Analysis of the reaction runaway in Al/Ni multilayers with combined nanocalorimetry and time-resolved X-ray diffraction

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Grapical Abstract

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Abstract:
Self-sustaining runaway reactions in reactive multilayers exhibit heat-up with over $10^6$ K/s to temperatures of higher than 1000 °C, which defines unprecedented kinetic regimes for metallurgical phase transformations. The latter allows for developing alternative concepts for microstructure design. In order to explore the phase transformations in these kinetic regimes, we combine nanocalorimetry with time resolved synchrotron X-ray diffraction. Nanocalorimetry allows us to perform thermal analysis of ignition as well as the reaction runaway and to develop necessary and mandatory quantitative criterions for ignition. In order to trace the temporal phase evolution, we use time-resolved synchrotron X-ray diffraction. We heat the Al/Ni multilayers with 5000 K/s and find that Ni starts to diffuse into the Al layer at 271 °C. Ignition occurs, dependent on the bilayer thickness, at about 400 °C in the solid state and atomic diffusion is revealed as the dominating mechanism. During the runaway, samples heat up in three stages with maximal $10^6$ K/s to 1100 °C. Ni$_2$Al$_3$ is the first phase to form which starts to nucleate once Al melts. The majority of the intermetallic phase grows after the runaway reaction in a fourth stage and reaches its maximum during cooling. This trend of the temporal phase evolution eventually enables us to propose a mechanism exhibiting conceptual similarities with the exothermic dissolution mechanism recently suggested for self-sustaining reaction fronts in Al/Ni multilayers.

Keywords: aluminum/nickel; reactive metallic multilayers; nanocalorimetry; synchrotron X-ray diffraction; phase transformations;
1. Introduction

Reactive materials are composed of two or more exothermically reacting elements in intimate contact. They release the energy in milliseconds during so-called runaway reactions after thermal, electric, or mechanical ignition. This self-sustaining type of reaction is characterized by the formation of stable (low free energy) intermetallic product phases [1]. A number of two-component materials systems have been reported (e.g., Al/Ni [2,3], Al/Ti [4], Al/Ru [5,6]) to show these characteristics. Applications range from the synthesis of high-temperature materials [7], microscale heat sources for propulsion or rapid soldering in microelectromechanical systems [8–10] to self-healing approaches for thin films [11]. Despite their potential exploitation in practical application, reactive materials are interesting model systems to study the fundamental mechanism of phase formation in highly non-equilibrium conditions. Only recently, effects of the predominate high heating rate conditions (>10⁶ K/s) and steep concentration gradients, which prevail at the interfaces of reactive materials, comes more into focus of research [12,13]. Assuming that the ability of mass transport in form of diffusion is the rate-limiting process, the specific reaction attributes, i.e., reaction time and temperature, enable to study metallurgical phase transformations in new kinetic regimes [14]. Potential effects on the properties of the product phases can be harnessed to develop new approaches for microstructure design.

Whereas the rate of intermixing and the phase transformations are extrinsically controlled by temperature and time, they are intrinsically determined by the diffusion lengths and the properties at the interfaces, such as local concentration gradients or contaminations [15]. The latter parameters can be precisely controlled in reactive metallic multilayers – a subclass of reactive materials. The nanometric periodical stack of exothermically reacting metals, represent a well-defined structure, which is well suited for fundamental investigations [13,16,17]. Hence, Al/Ni metallic multilayers became the prototype material for this purpose. We also use Al/Ni metallic multilayers in this study to explore the phase transformations in the kinetic regimes of the ignition and the self-sustaining reaction runaway. Although first studies revealed the relevance of phase transformations at the Al/Ni interfaces [18,19], the underlying mechanisms and pathways for control of these events are not yet fully understood. These pioneering works led to the conclusion that reactive Al/Ni multilayers are interface controlled materials where the bilayer thickness \( \Lambda \) is a critical parameter. Whereas \( \Lambda \) is not related to the local chemical potential (e.g., concentration gradient or contaminations) at the Al/Ni interfaces, which also affects the onset of the runaway [18,20], \( \Lambda \) is related to the interfacial density and pinpoints the maximal intermixing distances. The ignition temperature \( (T_\text{ig}) \) increases with increasing \( \Lambda \) suggesting the relevance of interdiffusion [21–24]. Several studies found that ignition is a solid state phenomenon that passes through several stages of intermixing and subsequent exothermic solid-state transformations at the interfaces [22–24]. Based on these findings Fritz et al. developed an analytical model to calculate the ignition temperature based on the balance of heat release and heat losses [21]. However, an open question still addresses the underlying phase transformation driving the ignition and the runaway.

