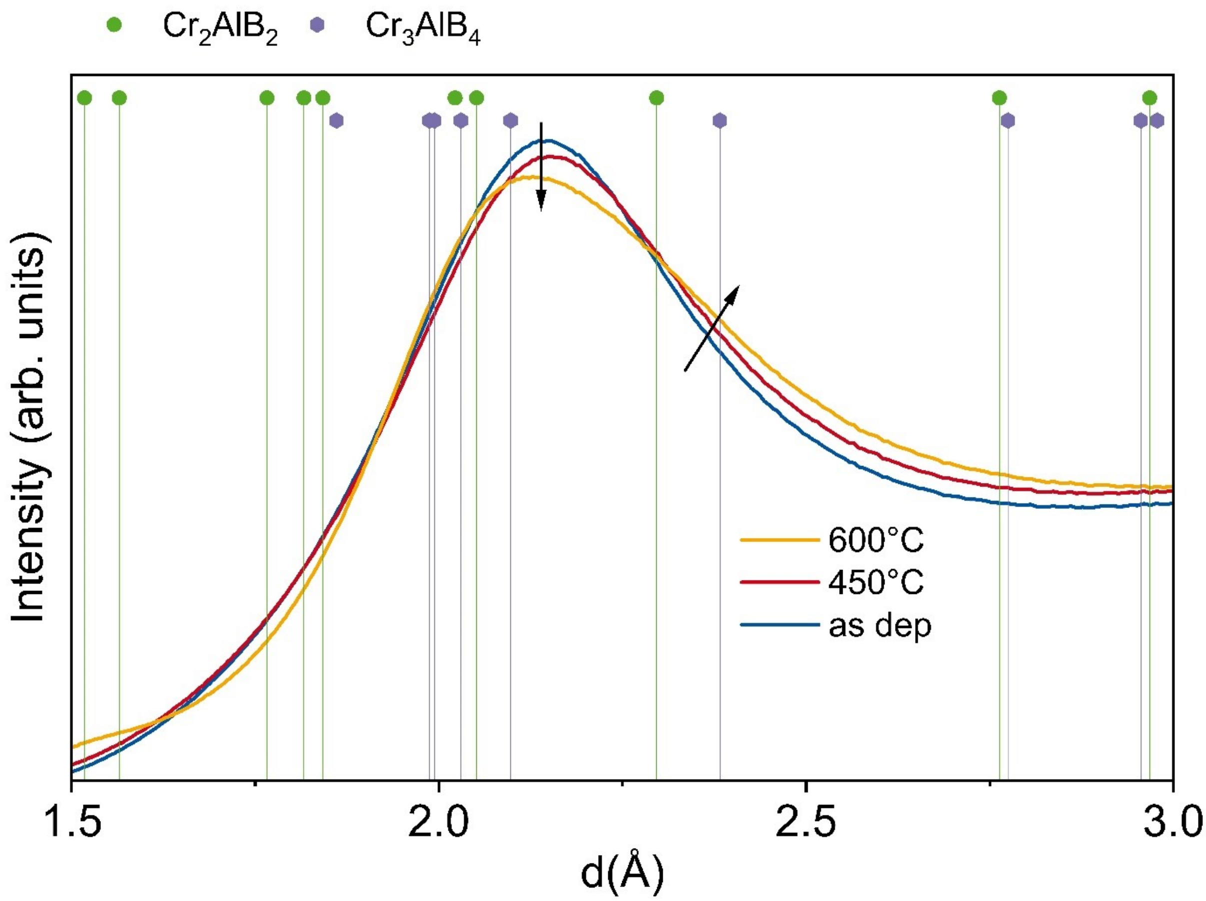
Annealing Temperature [°C]	**Composition**
As dep.	$Cr_{0.34}Al_{0.31}B_{0.35}$
400	$Cr_{0.37}Al_{0.31}B_{0.32}$
500	$Cr_{0.35}Al_{0.31}B_{0.34}$
600	$Cr_{0.35}Al_{0.31}B_{0.34}$
700	$Cr_{0.36}Al_{0.31}B_{0.33}$
800	$Cr_{0.35}Al_{0.30}B_{0.35}$



S 3: Integrated SAED patterns for various temperatures extracted during *in situ* annealing with no background subtraction performed. The data were corrected for thermal expansion. Up to 400 °C, no change to the amorphous as deposited state can be seen, while at higher temperatures the formation and grain growth of Cr_2AlB_2 and Cr_3AlB_4 can be seen.



S 4: Full 2θ range of X-ray diffraction carried out for samples annealed at the indicated temperatures. Formation and growth of MAB phases Cr_2AlB_2 and Cr_3AlB_4 can be observed.

