Femtosecond laser ablation and nanoparticle formation in intermetallic NiAl

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Abstract

The ablation behavior of a stoichiometric intermetallic compound β -NiAl subjected to femtosecond laser pulsing in air has been investigated. The single-pulse ablation threshold for NiAl was determined to be 83 ± 4 mJ/cm² and the transition to the high-fluence ablation regime occurred at 2.8 ± 0.3 J/cm². Two sizes of nanoparticles consisting of Al, NiAl, Ni₃Al and NiO were formed and ejected from the target during high-fluence ablation. Chemical analysis revealed that smaller nanoparticles (1-30 nm) tended to be rich in Al while larger nanoparticles (>100 nm) were lean in Al. Ablation in the low-fluence regime maintained this trend. Redeposited material and nanoparticles remaining on the surface after a single 3.7 J/cm² pulse, one hundred 1.7 J/cm² pulses, or one thousand 250 mJ/cm² pulses were enriched in Al relative to the bulk target composition. Further, the surface of the irradiated high-fluence region was depleted in Al indicating that the fs laser ablation removal rate of the intermetallic constituents in this regime does not scale with the individual pure element ablation thresholds.

keywords: femtosecond laser ablation; intermetallic alloy; nickel aluminum; NiAl; nanoparticles; rapid solidification segregation

1. Introduction

Femtosecond laser ablation is useful for many applications such as the creation of nanoparticles [1], thin film deposition [2], micromachining [3–5], 3D tomography [6], microfluidics [4, 7], and

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measuring the properties of thin films on substrates [8]. Paramount to all of these techniques is a detailed understanding of the fluence-ablation relationship of the materials systems. While the scientific literature contains a plethora of ablation characterization studies for simple systems such as pure metals [9–15], polymers [16, 17], glasses [18, 19], and semiconductors [9, 20–22] and for complex systems such as superalloys [23, 24] and biomaterials [25, 26], there is a relative dearth of information regarding systems of intermediate complexity such as intermetallics and simple compounds [1, 21, 27]. For this reason an in-depth study of the ablation behavior of the intermetallic β -phase NiAl is presented. This material is of industrial importance as a model high-temperature coating system that forms a thermally grown α -Al₂O₃ oxide.

NiAl has a B2 crystal structure (ordered BCC, CsCl prototype) meaning that all Al and Ni atoms are bonded to their nearest neighbors by eight identical bonds. The ablation threshold of the pure constituent metals is 105-135 mJ/cm² for Al [9, 28] and 40-42 mJ/cm² for Ni [9, 11]. The present study demonstrates that the ablation behavior of the intermetallic NiAl is fundamentally different from either of its metallic constituents. Furthermore, the formation of nanoparticles in the ablation process in both the low-fluence and high-fluence ablation regimes has been studied.

2. Experiment

The fs laser ablation experiments were carried out in ambient air (22.8°C, 49-72% humidity) with a Clark MXR CPA Series pulsed Ti:Sapphire laser with a 1 kHz repetition rate, 780 nm wavelength, and 150 fs pulse width. The variability in the laser output power was below 1% within the time frame of the experiment. The beam was attenuated with a combination of neutral density filters and a rotating half-wave plate followed by a p-polarized beam splitter before being focused by a 500 mm focal length plano-convex lens to a $54.4 \mu\text{m } 1/e^2$ radius.

A series of single pulse and 100-pulse experiments were conducted with the laser orthogonally incident onto the target, which was stoichiometric NiAl polished to a mirror finish (0.25 μm diamond suspension). The range of laser power used was between 0.92 and 590 mW, corresponding to average fluences ranging from 0.010-6.4 J/cm².

After the laser experiments were conducted, the samples were ultrasonically cleaned in deionized water and methanol for two minutes before profile measurements and microscopy. The depth of the ablation craters was measured with a Veeco white light optical interferometer (WYKO NT1100).

The single-pulse experiments were measured using the phase-shifting interferometry (PSI) mode wherein the optical path length is altered and a lateral shift in the fringe pattern is used to create interferograms to determine the surface height profile. This measurement mode has sub-nanometer vertical resolution. The 100-pulse craters, which were approximately one hundred times deeper than the single-pulse craters and too rough for continuous fringe patterns required in PSI, were measured with the vertical scanning interferometry (VSI) mode. This mode scans the measurement head vertically and determines the height at which pixels are in maximum focus with approximately nanometer vertical resolution.

