Laser Ablation of Al-Ni Alloys and Al-Ni Layer Systems simulated with Molecular Dynamics and the Two-Temperature Model

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Abstract. Laser ablation of Al-Ni alloys and Al films on Ni substrates has been studied by molecular dynamics simulations (MD). The MD method was combined with a two-temperature model to describe the interaction between the laser beam, the electrons and the atoms.

The challenge for alloys and mixtures is to find the electronic parameters: electron heat conductivity, electron heat capacity and electron-phonon coupling parameter. The challenge for layered systems is to run simulations of an inhomogeneous system which requires modification of the simulation code.

Ablation and laser-induced melting was studied for several Al-Ni compounds. At low fluences above the threshold ordinary ablation behavior occurred while at high fluences the ablation mechanism changed in Al$_3$Ni and AlNi$_3$ from phase explosion to vaporization.

Al films of various thicknesses on a Ni substrate have also been simulated. Above threshold, 8 nm Al films are ablated as a whole while 24 nm Al films are only partially removed. Below threshold, alloying with a mixture gradient has been observed in the thin layer system.

Keywords: laser ablation, molecular dynamics simulations, two-temperature model, aluminum, nickel, AlNi alloy, AlNi layers

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INTRODUCTION

Molecular dynamics simulations (MD) of laser ablation with femto-second pulses is well established nowadays [1, 2, 3]. To describe the interaction of the laser and the metal accurately, the molecular dynamics (MD) simulation method has to be enhanced by the two-temperature model (TTM) where electrons and the ions (or the lattice) are described by different temperatures [4].

Most studies of laser ablation to date deal only with pure metals. To our knowledge, there is only one publication on complex alloys [5], and a few on Au-Cu and Ag-Cu layer systems [6, 7, 8]. See also the femtosecond melting of Au-Cr layer systems [9, 10].

There are on the other hand very interesting studies of shock waves in AlNi multilayer materials [11, 12, 13, 14, 15, 16, 17]. They reveal exothermic reactions and alloying of the multilayer systems under shock wave treatment. Similar phenomena are expected to occur in the AlNi system under laser treatment.

Furthermore, nickel aluminides are technologically very interesting materials which may have better properties than steel for example. The melting points are higher than for pure aluminum, but they are lower than for pure nickel. The intermetallic phases
possess lattice structures which reduce the mobility of dislocations and defects and reduce diffusivity. This leads to superior mechanical properties at higher temperatures. The yield strength increases with temperature in contrast to steel. Increased thermal heat conductivity and corrosion resistivity renders them candidates for high temperature applications in airplanes and gas turbines. But these applications also require precise processing of the materials. This is were ablation with femto-second lasers comes into play.

Details of this work have been published already [18]. Therefore the method and results will only shortly be summarized. The influence of the materials anisotropy will be discussed and new results and analysis of Al films on Ni substrate will be reported.

**THE SIMULATION MODEL**

The basic equations of the two-temperature model are generalized heat conduction equation for the electrons and the atoms separately:

\[
\begin{align*}
C_e(T_e) \frac{\partial T_e}{\partial t} &= \nabla \left[ K_e \nabla T_e \right] - \kappa (T_e - T_a) + S(x,t) \tag{1} \\
C_a(T_a) \frac{\partial T_a}{\partial t} &= \nabla [K_a \nabla T_a] + \kappa (T_e - T_a) \tag{2}
\end{align*}
\]

Equations (1) and (2) describe the time evolution of the electronic \((T_e)\) and the atomic \((T_a)\) or lattice temperature within the material. \(S(x,t)\) is the external laser field. \(C_{e,a}\) are the heat capacities, \(K_{e,a}\) the heat conductivities, \(\kappa\) the electron-phonon coupling constant.

In general these physical properties are functions of \(T_e\) and \(T_a\). With these equations (1) and (2) the laser field is coupled physically meaningfully into the system: first the energy is brought into the electronic system via a source term \(S(x,t)\). Then the electronic system transports the heat into the bulk and at the same time interacts with the atoms.

To work on an atomic scale equation (2) has to be replaced by molecular dynamics. Instead of (2) the following equations of motion are solved together with (1) for each atom \(j\):

\[
\frac{m_j}{dt^2} = -\nabla_x U(\{x_k\}) - \frac{\kappa (T_a - T_e)}{C_a} \frac{m_j}{dt} dx_j. \tag{3}
\]

The velocity-dependent friction term represents the coupling between TTM and MD.