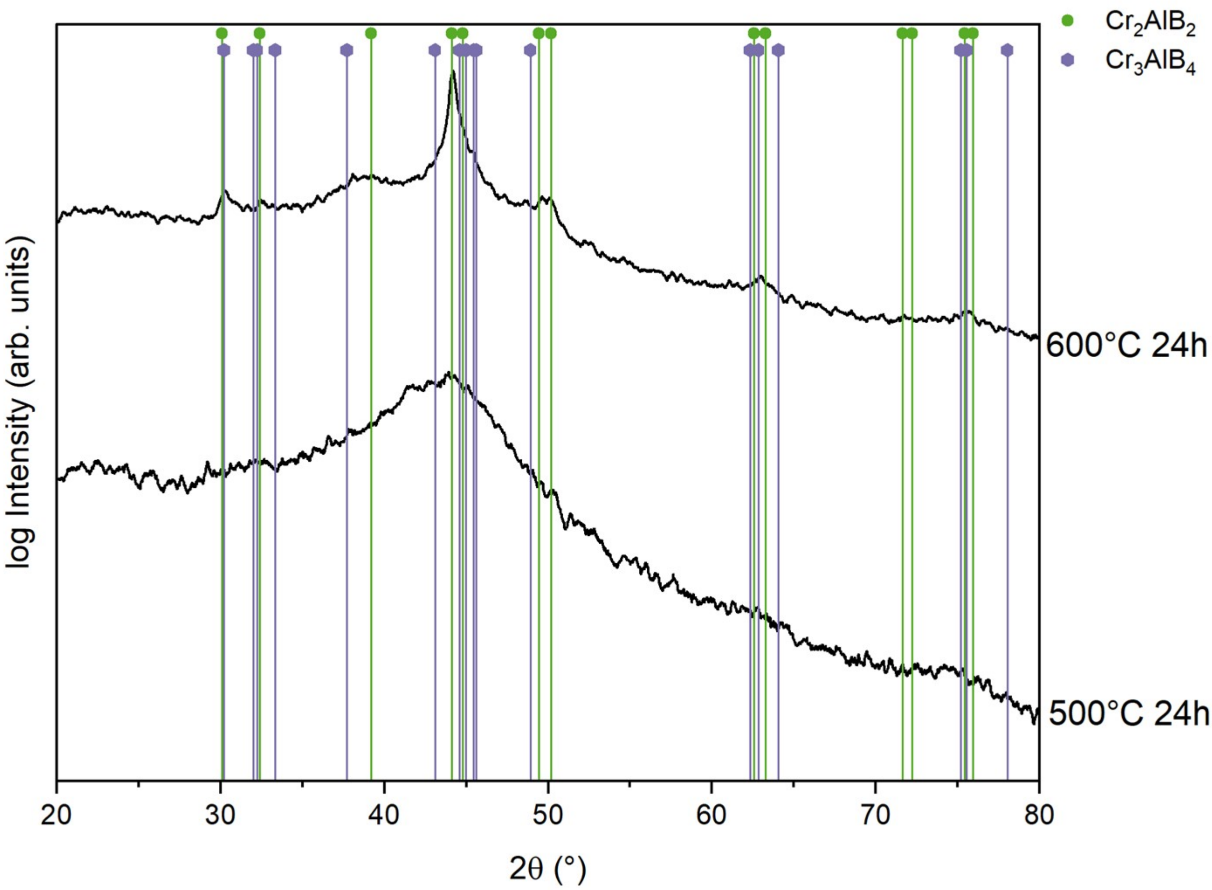


S 5: Comparison of the *in situ* SAED data for the as deposited state and at 450 °C between 1.5 and 3 Å. A shift in the ratio of the intensities below 2.25 Å and above 2.25 Å indicate the formation of a crystalline phase out of the predominantly amorphous matrix.