Ex-situ studies after slow heating (< 1.7 K/s) in a differential scanning calorimeter [16,17,25,26] and rapid heating (> 1000 K/s) in a nanocalorimeter (NC) [27,28], revealed a sequence of solid-state phase transformations starting with NiAl₃ or Ni₃Al₉. However, the samples did not ignite. The reaction power, determined by the composition, sample mass, interface density and heating rate is not sufficient to overcompensate the geometry dependent heat losses and self-sustain the reaction [21]. Therefore, it cannot conclusively stated whether the observed transformations dominate ignition and the following runaway. For example, Pauly et al. demonstrated in the Ru/Al system, that the formation of metastable phases might play a crucial role for ignition. The latter has not been observed during slow heating [6]. Another type of experiments used thermal, electrical discharge, and mechanical
shock ignition experiments [21,22,24] which allowed quantifying the kinetics of ignition and the determination of crucial parameters, such as $T_{ig}$ or activation energies of the underlying phase transformations. In case of local ignition, a self-sustaining reaction front propagates through the multilayer which is either explained by the precipitation of intermetallic compounds at liquid Al/solid Ni interfaces [29,30] or by an exothermic dissolution process [31,32], where solid Ni dissolves into molten Al. Despite these findings it is still unclear which transformations at the interface lead to ignition and dominate the early stages of the runaway reaction. Particularly the role of intermetallic phase formation for the initiation of the runaway reaction is still under debate [1,12,13,22].

The lack of advanced in-situ methods for correlated thermal and structural analysis with millisecond time resolution impedes an in-depth understanding [14,22]. Only few studies reported on the capability to reproduce conditions of ignition on the one hand and enable simultaneous structural characterization on the other hand [33–35]. In the past, stand-alone time-resolved synchrotron-X-ray diffraction already proved useful for exploring self-propagating reactions in nanolaminates [29,30] where, however, the temperatures and heating rates evolve uncontrolled. Nanocalorimetry is a novel, currently advancing method used to approximate the ignition and the reaction runaway under highly controlled conditions. It enables thermal analysis under heating rates up to $10^6$ K/s [36,37]. Hence, we choose time-resolved synchrotron-X-ray diffraction to probe the structural transitions and integrated nanocalorimetry for the thermal analysis. For the first time this methodical approach is used to investigate the underlying mechanism of ignition and the preceding runaway reaction in reactive multilayer materials.

Using this approach, which is explained in detail in Section 2, we are able to verify and thermally quantify the nature of chemical intermixing and phase formation under the relevant conditions. Whereas ignition of runaway reactions can be analysed via ex-situ experiments [6], an already self-sustaining reaction requires the in-situ analysis [29,30]. Accordingly, we analyse ignition in Section 3.1 and the reaction runaway in Section 3.3. Complementary the accessible phase transformations before ignition (solid-state) are discussed in Section 3.2. We will show that interdiffusion of Ni into the Al phase initiates the runaway reaction in Ni/Al multilayers for heating rates of about 5,000 K/s and significant phase formation starts close to the peak temperature of the reaction.

2. Materials and Methods
2.1. Materials
Al/Ni multilayers were deposited by magnetron sputtering in a Leybold Z 550 coater (Leybold GmbH, Germany) from pure elemental targets (purity: 99.999 %). The sputter rates of Al and Ni were 21 nm/min, and 39 nm/min, respectively. The base pressure of the vacuum chamber was better than 2×10^{-4} Pa and high purity argon (>99.999 % by volume) was used as a sputter gas. The multilayers were deposited on the calorimeter sensors through a shadow mask enabling the local deposition in the active area of the sensor downside. All specimens were fabricated with overall composition of 25 at.% attributed to the Al-rich side of the Ni-Al phase diagram. Since the runaway reaction is driven by the heat of formation, the stoichiometry of NiAl$_3$ was chosen to maximize the reaction power output ($\Delta H_{f}^{NiAl_3} = -38$ kJ/g at) [38]. The corresponding bilayer thickness $\Lambda$ was 166 nm (Al: 136 nm; Ni: 30 nm) and 83 nm (Al: 68 nm; Ni: 15 nm). In case of the in situ studies an overall sample thickness of 2 µm was chosen in order to enhance the diffracted intensity. All other experiments were carried out with a sample thickness of 1 µm.
2.2. Nanocalorimetry