The surface profiles of the craters were post-processed to remove optical aberrations created by the measuring system and then a 10×10 pixel box surrounding the lowest point in the crater was used to determine the maximum depth, d_0 , for the experiment. The uncertainty in the depth was taken as the standard deviation of the 100 values within the box. In a few cases with high fluences, the depth was determined manually due to a large amount of missing data confounding the automatic fitting routines.

Initial surface chemical analyses were performed with an FEI Versa 3D microscope with a 30 mm EDAX Octane silicon drift detector. Further analysis of the nanoparticles ejected during ablation was performed with an FEI T20 TEM equipped with an EDAX Si(Li) Energy Dispersive X-ray Spectroscopy (EDS) detector and an FEI XL30 equipped with an EDAX Apollo X EDS detector. No attempt was made to quantify the amount of oxygen or carbon in the samples with EDS due to unreliable measurements with light elements. To collect a sufficient quantity of nanoparticles for analysis, a series of twenty-five identical 100-pulse high-fluence regime or 1000-pulse low-fluence regime experiments were performed consecutively. A carbon support TEM grid (Formvar) was cut into a Pac-Man shape and held 1-3 mm away from the target approximately parallel to the surface. The laser beam passed through the “mouth” of the grid and irradiated the NiAl sample. Particles ablated from the target and impacted the grid to be analyzed by SEM and TEM. The crystal structures were analyzed using selected area diffraction patterns (SADPs) for various agglomerated particles. A gold standard was used to calibrate the TEM camera length. Powder diffraction simulations were carried out using JEMS for various metals, intermetallics, and oxides in order to determine the crystal structures.

3. Results

3.1. Ablation depth dependence on laser fluence

Figure 1 shows the experimental results from both the single-pulse and the 100-pulse series of tests as the maximum ablation depth, d_0 , per pulse as a function of average laser fluence, ϕ_{avg} , along with best fits as explained in Section 4. For the 100-pulse experiments, the ablation depth reported is the average depth per pulse. The diameter of the laser beam at focus is over 100 μm , so it is not expected that there are any steep edges affecting absorption or confining the ablated plume/particles because the aspect ratio of the crater is low (maximum depth in 100-pulse experiments is 10.5 μm).

3.2. Chemical analysis of the low-fluence ablation regime

As previously documented, the ablation behavior of many materials differs between the low-fluence and the high-fluence ablation regimes [10]. For metallic materials in the low-fluence regime, the ablated material is a liquid-like layer that is ejected from the surface without the formation of plasma [13, 29, 30] and leaves behind no appearance of surface melting. Laser-induced periodic surface structures (LIPSS) are formed with their orientation depending on the laser polarization after multiple pulses due to interactions with surface plasmons [30]. An example of LIPSS in NiAl is shown in Figure 3.

Energy dispersive X-ray spectroscopy (EDS) analysis of the center of the ablation crater produced after one thousand pulses with $\phi_{avg} = 250 \text{ mJ/cm}^2$ (upper inset of Figure 3) shows no significant deviation from the target composition, which was measured via EDS to be 50.3 ± 0.1 at% Al. However, analysis of the redeposition layer at the perimeter of the crater (bright contrast in the lower inset of Figure 3) shows 58.3 at% Al.

In addition, a high magnification EDS map was collected from the center of a low-fluence, one hundred-pulse crater made with a fluence similar to that in Figure 3. The signal from the peaks and valleys of the surface undulations (LIPSS) was segmented using the gray value from the associated electron image. The integrated composition of the peaks was measured to be 2 at% enriched in Al while the valleys were 2 at% depleted in Al compared to the average composition of the crater, which was the same as the bulk polished surface. Precise quantification of the chemical fluctuation is not possible with EDS due to the large interaction volume of the EDS signal in comparison

with the size of the LIPSS. This measurement is noteworthy, although prone to error due to the geometry of the surface as explained in Section 4.3.