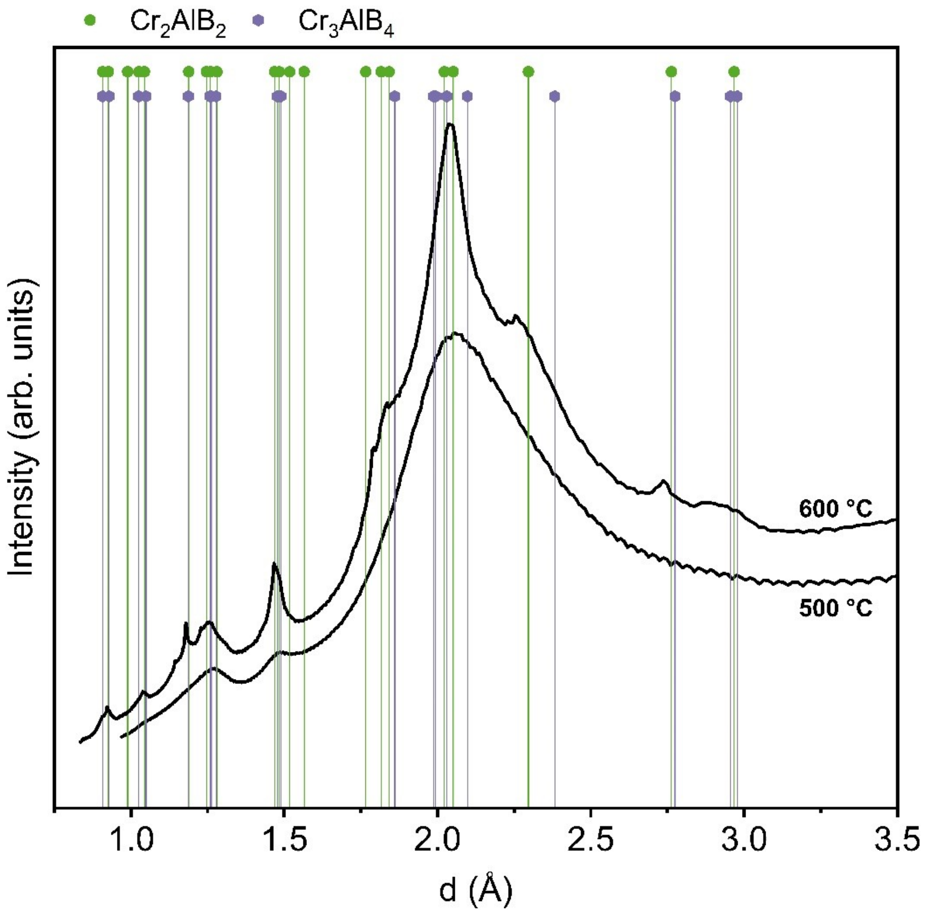
More detailed analysis of phase formation

To further study phase formation between 450 and 600 °C, longer annealing experiments with holding times of 24 h at 500 °C and 600 °C have been conducted. While SAED data of the sample annealed at 500 °C only reveal the formation of a crystalline Cr-Al-B phase (Figure S 7), the formation of the Cr_2AlB_2 MAB phase at this temperature is clearly shown by HRSTEM in Figure S 8a. This can be rationalized by the reported calculated enthalpies of formation predicting Cr_2AlB_2 to be energetically favored over Cr_3AlB_4, even though the experimental chemical composition here differs from the theoretically assumed [1]. However, due to the low reported energetic difference (0.044 eV/atom) between both phases, concurrent formation of Cr_3AlB_4 cannot be fully ruled out at this temperature.

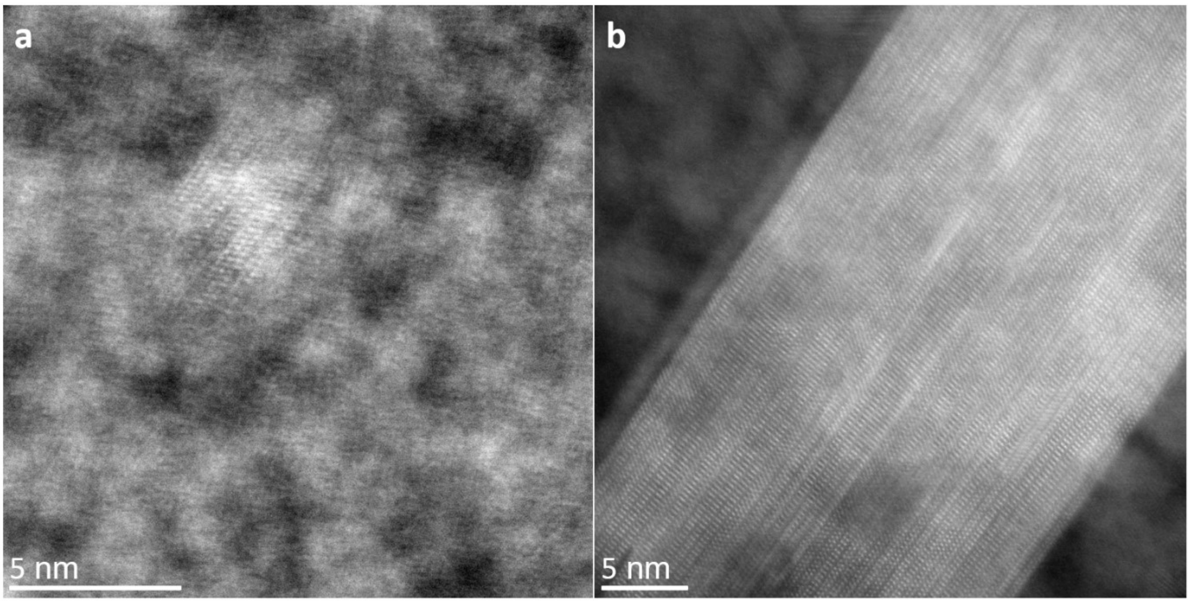
After annealing at 600 °C, the formation of both Cr_2AlB_2 and Cr_3AlB_4 can be observed (Figure S 7, Figure S 8b), whereby the observed phase fraction of Cr_2AlB_2 is significantly larger compared to Cr_3AlB_4. The higher amount of Cr_2AlB_2 correlates with the higher DSC peak intensity of the first transition (orange colored region Figure 2) and with the lower energetic barrier of formation, while the lower fraction of Cr_3AlB_4 correlates with the second transition (blue colored region Figure 2) and the slightly higher enthalpy of formation.[1] All of the above indicates that the first transition observed here (orange colored region Figure 2) corresponds to the formation of the Cr_2AlB_2 MAB phase, whereas the second transition (blue colored region Figure 2) corresponds to the formation of the Cr_3AlB_4 MAB phase while concurrent formation due to structural and energetic similarity cannot be fully ruled out.