For this study a custom made chip-based nanocalorimeter was used. All experiments were performed in a non-differential, quasi-adiabatic configuration. The sensor is based on the design presented by Allen et al. [39] and was fabricated under clean room conditions in cooperation with IMTEK, University of Freiburg. A schematic illustration of the sensor is shown in Figure 1 (a). A silicon frame serves as a support structure for a (150-nm- or 300-nm-thick) SiNₓ membrane. A 75-nm-thick Pt heater with a 10-nm-thick Ti adhesion layer is structured on top of the membrane. Two voltage probes contact the heater strip with a spacing of 3.7 mm. The section of the heater between the voltage probes is the sensing area. To prevent thermally induced changes of the sensor during calibration and the experiments, the sensors were annealed for 1 h at 700 °C in air [40]. Afterwards, every sensor was optically calibrated via an infrared pyrometer (KS 740 – LO, Kleiber Infrared GmbH, Germany) in a temperature range between 300 and 700 °C [41]. To confirm reliability of the optical calibration procedure, melting experiments of Al \((T_{m,Al} = 660.3\ \degree C)\) and Sn \((T_{m,Sn} = 231.0\ \degree C)\) nanoparticles with a diameter of 100 - 150 nm were performed. Measurements on six randomly selected chips results in a melting temperature of \(660.3 \pm 5.8\ \degree C\) for Al and \(231.3 \pm 2.4\ \degree C\) for Sn. To exclude sample thickness induced temperature errors complementary measurement were performed on 2000 nm-thick sputter-deposited Al thin films. As shown in the Supplementary, the onset of the melting signal validates the calibration for thick samples. Figure 1 (b) sketches the circuit controlling the power output and the data acquisition of the nanocalorimeter. A current pulse \(I(t)\) from a source measuring unit (PXIe-4138, National Instruments, USA) resistively heats the Pt-strip and indirectly the sample. Simultaneously the voltage drop \(\Delta V_{chip} = V_{chip}^+ - V_{chip}^-\) in the sensing area is measured with data acquisition unit (PXIe-4464, National Instruments, USA) at a rate of 200 kHz. This is used for both, the calculation of \(\dot{Q}_{in} = \Delta V_{chip} \cdot I(t)\) and the calculation of the electrical resistance \(R(T) = \Delta V_{chip} / I(t)\). Knowing the resistance-temperature relationship \(R(T)\), the temperature \(T\) of the sensor is given by:

\[
T = T_0 + T_1 \cdot (R(T) - R_0) + T_2 \cdot (R(T) - R_0)^2
\]

where \(T_0\) and \(R_0\) is the temperature and the resistance at ambient conditions and \(T_1, T_2\) are fitting constants. The recorded data were carefully smoothed using the Lowess algorithm [42]. All experiments employ heating rates of about 5,000 K/s.
2.3 Thermal analysis and the necessary criterion for ignition

Nanocalorimetry data can be used to determine the individual power contributions during the reaction of reactive materials. On this basis the critical temperature, where the ignition of the runaway reaction occurs is calculated. It is based upon theoretical considerations for combustion [43], which discuss entities like the reaction power \( \dot{Q}_{\text{rc}} \) and the heat losses \( \dot{Q}_{\text{loss}} \) and propose the following necessary criterion for ignition:

\[
\dot{Q}_{\text{rc}} > \dot{Q}_{\text{loss}} \; ; \; \dot{Q}_{\text{in}} = 0 \tag{2}
\]

Since the external input power \( \dot{Q}_{\text{in}} \) equals zero or becomes negligible compared with \( \dot{Q}_{\text{rc}} \) the reaction exhibits a self-sustaining behaviour. The nanocalorimeter enables us to measure the power contributions \( \dot{Q}_{\text{rc}}, \dot{Q}_{\text{loss}} \) and \( \dot{Q}_{\text{in}} \) during a reaction based upon the thermal description of the nanocalorimeter system (i.e. sensor and sample):

\[
C_{P,\text{total}}(T) \cdot \dot{T} = \dot{Q}_{\text{in}} + \dot{Q}_{\text{loss}} + \dot{Q}_{\text{rc}} \tag{3}
\]

and

\[
\dot{Q}_{\text{rc}} = C_{P,\text{total}}(T) \cdot \dot{T} - \dot{Q}_{\text{in}} - \dot{Q}_{\text{loss}} \tag{4}
\]

where \( C_{P,\text{total}}(T) \) and \( \dot{T} \) denote the total heat capacity of the system (sensor and sample) and the heating rate, respectively. We will use \( \dot{Q}_{\text{rc}} \) to define ignition. According to Equation (4) \( \dot{Q}_{\text{rc}} \) can be calculated if \( C_{P,\text{total}}(T) \), \( \dot{Q}_{\text{in}}(T) \) and \( \dot{Q}_{\text{loss}}(T) \) are known. As already shown \( \dot{Q}_{\text{in}} \) can be directly calculated using the applied Voltage \( V_{\text{in}} \) according to \( \dot{Q}_{\text{in}} = V_{\text{in}}I \). \( \dot{Q}_{\text{loss}}(T) \) is determined in slow heating calibration experiments (typically at a heating rate of 20 K/s) using identical sensors. Under slow heating conditions, it can be assumed that \( \dot{Q}_{\text{in}} = \dot{Q}_{\text{loss}} \) [13]. \( C_{P,\text{total}}(T) \) is determined in a temperature regime, where no reaction is detected (typically < 200 °C). To apply \( C_{P,\text{total}}(T) \) to the full temperature range of interest, we use the temperature dependent values for \( C_{P} \) of Al and Ni as listed in Dinsdale [44]. Finally, Equation (2) and (4) are utilized to calculate the critical temperature for ignition of the runaway reaction.