Analysis of the TEM grid that collected material ablated from twenty-five, one thousand-pulse low-fluence ablation events (see red diamond in Figure 1) shows a thick film consisting of Ni, Al, and O atoms. At the edge of the film it was possible to distinguish clusters of smaller nanoparticles (1-30 nm) that will henceforth be referred to as “nanoclusters” and larger nanoparticles that were (100-200 nm). An SEM EDS point-scan analysis of four nanocluster groupings (such shown by the orange triangles in Figure 5) indicated a 54 ± 4 at% Al composition whereas five measurements of the nanoparticles gave 46 ± 8 at% Al (such shown by the blue squares in Figure 5). TEM analysis produced similar results. The film in bulk was found to be stoichiometric.

3.3. Chemical analysis of the high-fluence ablation regime

The high-fluence ablation regime is characterized by a melting appearance in the target and the detection of a laser induced breakdown spectroscopy (LIBS) signal [13, 29, 30], indicating the formation of plasma from the target. The target surface no longer forms LIPSS after multiple pulses, but rather has the appearance of a melted and re-solidified layer.

EDS spot scans were performed on a collection of nanoparticles remaining at the bottom of a single-pulse crater with $\phi_{\text{avg}} = 3.7 \text{ J/cm}^2$ (see Figure 4a) and a 100-pulse crater with $\phi_{\text{avg}} = 1.7 \text{ J/cm}^2$ (see Figure 4b) following high-fluence ablation experiments. The nanoclusters remaining in both craters are rich in Al compared to the target composition. The X-ray signal interaction depth is estimated to be approximately $0.5 \text{ }\mu\text{m}$ by Monte Carlo simulations [31], meaning that the EDS measurements are sampling some of the surface below the nanoclusters. For this reason, the composition of the nanoclusters is likely to be more enriched in Al than measured. In addition, Figure 4b shows the surface of the high-fluence irradiated area covered in nanoclusters, which interfere with measurements of the irradiated surface due to an enhanced signal caused by their spherical shape. For this reason, twelve spot scans were taken from both the particles and the irradiated surface of the crater in Figure 4b to acquire a statistical representation of the chemistry. The chemical composition of the nanoparticles on the surface was 51.4 ± 0.2 at% and 55 ± 1 at% Al for the single pulse ($\phi_{\text{avg}} = 3.7 \text{ J/cm}^2$) and 100-pulse ($\phi_{\text{avg}} = 1.7 \text{ J/cm}^2$) experiments, indicating that segregation increases with more pulses in the high-fluence regime.

The chemical composition of the nanoparticles that were ejected from the surface and impacted

the TEM grid during twenty-five, one hundred-pulse experiments at a fluence of 1.7 J/cm^2 (see red square in Figure 1) was measured *via* EDS in both the TEM and SEM. A typical TEM bright field image of the particles is shown in Figure 5. It is apparent that two populations of particles were present —those nanoparticles having a diameter approximately 100-200 nm and nanoclusters of particles with diameters in the range of 1-30 nm. The nanoclusters settled onto the grid in large agglomerates while the larger nanoparticles tended to be isolated. Fifty-three SEM EDS and fifteen TEM EDS measurements gave a composition $42 \pm 15 \text{ at\% Al}$ for the large particles and $56 \pm 12 \text{ at\% Al}$ for the nanoclusters, where the uncertainty is the standard deviation of all the measurements. No outliers were excluded from the analysis above. In addition, the combined nanoparticle and nanocluster chemical concentrations varied between the TEM grid spaces analyzed, suggesting an angular dependence to the ablation of Al and Ni atoms. Both the nanoparticles and nanoclusters were Al-rich compared to the target in some grid spaces and Al-lean in other grid spaces. However, regardless of the local composition in the grid space, the nanoclusters were always enriched in Al relative to the larger nanoparticles. Due to the experimental setup, it was not possible to quantify the spatial/angular dependence of the composition as in other studies [20, 32].

Selected area diffraction patterns (SADPs) were acquired on the agglomerates of nanoclusters and nanoparticles to determine the crystallinity and crystal structures. In all cases, both the nanoparticles and nanoclusters were determined to be crystalline. The best fit of the diffraction rings and lattice spacings from the SADPs suggested a combination of NiAl, NiO, Ni₃Al, and metallic Al. The patterns were evaluated against all intermetallic compounds in the Ni-Al binary and possible Ni-Al-O oxides, as shown in Table 1.