The differential equation (1) for the electrons is solved on a lattice by a finite difference scheme (FD). For pure metals and alloys all FD cells are equivalent.

**Generalization of the model**

The electron heat conductivity parameter \(K_e\) is a scalar function as long as the material is isotropic, cubic or nearly cubic which is the case for the AlNi system. In general equation (1) has to be generalized to a tensorial function. Fortunately Al\(_{13}\)Co\(_4\) can be treated as orthorhombic, thus only diagonal terms are required. But since Al\(_{13}\)Co\(_4\) is a layered material it strongly deviates from isotropy. The other electronic parameters
remain unchanged since no spatial gradients of the heat capacity and electron-phonon coupling are present in equation (1).

In the simulations of layered systems FD cells will be present with varying and mixed occupancy. The question is then how to find the correct averages for the electronic parameters.

The gradient term of the temperature in Eq. 1 can be replaced by the second derivative as long as the electron heat conductivity \( K_e \) is a constant. If \( K_e \) becomes position dependent it is computed as the harmonic average of two neighboring FD cells at \( x - 1 \) and \( x \) as recommended in [19]

\[
K_e = \frac{K_e^{x-1} K_e^x}{K_e^{x-1} + K_e^x}.
\] (4)

This definition works even if the heat conductivities deviate strongly. Thus it is possible to simulate the electron part of multi-component samples.

Usually, the inverse absorption length \( \mu \) of the laser radiation is regarded as a constant and the absorption is modeled by the standard Lambert-Beer-law. This approach is no longer valid for the layered systems. Therefore, the absorption length is replaced by an effective length. For example, a layer which absorbs twice as much energy as the reference layer is taken into account with twice its thickness. The energy absorbed in a certain cell is then computed by comparing the difference of the laser intensity to the left and right:

\[
\Delta E = \Delta t_{FD}(S(d_l, x) - S(d_r, x))
\] (5)

with the absorbed energy \( \Delta E \), FD-timestep \( \Delta t_{FD} \), laser intensity \( S \), position \( x \) and effective depths \( d_r \) and \( d_l \). The laser absorption can still be modeled by an exponential law \( \exp(\mu_{\text{eff}}d) \) with an effective inverse absorption length \( \mu_{\text{eff}} \). The dependency of the injected energy on the decrement of the laser power guarantees that the applied fluence \( S_0 \) is deposited in the sample.

### Simulation code and interactions

All simulations have been carried out with IMD, the ITAP Molecular Dynamics package which is described in detail in [20, 21] and for laser ablation in [3]. The program is available from github [22].

The atomistic interactions were modeled by EAM potentials. For the AlNi system a set of potentials was computed by Purja Pun and Mishin [23]. For Al\(_{13}\)Co\(_4\) the potentials [24] were computed by fitting effective potentials to ab-initio simulations with potfit [25].

### OVERVIEW OF LASER ABLATION OF AL-NI ALLOYS

Details of the laser ablation and laser induced melting have been presented in [18]. The pure phases and alloys Al, AlNi and AlNi\(_3\) are cubic. Thus the isotropic equations apply. Only Al\(_3\)Ni is orthorhombic but it weakly deviates from isotropy. Thus it is also treated
as an isotropic material. Fortunately, all required parameters could be obtained from literature except for the electron-phonon coupling constant which was calculated with the formula of Wang et al. [26]:

\[ \kappa = \frac{\pi^4 (k_B v_s n_e)^2}{18 K_e(T_e)} \]  

which gives the relation of \( \kappa \) to the velocity of sound \( v_s \), the electron density \( n_e \), and the electronic heat conductivity \( K_e(T_e) \).

### Results for the pure metals Al and Ni

The pure metals have been used as a benchmark for the generalized simulation program. The laser ablation and laser-induced melting results compare well with data from different sources, experiment and simulation.