2.4 Synchrotron X-ray Diffraction

In order to identify the underlying phase transitions, which drive the reaction, in situ X-ray diffraction (XRD) experiments were performed. For this purpose nanocalorimetry experiments were conducted at the X04SA powder diffraction beamline of the Swiss Light Source (SLS) at the Paul Scherrer Institute (PSI) in Villigen, Switzerland [45]. The active area of the nanocalorimetry sensor was exposed with an X-ray beam in transmission geometry. A beam energy of 12.6 keV (0.984 Å) and a spot size of 500 x 500 µm² was selected. The diffracted signal was captured with a PSI developed 2D single photon counting detector (Eiger 500k) [46,47]. This setup enabled us to perform experiments with an acquisition rate of up to 22 kHz (\( t_{\text{frame}} = 45.5 \mu s \)). Up to now, comparable in situ nanocalorimetry experiments were limited to a XRD frame rate of 50 Hz [48–51]. However, we reduced the acquisition
rate in the current study to 5 kHz (200 µs/diffractogram) to optimize the signal-to-noise ratio. Since the dead time to read out the data during the experiment is only 5 µs, quasi-continuous measurements were performed. All experiments were performed in air under ambient pressure. Each sample was carefully aligned with a motorized XYZ-stage. In a post experimental step, the 2D data, were radial integrated and the background was fitted with a 3rd order polynomial function and subtracted from the data.

3. Results and discussions

Figure 2 shows a typical temperature profile of a runaway reaction for samples with \( \lambda = 166 \) nm. The temperature rises linearly due to external heating from 50 to about 350 °C with an average heating rate of \( 5690 \pm 130 \) K/s. At 425 °C \( (t = 59.2 \) ms) there is a sudden increase of the temperature indicating the exothermic runaway reaction. The peak temperature is 1134 °C where a maximum heating rate of \( 2.8 \times 10^5 \) K/s is measured. Afterwards, the sample cools down to 708 °C \( (t = 117.6 \) ms) by heat losses to the surrounding. The cooling curve shows two retardations (“plateaus”) at 1073 °C and 788 °C. Due to external heating up to \( t = 148.5 \) ms, there is a second temperature increase before the current is shut down completely. This solely externally driven temperature increase is approximated with a dashed line.

![Figure 2: Nanocalorimetry measurement with time-resolved X-ray diffraction. The sample with 25 at.% Ni (\( \lambda = 166 \) nm) was heated with an initial rate of 5690 ± 130 K/s. The temperature evolution during the runaway reaction is shown (black). The in-situ diffraction signal (red) give evidence of the formation of Ni_2Al_3 and NiAl_3 during the reaction.](image)

The temporal evolution of the corresponding diffracted X-ray intensity is shown in the background of Figure 2. Initially, four diffraction peaks were identified, namely Al \( (2\theta_{Al(111)} = 24.14°) \), Pt \( (2\theta_{Pt(111)} = 24.96°, 2\theta_{Pt(200)} = 28.97°) \) and an overlapping Al and Ni peak at \( 2\theta_{Al(111),Ni(200)} = 28.02° \). Since we measure in transmission, the Pt peaks are generated by the heating strip of the chip. Generally, a slight shift of the peak positions with increasing time (or temperature) is observed. We attribute this superimposed effect of thermal expansion and stresses due to the mismatch of the coefficient of thermal expansion in the layer stack. Once the sample is ignited at \( t = 59.2 \) ms, the Al peak disappears. Simultaneously, the formation of new diffraction peaks between 15.72° and 30.10° can be observed. These peaks were assigned to the Ni_2Al_3 phase. A second phase transformation occurs in a later cooling stage of the sample. Peaks belonging to the NiAl_3 phase can be identified for \( t > 77.6 \) ms.
3.1 The ignition

To analyse the phase transformations up to the point of ignition, we started with an nanocalorimetry based thermal analysis. While the temperature signal is not sensitive enough, $\dot{Q}_{\text{rec}}$ exhibits the required sensitivity to analyse the small amounts of heat released during the very early stages of ignition and the reaction runaway. Figure 3 shows the power contributions of Equation (3) as function of the temperature for $\Lambda = 166$ nm (Figure 3(a)) and $\Lambda = 83$ nm (Figure 3(b)).

![Figure 3: Power contributions according to Equation (3) during ignition and the early stages of the runaway reaction for (a) a $\Lambda=166$ nm sample and (b) a 83 nm sample. The reaction power $\dot{Q}_{\text{rec}}$, heat losses $\dot{Q}_{\text{loss}}$, input power $\dot{Q}_{\text{in}}$, and $C_p \cdot \dot{T}$ were measured by NC. The stars in (a) denote the results from quenching experiments where (a) and (b) indicate the two potential conditions for the definition of ignition (for details see text).](image)