4. Discussion

The experimental results detailed above support three key ideas —that the fs ablation behavior of NiAl is distinct from both Ni and Al, that there is size-dependent segregation of Ni and Al in the nanoparticles and nanoclusters formed during pulsed laser ablation, and that there is preferential removal of Al from the laser target during high-fluence pulsed laser ablation.

4.1. Ablation thresholds

The two temperature model was used to fit the data from both experiments to the following dependencies [14, 15].

$$\begin{aligned} d_0 &= \delta \ln \frac{\phi_{\text{avg}}}{F_{\text{th}}^\delta} \\ d_0 &= l \ln \frac{\phi_{\text{avg}}}{F_{\text{th}}^l} \end{aligned} \tag{1}$$

where d_0 is the maximum ablation depth of the crater, δ and l are the optical and electronic heat penetration depths in the material relating to the low-fluence and high-fluence ablation regimes, and F_{th} is the threshold for the respective dependency. The data from the single-pulse experiments were fit using the weighted least squares method and the data in the 100-pulse experiments were fit using a modified weighted least squares method allowing for a transition region between the two regimes [that has zero weight](#). This modification was motivated by results such as in Figure 2 where both high and low-fluence regimes coexist in substantial fractions near the crossover between the two models. [The fit to the 100-pulse data determined the transition region to be 0.59-1.26 J/cm²](#). The best fit parameters are listed in Table 2.

As stated in Section 1, the single-pulse ablation thresholds of the pure constituent metals are 105-135 mJ/cm² for Al [9, 28] and 40-42 mJ/cm² for Ni [9, 11]. Interestingly, a simple rule of mixtures argument to estimate an ablation threshold in the range 73-89 mJ/cm² can explain the single-pulse ablation threshold of the intermetallic compound, which is 83 ± 4 mJ/cm². This is an unexpected agreement because the bonding of NiAl is stronger and more directional compared to Ni or Al, giving the intermetallic a much higher melting point than either of the constituents [33]. This result suggests that the fs ablation threshold is not directly linked to atomic stability in a material. Further, as discussed in Section 4.3, this result complicates the understanding of preferential ablation in the high-fluence regime.

The differences between the fitting parameters δ and l for the single pulse and 100-pulse tests are not significant whereas the differences in the thresholds, F_{th}^δ and F_{th}^l , are significant. This incubation effect has been studied previously [10, 34]. In both cases the threshold is lower for the 100-pulse experiment, which leads to a lower value of ϕ_2^* , the fluence at which high-fluence regime dominates. Following Mannion *et al* [10], one can solve for the incubation coefficient S in

$$F_{\text{th}}(N) = F_{\text{th}}(1)N^{S-1} \tag{2}$$

where N is the number of pulses incident on the sample and F_{th} is the ablation threshold. This gives $S = 0.95 \pm 0.01$ and $S = 0.84 \pm 0.02$ for the low-fluence and high-fluence regimes where the error results from propagation of the uncertainties in Table 2. These values are in good agreement with incubation coefficients reported for other metals ($S = 0.83\text{-}0.92$) [10, 34].

4.2. Size-dependent segregation of nanoparticles

As shown in Figure 4, nanoclusters remaining on the surface after a 100-pulse exposure are enriched in Al compared to the surrounding irradiated surface. While it is unlikely that the EDS technique is accurately measuring the true concentration of the particles, there is little doubt of the trend. The TEM and SEM analysis of the size-dependent segregation of particles ejected from the surface during a 100-pulse high-fluence or 1000-pulse low-fluence experiment has demonstrated that the nanoclusters tend to be rich in Al compared to the bulk composition while the larger nanoparticles tend to be Al-lean. The diffraction patterns of the nanoclusters were consistent with a combination of FCC Al, Ni_3Al , and NiAl . NiO did not improve the fit of the diffraction rings, but is likely present based on the presence of oxygen in the EDS signal.

To the authors' knowledge, this is the first observation of size-dependent chemical segregation in nanoparticle formation from fs laser ablation. This observation is in stark contrast to the analysis of other nanoparticle compounds such as PtPb nanoparticles formed *via* low-fluence fs pulsed laser ablation in methanol wherein the nanoparticles (measured *via* EDS, SAD, XRD) "reserved the composition of the bulk target," although it was noted that particles smaller than 30 nm were amorphous while those larger were crystalline [1].