### Results for the Al-Ni alloys

Laser ablation and laser-induced melting has been studied for the alloys Al\(_3\)Ni, AlNi, and AlNi\(_3\). Other intermetallic phases exist in the Al-Ni system but these are more complicated. The laser induced melting behavior has been simulated for several sample sizes. The melting depths increases as predicted by the well-known model of Preuss et al. [27] for fluences up to at least 1000 J/m\(^2\), but then levels off for the short samples. The ablation depth shows strong fluctuations but can also be modeled by the Preuss formula. At low fluences phase explosion is observed. For Al\(_3\)Ni the mechanism changes to vaporization at about 3000 J/m\(^2\). The same is true for AlNi\(_3\) at 900 J/m\(^2\). The behavior of this phase is more erratic, however, since it is accompanied by a phase transition from the orthorhombic phase to fcc. Only for AlNi\(_3\) it was possible to find some experimental data [28] but even these data had to be reanalyzed. The experimental data are rather close to the high fluence behavior observed in the simulations. A further discussion of the results of the other compositions is postponed due to the lack of comparable data.

### ANISOTROPIC MATERIALS

All the structures simulated in the Al-Ni-system where more or less isotropic. Thus no directional-dependent behavior was expected.

Previously we also studied a strongly anisotropic material, the approximant Al\(_{13}\)Co\(_4\)[5] of the decagonal quasicrystal phase Al-Ni-Co. The structure of this alloy features properties of periodic and quasiperiodic solids: it consists of quasiperiodic planes stacked periodically with a period of 14 Å. Therefore the heat conductivity \( K_e \) possesses a directional dependency, while the smaller effect on the electron-phonon coupling is neglected. Due to the great interest in quasicrystals it was possible to find
the electronic parameters for this structure. Interactions were computed with potfit as described in the section about the interactions.

The melting depth turned out to be less than half the size of aluminum at the same fluence. The melting depth was at most 20% higher perpendicular to the layers than in the layers, although the heat conductivity perpendicular to the layers was about 2.2 times larger than in the layers. An explanation for the weak direction dependence is given by the relatively high electron-phonon coupling of Al-Co (five times larger than that of aluminum). This leads to a very short electron-lattice relaxation time \( \tau_{el-ion} \approx C_e/\kappa \) which shortens the diffusive heat conduction of the electrons considerably.

**LASER ABLATION OF AL FILMS ON NI SUBSTRATE**

Two cases of an Ni substrate covered with Al were studied. The thin layer sample is covered by a 8 nm Al film, the thick layer sample by 24 nm Al. A sketch of the observed mechanisms is given in Fig. 1. In the figure at the center alloying was found below threshold, at the bottom the roll off of most of the Al-layer was observed above threshold with a sheet of an AlNi mixture staying behind.

**FIGURE 1.** Top: initial state of the thin layer sample before irradiation, center: irradiation below threshold, bottom: irradiation above threshold. Green: Al, red: Ni. Picture prepared with OVITO [30].

For the layer simulations samples have been prepared with about two million atoms and a volume of \( 230 \times 11 \times 11 \text{ nm}^3 \).

**Results for the thin Al-layer**

Since Al has a much lower melting point than Ni it will melt already at a low fluence of less than 40 J/m\(^2\). Together with the lower heat conductivity of Ni this leads to a plateau in the melting depth vs. fluence at 8 nm until Ni starts to melt at 250 J/m\(^2\). In general the behavior is as given by the model of Preuss et al. [27].
The ablation fluence of the Al film is 500 J/m$^2$ at a depth of 10 nm, which indicates that the Al film is ablated as a whole. Below the ablation threshold voids are formed in the Al film and phase explosion occurs above threshold.

**Results for the thick Al-layer**

The exponential decay of the absorbed laser fluence causes the absorption of the major part of the energy within the Al-layer. The melting of the Ni-substrate occurs preferably by propagation of the energy through heat conduction.

The melting depth again shows a plateau at about 24 nm if plotted vs. fluence. This is caused by the complete melting of the Al-layer at fluences of about 60± 20 J/m$^2$ until Ni starts to melt at a fluence of 360 J/m$^2$. The general behavior is as predicted by the model of Preuss. The reason for the slightly higher damage threshold as compared to the thin layer is the higher heat conductivity of the thick layer which removes energy from the top of the sample. This behavior has been confirmed in experiment [29].

Below the ablation threshold bubbles are formed in the Al-film. Ablation now occurs at 460 J/m$^2$. The ablation depth indicates that the Al-layer is again ablated completely. But the behavior changes above about 900 J/m$^2$. The ablation depth decreases. The reason is that the Al is vaporized now, but part of the material precipitates on top of the liquid Ni-substrate. A mixed zone is generated where nickel aluminides can form.