Independent of $\Lambda$, the $\dot{Q}_{\text{rec}}$ signal shows first evidence for an exothermic reaction starting at 271 °C. $\dot{Q}_{\text{rec}}$ continuously decrease with increasing temperature and, dependent on $\Lambda$, accelerates substantially at about 381 °C and 340 °C for $\Lambda = 166$ nm and $\Lambda = 83$ nm, respectively. At the intersection between $\dot{Q}_{\text{rec}}$ and $\dot{Q}_{\text{loss}}$, the reaction power starts to overcompensate heat losses. According to Equation (1) the intersection temperature is considered as a necessary condition for ignition of the runaway reaction. The as-defined ignition temperature strongly depends on $\Lambda$. Increasing $\Lambda$ from 83 nm to 166 nm increases the ignition temperature from 409 °C to about 490 °C. Interestingly, we found ignition starts at temperatures lower than that defined by the necessary condition where $\dot{Q}_{\text{rec}} > \dot{Q}_{\text{loss}}$. Figures 3 (a) and (b) indicate the quenching temperatures of the experiments (filled and unfilled stars) and reveal that under the existing cooling conditions sample quenching is only possible below temperatures of about 410 °C for $\Lambda = 166$ nm and around 370 °C for $\Lambda = 83$ nm. In fact, the mandatory criterion $d\dot{Q}_{\text{rec}}$...
\[ \frac{d\dot{T}}{dT} > \frac{dQ_{\text{act}}}{dT} \]
seems to be more reasonable for the definition of ignition. To shed light on the underlying mechanism which drives ignition, we heated samples with \( \Lambda = 166 \) nm close to the ignition temperature up to \( 412 \) °C and quenched them with a cooling rate of \( \sim 2 \times 10^4 \) K/s by switching off the power supply. This experiment mimics hot plate approaches to explore phase transitions leading to ignition, such as those in [6,21]. Contrasting hot plate experiments, the NC approach, however, allows uniform heating with a constant heating rate. The phase composition of a quenched sample was analysed via ex situ synchrotron X-ray diffraction with an extended acquisition time of 20 s shown in Figure 4. At this acquisition time, a minimum thickness of detectable NiAl\(_2\) phase of about 2.6 nm was calculated. Elemental peaks of Al, Ni and Pt can be identified. We found no evidence for the Al-rich intermetallic compounds, such as Ni\(_2\)Al\(_9\), NiAl\(_3\) and Ni\(_2\)Al\(_3\), which are expected to form during heating. In addition, we do not observe a change in the integrated peak area of the Al peak at \( \sim 24.3^\circ \) (as-deposited: 1851 vs. quenched: 1846) indicating the absence or negligible phase formation in the course of quenching and cooling. The overlapping peak at \( \sim 28.1^\circ \) contains contributions of Ni (28.01°) and Al (28.15°). An increase of the overall intensity can be observed after thermal pulsing to 412 °C. The nanocalorimeter data in Figure 3 (a) suggest that atomic intermixing starts at \( 271 \) °C, probably dominated by asymmetric Ni diffusion into Al [15–17]. The latter should correlate with a decrease in intensity, particularly that of the Ni peak. Instead, we observe an increase of the overall intensity suggesting that thermally induced microstructure changes of the layers, such as grain growth, occur simultaneously and balance out the intensity decrease by intermixing.

![Figure 4: Ex situ X-ray diffraction before (black) and after (blue) quenching of a Ni/Al multilayer with 25 at% Ni (\( \Lambda = 166 \) nm). The specimen was heated up to 412 °C (close to ignition) via nanocalorimetry and subsequently quenched. While the temperature pulse causes a small peakshift of the Al peak, no phase formation of Ni\(_2\)Al\(_9\), NiAl\(_3\) or Ni\(_2\)Al\(_3\) is observable. Small peaks at an angle of 22.64°, 26.45° and 29.36° cannot be assigned to any of the latter phase. They probably indicate the presence of small amounts of Ti, Ti\(_2\)O, or Pt/Ti intermetallic compounds between Ti adherence layer and the heater strip.](image)

### 3.2 Accessible phase transitions before ignition

To reveal accessible phase transitions in this temperature range, we performed a multiple pulse experiment on a \( \Lambda = 83 \) nm multilayer specimen. The pulse length was kept constant at 100 ms, while the maximum temperature was incrementally increased. This results in a heating rate between 3,000 K/s and 5,000 K/s. After every pulse with the nanocalorimeter we recorded a long-acquisition diffractogram to determine the phase composition. To understand how the reaction rate change with
temperature, Figure 5 (a) plots $dH/dT$ vs. temperature for every pulse, where $dH/dT$ denotes the heating rate normalized reaction power. The successive pulses are labelled with P1-P12, whereby selected ones are highlighted with colour. Corresponding diffractograms are shown in Figure 5 (b). The reaction rate for Pulse 1 starts to increase at about 234 °C indicating an exothermic process in the sample. The change of heat release for Pulse 1 is more pronounced as that for the Pulses 2-5. Except for Pulse 1, $dH/dT$ evolves similarly up to 285 °C independent of the thermal history (number of pulses). For temperatures greater than 285 °C, $dH/dT$ decreases with the number of pulses for a given temperature. For Pulses 6–12 the reaction rate exhibits a substantially stronger exothermic behaviour with generally higher maximal reaction rates. In addition, the $dH/dT$ traces for the Pulses 7–12 start to form a step at around 285 °C which is observed at similar levels for all traces ($\approx 7.7 \cdot 10^7$ J/K).