There are a few possible explanations for this observation:

- (i) Ni, which has a higher melting and boiling point than Al, may nucleate from the cooling liquid-like or plasma phase first and grow into larger Ni-rich nanoparticles. The Al atoms have more time to coalesce into Al-rich vapor agglomerates from the Al-rich vapor/plasma plume because they cool to a lower temperature before condensing. They then re-solidify into clusters of small nanoparticles that are Al-rich without much time for particle growth.
- (ii) Al atoms will vaporize from both the hot target and ablated particles after the laser pulse because Al has a higher vapor pressure and lower boiling point than Ni. This leaves the surface and larger nanoparticles Al-depleted and provides a source for Al-rich nanocluster growth before settling on the TEM grid or inside the laser crater.

- (iii) There is plasma phase segregation of the Ni and Al atoms due to relative masses. The ions and atoms ejected from the surface collide with air molecules and the more massive Ni atoms/ions are less impeded by these collisions and travel in a narrower path than the Al atoms/ions. This causes a spatial segregation of Ni and Al particles because the Al particles are scattered to a larger volume. The resulting difference in particle density affects the relative potential for the nucleated particles to grow, meaning that it is expected that the lighter element (which is scattered to a larger degree) would form smaller nanoparticles.

As expanded upon in Section 4.3, the third possibility (mass-based segregation) is the most likely explanation for size-dependent segregation of the nanoparticles.

4.3. Target surface enrichment

As in Section 3.3, it was observed during the high-fluence multiple-pulse experiments that the composition of the surface of ablation craters in the target becomes increasingly depleted in Al. To further corroborate this observation, EDS analysis was performed on a 100-pulse very high fluence experiment ($\phi_{\text{avg}} = 6.4 \text{ J/cm}^2$) and found that the center of the crater had a composition of 40.5 at% Al that monotonically approached the bulk composition at the edge of the laser crater. In contrast, as stated in Section 3.2, pulsed laser ablation in the low-fluence regime did not cause the target to deviate from the initial composition. There are a few common explanations for the preferential removal of Al over Ni atoms from the target in the high-fluence ablation regime:

- (i) Al may become depleted from the target due to preferential evaporation from the hot surface of the target in the high-fluence region of the pulse. Al has a significantly higher vapor pressure than Ni and therefore has more time to evaporate after each laser pulse. Continued laser pulsing of the same spot will result in depletion of Al from the target and enrichment of Al in any nanoclusters that condense back on the target surface. Figure 4a corroborates this argument because the enrichment of Al in the nanoclusters from the single pulse is only 1.4% greater than stoichiometric versus 5% from 100 pulses at a lower fluence.
- (ii) There is diffusive segregation of Ni to the surface of the target upon cooling, which causes Ni enrichment near the surface only.
- (iii) The relative ablation rates of Ni and Al in the high-fluence regime *are not* dependent on their individual ablation thresholds (105-135 mJ/cm² for Al [9, 28], and 40-42 mJ/cm² for Ni

[9, 11]), but rather depend on some other property such as the respective vapor pressures at the temperatures of interest. According to the CRC handbook, $\log(VP_{Al}) - \log(VP_{Ni}) = 9.6 - 4.3$ over the range 500 to 1000 K [35].

It is relevant that previous low-fluence fs ablation studies in vacuum on the formation of CoPt (L1₀ structure) thin films observed consistent Co-enrichment in the deposited film and Co-depletion in the laser target (as measured *via* XRD) and attributed it to the large variation in vapor pressures [2]. Similar vapor pressured-attributed enrichment has also been observed with high-fluence ns pulsed laser deposition of Al-Sn (immiscible system) thin films in vacuum [36]. Further, a study on the low-fluence fs laser ablation in air of TiN found the irradiated zone to be depleted in N, which has a higher vapor pressure than Ti [27].

However, preferential ablation of one species based on vapor pressure is not always the case. High-fluence ns pulsed laser deposition films of NbAl₃ in vacuum were found to be “very nearly stoichiometric” [37, 38] despite an enormous difference in vapor pressure ($\log(VP_{Al}) - \log(VP_{Nb}) = 40.1 - 19.5$ over 500-1000 K [35]). Further, a study of the fs pulsed laser formation of PtIr nanoparticles in acetone found no deviation from the target composition [39] and a study of the fs pulsed laser formation of PbPt nanoparticles in methanol also found no deviation from target composition [1]. The difference in vapor pressures of these systems over the same temperature range is 11-5.6 and 36-16 orders of magnitude for PtIr and PbPt [35]. This suggests that vapor pressures are not the only controlling factor for enrichment of alloys and compounds during pulsed laser ablation and deposition.