S 6: XRD measured of samples annealed for 24 h at the indicated temperatures to narrow down phase formation. After 600 °C peaks corresponding to Cr_2AlB_2 start emerging which cannot be seen at the lower temperature.



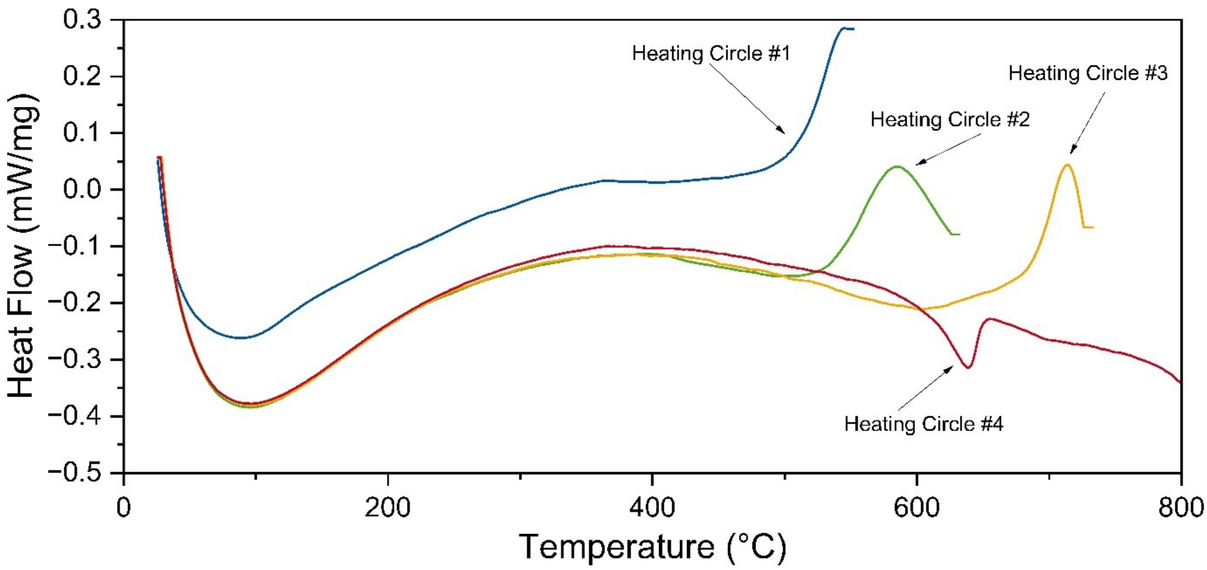
S 7: Integrated intensity of SAED patterns of samples annealed at 500 and 600 °C for 24 h. The formation of a MAB phase is indicated by the presence of three distinct peaks after 500 °C, while the presence of Cr_2AlB_2 and Cr_3AlB_4 as well as a significant increase in crystallinity and crystal size is visible after annealing at 600 °C.



S 8: *Ex situ* HRSTEM micrographs of 24 h annealed samples at 500 °C (a) and 600 °C (b). MAB crystallites containing the Cr_2AlB_2 phase are formed after 500 °C. The crystal size is significantly increased after 600 °C, whereby the Cr_2AlB_2 as well as the Cr_3AlB_4 phase can be identified.

S 9: Supplementary Video

Available electronically



S 10: DSC curves for repeated heating. In addition to the peaks corresponding to exothermic amorphous crystalline transformations (heating cycles 1 to 3), an endothermic peak corresponding to Al melting can be observed in the 4^{th} heating cycle (red curve).

References

1. Khazaei M, Wang J, Estili M, et al. Novel MAB phases and insights into their exfoliation into 2D MBenes [10.1039/C9NR01267B]. Nanoscale. 2019;11(23):11305-11314.