To elucidate the reaction rate evolution with temperature, the underlying transformations have to be revealed. The diffraction patterns recorded after the individual thermal pulses are shown in Figure 5 (b). Up to Pulse 5 there is no evidence for phase formation. First indications of the formation of an intermetallic compound can be stated after Pulse 7, Figure 5 (b). NiAl$_3$ peak formation is observed where the peak intensities constantly increase with pulsing, while the peak intensity of the Al peaks generally decrease. At the same time, we note a significant increase in the maximal reaction rates, which are plotted vs. temperature in Figure 6. This allows us to define two temperature ranges with significantly different maximal reaction rates. Up to 342 °C, we observe low reaction rates. For temperatures > 389 °C the maximal reaction rates increase by a factor of 2.75 and roughly plateaus for Pulses 7–12. Between 342 °C and 389 °C we assume that the reaction rates show a transition with increasing values. The diffraction data enable us to infer the dominating mechanism in the mentioned temperature ranges. The diffraction data up to Pulse 5 do not indicate any phase formation. We note that interdiffusion has to precede phase nucleation in metallic multilayers. This is a common observation in conventional differential calorimetry experiments as well as nanocalorimeter experiments [13,52,53]. During heating, the heat of mixing for forming a solid solution is released which is recorded as a shoulder by the calorimeter instead of a strong peak as it is the case for phase transformations. The heat of mixing is usually substantially lower than the heat of phase formation, resulting in lower reaction rates during heating [17]. Hence, we conclude that interdiffusion perpendicular to the Al/Ni interfaces, probably asymmetric diffusion of Ni into Al, dominates up to
For temperatures > 389 °C the diffraction data indicate NiAl₃ growth. During growth, the heat of formation of the intermetallic is released which increases reaction rates. Thus, the transformation behaviour for temperatures > 389 °C is dominated by NiAl₃ growth.

In conclusion a low and high level dH/dT-regime can be identified with a transitional region in between (Figure 6). According to the discussion above we relate interdiffusion and phase growth to the low- and high-level regime, respectively. The diffractograms recorded in the transitional regime between 342 °C and 389 °C do not show any peaks which would indicate intermetallic phase formation. Nonetheless, we cannot ultimately rule out that minor amounts of intermetallic nuclei have been formed at the interfaces. At very low amounts of phase, the corresponding diffracted signal is not strong enough to be distinguished from the background/noise. Although not detected in the diffracted signal, the local formation of nuclei would explain the significant increase in dH/dT signal. Hence, we assume that local nucleation at the Al/Ni interfaces occurs in the transitional regime.

Figure 6: The maximal dH/dT values of every pulse shown in Figure 5 (a) vs. the corresponding temperature. The data points are averaged values to define the dH/dT levels representing the temperature range of interdiffusion and phase growth.

3.3 The reaction runaway

Once ignited, the reaction proceeds self-sustained where the temperature rapidly increases up to 1,100 °C within 400 µs. Figure 7 (a) plots the temporal evolution of temperature and heating rate after ignition took place and enables us to characterize the reaction runaway. The major temperature increase which indicates the runaway starts about 7.75 ms after the instant of time where the reaction became self-sustaining (indicated by the yellow star). The heating rate evolution during the runaway passes through four stages which was also found by Fritz et al. [22]. At 425 °C, the heating rate rapidly increases up to 3⋅10⁶ K/s before it decreases to 2⋅10⁶ K/s followed by a regime where the heating rate constantly increases again. After reaching the maximal temperature of about 1100 °C the sample cools down. Qualitatively, we observe the four stages in the heating rate signal during the runaway for several multilayers with the same total thickness and Λ (not shown here). Consequently, according to
the heating rate evolution, we define four stages characterizing the reaction runaway for Al/Ni multilayers with \( A = 166 \text{ nm} \) that were ignited with 5,000 K/s. The four stages are denoted in Figure 7 (a). To identify the corresponding phase evolution, the time-resolved diffractograms recorded in the corresponding \textit{in situ} measurement were plotted in Figure 7 (b).

**Figure 7:** (a) Temperature and heating rate during the runaway reaction. The heating rate signal allows the definition of four stages I-IV. The ignition of the runaway reaction is indicated by the star. (b) Corresponding X-ray diffraction patterns during the runaway reaction. There is a significant decrease of the Al peak intensity in stage III (\( T = 678 \text{–} 1134 \text{ °C} \)), which is attributed to the onset of melting. At the same time first indication for the formation of Ni\(_2\)Al\(_3\) can be detected. Ni\(_2\)Al\(_3\) growth continues in stage IV.