A fourth possibility to explain the difference in ablation rates for the fs laser experiments is the difference in atomic mass between the elements. Some of the energy absorbed by the target during a laser pulse is converted into kinetic energy. Assuming that each atom inherits the same amount of kinetic energy, lighter elements/ions will obtain a faster velocity and therefore can travel further away from the target on average before condensing back into the solid phase. In the above examples, this simple argument explains the segregation behavior for all of the fs pulsed laser systems. The principal systems showing no preferential ablation during fs pulse laser experiments were PbPt and PtIr wherein the atomic mass difference of these systems is only about 2 and 6%. In systems exhibiting significant differences in relative atomic mass ($> 50\%$, e.g. CoPt, NiAl, TiN), the target was always depleted in the lighter element. Moreover, mass-based segregation was observed in fs

pulsed laser deposition of BaTiO₃ [32]. It was found that the lighter element, Ti, preferentially deposited at smaller angles compared to Ba, which segregated to wider angles. However, the authors did not specify whether the target experienced preferential removal of the lighter element. This argument does not explain the segregation in ns laser ablation, but femtosecond and nanosecond ablation experiments are fundamentally disparate because the fs pulse length is much shorter than required for atoms or ions to move. None of the fs laser pulse is absorbed by melted target or the vapor/plasma plume during ablation as it is in ns ablation [30]. **Therefore, mass-based chemical enrichment of the surface is the most likely explanation, although more experiments are needed to confirm this.**

To address the peak-valley chemical segregation observed in the LIPSS of the one hundred low-fluence pulse experiment, there are two likely explanations for Al enrichment at the peaks. The first option, there is near-surface diffusion or convective currents causing Al atoms to move to the peaks while Ni atoms preferentially move to the valleys. This movement could be due to a combination of dynamic strain, temperature, and pressure gradients involved in the fs laser ablation event. Recent hydrodynamical models based on Marangoni convection suggest that this is a feasible explanation for atomic segregation in the low-fluence regime [40]. Second, it is likely that the characteristic X-rays emitted from the valleys of the LIPSS will pass through the nearby peaks on the way to the EDS detector and so, on average, pass through more attenuating material than the X-rays emitted from the peaks of the structures. The signal from lower energy photons is more significantly shielded than the higher energy photons because mass attenuation coefficients of X-rays are a strong function of energy [41]. Therefore, the low-energy EDS signal from Al ($K\alpha= 1.48$ keV) is expected to be attenuated to a greater degree than the high-energy signal from the Ni ($K\alpha= 7.47$ keV) when measured in the valleys of the LIPSS. It is therefore possible that the EDS chemical segregation measurement is not accurate, but rather a figment of the surface geometry. However, the degree of segregation (± 2 at% Al) gives credence to the possibility that true surface segregation is occurring between the peaks and valleys of the LIPSS. Further studies of the fs ablation behavior of compounds are required to determine the true mechanism for the apparent chemical segregation.

Figure 6 shows a schematic summarizing the observed fs pulsed laser ablation behavior of NiAl in this study. In the high-fluence regime, the target becomes depleted in Al. Large nanoparticles

that are Al-depleted impact the TEM grid while groups of Al-rich small nanoclusters settle on the TEM grid and the target laser crater. In the low-fluence regime, the target composition does not change and similar size-dependent segregation is seen as in the high-fluence case. More controlled experiments of fs pulsed laser ablation of compound materials are needed to elucidate the nature and causes of size-dependent segregation and preferential ablation. Further studies of compound ablation behaviors as a function of fluence and ambient environment (vacuum, air, solvent) will be needed to elucidate these observations and determine whether or not atomic mass controls this behavior.