**Stage I**

The combined nanocalorimeter-XRD data (Figure 7b) does not reveal phase formation up to 426 °C (up to the end of Stage I). However, the thermal analysis shown in Figure 3 demonstrates that there is an exothermic reaction already starting at 271 °C. The incremental pulse experiments corroborate that ex situ. They also show substantial heat release without notable phase formation for the first pulse (Figure 5a and 5b). Since interdiffusion has to precede phase nucleation [52] we assume that the nanocalorimeter signal is the release of the heat of mixing due to atomic diffusion. This is also consistent with findings for slow [17] and rapid [13,33] heating. In addition, we calculated the critical ignition energy required to initiate the runaway. Based on the measurement of the external input power, we deduced an ignition energy of \( 1.80 \times 10^3 \text{ J/cm}^3 \), which is in good agreement with measured ignition thresholds for Al/Ni(V) multilayers [22]. Hence, the exothermic power based on the release of the heat of mixing is sufficient to initiate the runaway reaction and we conclude: interdiffusion is the dominant mechanism for ignition under the given heating rate of \( \sim 5,000 \text{ K/s} \). A similar conclusion for the propagation of a reaction front in free-standing Al/Ni multilayers was drawn in [32]. It is suggested that the formation of a liquid Al-rich solution drives the propagation of the reaction front and solid state diffusion occurs up to ignition. From a thermodynamic perspective they assumed that the heat released during this solution formation is sufficient to initiate the runaway and the massive formation of an intermetallic compound is not required. We note that interdiffusion may not be the only mechanism to initiate the runaway reaction. Depending on the heating rate, the resulting reaction power from diffusion may be too low to reach a critical amount of energy release. In these cases, additional phase nucleation might be required.
Stage II

The major temperature increase takes place in Stage II, well after the thermodynamically calculated ignition temperature of 338 °C. A delay between ignition and runaway is generally observed for reactive materials [22,23]. Figure 7 (a) reveals a delay of about 7.75 ms. In stage II, the temperature increases up to the maximum temperature and the heating rate takes the maximal value of about \(3 \times 10^6\) K/s at about 693 °C. The diffracted intensities of Stage I and II show no differences. We also observe that the onset melting of Al at 660 °C does not affect the heating rate and the diffracted signal, i.e. the intensity of the Al peak at 24°. We relate that to the substantially accelerated intermixing close to the melting point of Al. The Arrhenius temperature dependence of diffusion enhances intermixing and, accordingly, the exothermic heat release by the formation of a solid solution overcompensates the endothermic melting of Al - at least during the onset of Al melting.

Stage III

First significant changes in the diffracted signal can be observed in Stage III (Figure 7b). The Al peak intensity at 24° starts to decrease for temperatures > 693 °C. Simultaneously, first indications of the Ni2Al3 phase can be identified. The heating rate decreases to a lower level between \(2 \times 10^5\) K/s - \(2.5 \times 10^5\) K/s (Figure 7a). It is unlikely, that pronounced heat losses are causing this drop. The heat losses are negligible compared to the reaction power in this temperature range. Overcompensation of \(\dot{Q}_{loss}\) by \(\dot{Q}_{rc}\) already occurs at 404 °C. In fact, we assume that endothermic melting of Al now dominates the reaction, which is represented in the heating rate. The observed temperature of 693 °C is above the expected melting temperature of Al (\(T_m = 660 °C\)) indicating that the high heating rates of about \(2 \times 10^6\) K/s, result in superheating of solid Al [54]. We note that we cannot completely rule out, that lateral temperature inhomogeneities in the sample leading to this overestimation. With further reaction progress, the heating rate stabilises and increases again by the end of Stage III (Figure 7a). We assume that the heat release related to significantly enhanced Ni diffusion in liquid Al [55] dominates the observed heating rate behaviour. This is in reasonable agreement with findings for self-propagating reaction fronts in free-standing Al/Ni multilayers where a so called exothermic dissolution process drives the front through the sample [31,32]. This mechanism also assumes that prominent phase formation is observed during late stage of the runaway. The latter finding is also consistent with our observations, where the initial stages of Ni2Al3 formation occur in a relative late stage of the runaway (Stage III), see Figure 7b. The nucleation will also contribute to the heating rate signal. The diffractogram of Stage III indicates only minor amounts of Ni2Al3 showing that presumably intermixing of solid Ni into liquid Al dominates.

Stage IV

At the transition from Stage III to Stage IV there is a sudden drop of the heating rate and the maximal temperature of 1134 °C (\(t = 59.6\) ms) is reached. Within Stage IV the Al peak disappears, indicating that Al is completely in the molten state (Figure 7b). Stage IV is generally characterized by the Ni2Al3 formation as can be seen by the evolution of the respective diffraction peaks. Assuming that Ni2Al3 forms at least to some extend a continuous layer at the solid Ni/liquid Al interface the formation of the intermetallic impedes the Ni dissolution and makes Ni diffusion through the Ni2Al3 to the rate limiting process [56]. Consequently, there is a related drop in the heat release rate and the sample is cooling down. On a preliminary view, the formation of Ni2Al3 as first phase seems to contradict observations.
in other studies. Whereas nanocalorimetric experiments show the formation of NiAl \(_3\) \([13,33]\) in the solid state, studies of the self-propagating reaction on free standing reactive multilayers suggest NiAl as the first phase to form \([29,30]\) in saturated Al(Ni) liquid. It can be generally stated that the formation of Ni-enriched compounds, such as Ni\(_2\)Al\(_3\) and NiAl, is preferred for nucleation on liquid Al solutions. From the thermodynamic point of view, the formation of Ni\(_2\)Al\(_3\) \((\Delta H^\circ = -57 \text{ kJ/g at})\) and NiAl \((\Delta H^\circ = -59 \text{ kJ/g at})\) are preferred over that of NiAl\(_3\) \((\Delta H^\circ = -38 \text{ kJ/g at})\) \([38]\). In addition, the enhanced Ni diffusivity in liquid Al \((10^{-8}–10^{-9} \text{ m}^2/\text{s})\) \([31]\) compared to that in solid Al \((10^{-12}–10^{-16} \text{ m}^2/\text{s})\) \([57]\) allows the nucleation of Ni-enriched phases. We assume that Ni\(_2\)Al\(_3\) forms in the current study due to the overall composition of about 30 at.\% Ni.

The temporal evolution of the phase composition for extended durations in Stage IV gives valuable insight into the reaction mechanism. Hence, we used the \textit{in situ} data and calculated the integrated intensities of well separated diffraction peaks of Al, Ni\(_2\)Al\(_3\), and NiAl. Figure 8 plots the temporal development of the normalized integrated peak area together with the temperature profile. The majority (more than 50\%) of Ni\(_2\)Al\(_3\) forms after the peak temperature is exceeded during cooling to 882 °C. At 882 °C NiAl\(_3\) starts to nucleate, while Ni\(_2\)Al\(_3\) begins to decompose. Since the majority of Ni\(_2\)Al\(_3\) formation occurs during cooling, the Ni\(_2\)Al\(_3\) formation is not able to primarily contribute to the temperature evolution of the reaction runaway in Stage I-III. In turn, this corroborates the proposed mechanism deduced from Stage I-III where solid state diffusion ignites the runaway and the runaway itself is dominated by solid/liquid dissolution with Ni\(_2\)Al\(_3\) nucleation.

\textbf{Figure 8:} The normalized integrated peak area of Al, Ni\(_2\)Al\(_3\) and NiAl\(_3\) and the corresponding temperature signal for a runaway reaction. Peak fitting with Voigt functions were used to calculate the integrated peak area. The Ni peak is not shown due to strong overlapping with other peaks.

In order to explain the observation that the majority of Ni\(_2\)Al\(_3\) forms during cooling, we assume that the intermetallic phase covers Al/Ni interfaces during Stage III of the runaway. Only minor amounts need to be considered to assume a significant decrease of the diffusion rates for the in-diffusion of Ni which reduces the growth rate of Ni\(_2\)Al\(_3\). Since the exothermic $\dot{Q}_{\text{react}}$ is proportional to the diffusion and growth rate, $\dot{Q}_{\text{react}}$ is reduced and insufficient to maintain the temperature level. The sample starts to cool. However, cooling creates the thermodynamic driving force for the growth of Ni\(_2\)Al\(_3\). This post-
runaway reaction is also observed for self-propagating reaction waves in Al/Ni multilayers [31,32]. A similar phase formation behaviour was reported for macroscopic solid Ni/liquid Al reaction couples [58]. Although the lateral and temporal dimension differ in the latter study, the results show dissolution of solid Ni into liquid Al during heating and isothermal holding. Ni$_2$Al$_3$ formation does not occur. Only cooling creates the driving force for the Ni$_2$Al$_3$ formation.

4. Conclusion

We explored the ignition and the early stages of reaction runaways in reactive Al/Ni multilayers employing NC in combination with synchrotron X-ray diffraction. The samples were heated with an average heating rate of 5,000 K/s. Using nanocalorimetry based thermal analysis of the ignition, we show that atomic intermixing starts at 271 °C and, depended on the bilayer thickness, ignition occurs without phase formation at about 400 °C in the solid state. In addition, nanocalorimetry allows us to develop and test mandatory and necessary ignition criterions. Time-resolved synchrotron X-ray diffraction revealed that elemental intermixing is the major mechanism for runaway initiation under the given heating conditions. The analysis of the reaction runaway shows that melting of Al accelerates the intermixing, increases the reaction power and Ni$_2$Al$_3$ starts to form once Al starts to melt. The formation of Ni$_2$Al$_3$ instead of the most Al-rich one NiAl$_3$ (as it is usually observed during solid-state transformations) seems to be assisted by the formation of the solid Ni/liquid Al interface. The results suggest that the underlying mechanism has similarities to the exothermic dissolution mechanism recently proposed for self-propagating reactions in Al/Ni multilayers.

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Declaration of Interests

None
6. Literature