5. Summary and Conclusions

- i. The single-pulse fs laser ablation threshold of NiAl was distinct from both Ni and Al and was found to be $\phi_{\text{avg}} = 83 \pm 4 \text{ mJ/cm}^2$ with the transition to the high-fluence ablation regime at $\phi_2^* = 2.8 \pm 0.3 \text{ J/cm}^2$.
- ii. There is chemical segregation and departure from the bulk composition during the formation of the nanoparticles during both the high-fluence and low-fluence ablation regimes.
 - (a) The material that ejected from the target surface and deposited on a TEM grid as clusters of smaller nanoparticles (nanoclusters) tended to be rich in Al.
 - (b) The material that ejected from the target surface and deposited on a TEM grid as larger nanoparticles tended to be Al depleted.
 - (c) The small nanoparticles that adhere to the surface of the irradiated crater after multi-pulse or single-pulse experiments in the high-fluence regime tend to be rich in Al.
- iii. The surface of the target becomes progressively leaner in Al with high-fluence pulsed laser ablation. The surface of the target does not change composition during low-fluence pulsed laser ablation.
- iv. The crystal structure of both larger and smaller nanoparticles was consistent with a combination of FCC Al, NiAl, Ni₃Al, and NiO at high fluence.

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Appendices

A. Powder diffraction simulations

Selected area diffraction patterns (SADPs) were obtained using two different camera lengths in an FEI T20 TEM. A Au standard was used to calibrate the camera lengths. SADPs were taken both over large regions of the Cu (Formvar) grid, and over small groupings of nanoparticles. JEMS software was then used to simulate powder diffraction patterns of various phases along the Ni-Al binary systems, as well as other oxide phases commonly found in the Ni-Al system. The phase matching criteria was based primarily on d-spacings, but relative intensities were also considered.

SADPs and simulated patterns for the two best matching phases, NiO and β -NiAl, are shown in Figure 7. The NiO phase matched the higher intensity experimental diffraction rings very well. These included the (111), (200), (220), (311), (222), and (400) rings, as shown in Figure 7a. The simulated β -NiAl phase contains a (100) superlattice reflection with relatively low intensity, which matched the corresponding SADP well. In addition, the (111), (200), and (211) rings matched the SADP well with respect to d-spacings, as shown in Figure 7b.

The experimental SADPs and simulated ring patterns for the partially matched phases, including γ -(Al) and γ' -(Ni₃Al), are shown in Figure 8. The γ -(Al) simulated pattern matched the intensities of the nearby diffraction rings very well, but the lattice spacings are slightly smaller in the simulated pure Al compared to the experimental SADP, as shown in Figure 8a. The γ' -(Ni₃Al) simulated pattern d-spacings matched the most intense d-spacings from the SADP, but the intensities at each ring were not consistent with the SADP, as shown in Figure 8b. The (110) superlattice reflection matched the d-spacing from a very faint ring in the SADP.

Figure 1: The maximum ablation depth, d_0 , of NiAl as a function of the laser fluence with 150 fs pulses for single pulses (dashed blue line) and 100-pulses (solid green line). The 100-pulse data are presented as the average ablated depth per pulse. The ablation thresholds are 83 ± 4 and 65.3 ± 0.4 mJ/cm² for the single and 100-pulse experiments. The thresholds for the high-fluence ablation regime, defined by the intersection of the low-threshold and high-threshold lines are 2.8 ± 0.3 and 1.2 ± 0.2 J/cm² for the single and 100-pulse experiments. The red diamond and square ($\diamond, \square$) indicate the fluences at which nanoparticles were collected on TEM grids during multi-pulse experiments (250 mJ/cm² and 1.7 J/cm²).

Figure 2: A secondary electron image, 40° tilted view, of a 100-pulse fs ablation experiment of NiAl with $\phi_{\text{avg}} = 1.7 \text{ J/cm}^2$. This is the same ablation crater shown in Figure 4b. Inside the solid red line but outside the dashed yellow line, one can see the LIPSS, characteristic of low-fluence ablation, while inside the dashed yellow line the fluence has exceeded the high-fluence threshold as evidenced by the formation of nanoparticles and the presence of a re-solidified layer. The inset shows a magnified view of the center of the pulse crater (at 40° tilt) where the nanoparticles are more clearly visible.

Figure 3: Example of a NiAl ablation crater after one thousand pulses with $\phi_{\text{avg}} = 250 \text{ mJ/cm}^2$. The upper inset is a magnified image of the center of the crater and highlights the clearly defined LIPSS. The lower inset shows more detail of the Al-rich redeposition layer on the edge of the crater.

Figure 4: a. Example of the smaller nanoclusters that remained in the NiAl ablation crater after a single pulse with $\phi_{\text{avg}} = 3.7 \text{ J/cm}^2$. b. Example of nanoclusters remaining in the ablation crater after 100-pulses with $\phi_{\text{avg}} = 1.7 \text{ J/cm}^2$. This close up image is taken in plan view from the crater in Figure 2. The blue crosses (+) indicate points where the EDS measurements for the nanoclusters were taken and the orange asterisks (*) indicate the locations where the background target chemistry was measured. A total of four measurements of each type were taken for (a) and twelve of each type for (b). The uncertainty is the standard deviation between these measurements.

Figure 5: Bright field TEM image showing the bimodal distribution of particles created during a series of 100-pulse ablation experiments on NiAl. The laser fluence was 1.7 J/cm^2 , the same as in Figures 2 and 4b. The average composition and standard deviation of the four measurements of nanoclusters denoted by the orange triangles ($\triangle$) was found to be $72 \pm 5 \text{ at\% Al}$. The composition of four of the the larger nanoparticles, denoted by the blue squares ($\square$) was $46 \pm 19 \text{ at\% Al}$. The large variability in the large particle measurements was likely due to significant overlap and close proximity of the nanoclusters to the large nanoparticles.

Figure 6: A schematic of the observed ablation behavior for high-fluence fs pulsed laser ablation of NiAl. Following a number of laser pulses the TEM grid positioned parallel to the target has many tightly grouped Al-rich nanoclusters with diameter 1-30 nm. There also exists larger isolated nanoparticles that are Ni-rich. A large number of Al-rich nanoclusters remain on the surface inside the target crater after laser pulsing.

Figure 7: Simulated powder diffraction patterns overlaid on top of the experimental SADP of (a) NiO and (b) β -NiAl. These two phases matched the experimental SADPs well with respect to d-spacings, and partially agreed with the intensities for each d-spacing.

Figure 8: Simulated powder diffraction patterns overlaid on top of the experimental SADP of (a) $\gamma\text{-(Al)}$ and (b) $\gamma'\text{-(Ni}_3\text{Al)}$. These two phases matched the experimental SADPs well with respect to intensities, and partially agreed with the d-spacings.

Table 1: Phases and crystal structures investigated using simulated powder diffraction patterns compared to selected area diffraction patterns showing degree of agreement. Al and Ni₃Al show partial agreement due to a slight d-spacing discrepancy with the bulk phase. Figures of the measured and simulated diffraction patterns are in the Appendix.

Phase	Prototype	Space Group	Lattice Parameters (Å)	Match?
Al	Cu	Fm $\bar{3}$ m	$a = 4.049$	partial
Ni	Cu	Fm $\bar{3}$ m	$a = 3.524$	no
NiAl ₃		Pnma	$a = 6.598, b = 7.352, c = 4.802$	no
Ni ₃ Al ₅		P $\bar{3}$ ml	$a = 4.053, c = 4.904$	no
NiAl	CsCl	Pm $\bar{3}$ m	$a = 2.885$	yes
Ni ₃ Al	AuCu ₃	Pm $\bar{3}$ m	$a = 3.572$	partial
F-Al ₂ O ₃		Fd $\bar{3}$ m	$a = 7.914$	no
R-Al ₂ O ₃	Al ₂ O ₃	R $\bar{3}$ c	$a = 4.754, c = 12.990$	no
NiO	NaCl	Fm $\bar{3}$ m	$a = 4.178$	yes
NiAl ₂ O ₄		Fd $\bar{3}$ m	$a = 8.053$	no

Table 2: Weighted least squares fit [42] parameters for Eqn. 1. The uncertainties arise from the combination of errors in each individual measurement and the confidence of the weighted fit. ϕ_2^* is the intersection between the two dependencies, indicating the value at which the high-fluence ablation behavior dominates the material response.

	δ (nm)	F_{th}^δ (mJ/cm ²)	l (nm)	F_{th}^l (mJ/cm ²)	ϕ_2^* (J/cm ²)
1-pulse	10.3 ± 0.3	83 ± 4	56 ± 3	1470 ± 50	2.8 ± 0.3
100-pulse	9.5 ± 0.3	65.3 ± 0.4	50 ± 5	690 ± 60	1.2 ± 0.2