Thomas et al. [6] have studied 30 nm gold films on copper substrate. This system is similar to our thick Al layer. They observe sub-surface melting of the copper which they attribute to the higher electron-phonon coupling of gold. In the Al-Ni system such an effect was not observed. The reason are the melting temperatures. The electron-phonon coupling of Al is also larger than that of Ni, but the melting temperatures of Au and Cu differ by about 20% while the melting temperature of Al is about half the value of Ni measured in Kelvin.

**Formation of nickel aluminides**

The formation of nickel aluminides in the thin layer sample is shown in Fig. 2 at depths from 5.5 to 10.5 nm. Obviously the atom fractions are not constant but vary with depth. The reason is diffusion. It has to be kept in mind that Al is still molten down to 7.5 nm, while Ni has solidified largely. Starting at 8.5 nm a fairly regular structure is seen which indicates the formation of non-stoichiometric Al-Ni mixed crystals. Deeper into the sample the Ni fraction increases and the formation of AlNi$_3$ crystals and the substitution of Ni by Al occurs. Diffusion will further generate all kinds of AlNi alloys with varying concentration. Obviously this will not be the equilibrium crystal structures.

Fig. 3 shows the transition from the Al film to the Ni substrate after irradiation. The transition is asymmetric, since the Al film is liquid while the Ni substrate is recrystallized. Thus the mobility of the minority atoms is different in addition to different diffusivities. The number of vacancies in the solid is measurable, but is at most 2%. In
FIGURE 2. Slices through the sample at depths 5.5, 6.5, 7.5, 8.5, 9.5, 10.5 nm (left to right, top to bottom). A few defects are indicated in the 8.5 and 9.5 nm slices. Picture prepared with OVITO [30].

The liquid vacancies cannot be defined. In contrast to the observations of Cherukara et al. [17] in shock simulations no preference for the formation of Al$_3$Ni was found. The density in the liquid phase is that of liquid Al and increases linearly starting at 4 nm until it reaches the density of solid Ni at 10 nm. The transition region is about twice as wide as the region observed by Thomas et al. in AuCu under similar conditions.

FIGURE 3. Transition of the composition from the sample surface to the bulk. The original surface was at 8 nm, after irradiation the interface between liquid and solid lies at about 7 nm. Vacancies cannot be defined in the liquid part.

Wu et al. [7] have studied the lattice misfit and misfit dislocations in a silver on copper system with a 30 nm film of silver. After irradiation they observe a lattice-mismatched
interface below an epitaxial layer, both in the copper substrate, covered by a 6 nm mixing region. The 2 nm epitaxial Cu layer is nearly perfect bcc, while the mixing region shows a transitional centered tetragonal structure. In their simulation the Ag and part of the Cu substrate was molten. In the present simulations of Al on Ni no lattice misfit was studied. The number of Ni to Al unit cells was optimized before irradiation for minimal distortion leading to a fraction of Ni:Al = 27:31. After the irradiation the recrystallized structure is only 1 nm thick while the Al film is still liquid and will turn amorphous if quenched. There is no epitaxial layer although AlNi also solidifies into the bcc or B2 phase. However, there are lattice defects visible in the 8.5 and 9.5 nm slice in Fig. 2. Since they are diagonal in the slices it is most likely that they represent stacking defects in the fcc structure.

**Shock simulations**

The group of Strachnan [11, 15, 16, 17] has intensively studied Al/Ni nanolaminates with different geometries and composition, among them layered systems which are close to the Al films on Ni presented here. They observe the exothermic reaction between Al and Ni as expected. No additional heat production was observed here. The reason might be that Strachnan et al. start with cold samples which are heated by shock wave and the reaction, while laser irradiation adds a large amount of energy, such that the additional reaction energy adds only a small effect. To find the effect would thus required precise simulations with increasing fluences, which have not yet been carried out.

**SUMMARY AND CONCLUSIONS**

Molecular dynamics simulations of laser melting and ablation of the AlNi system have been reported. For pure metals experimental and simulation results from other references could be reproduced. For the nickel aluminides reasonable results where obtained which largely confirm to the general formula of Preuss et al. [27]. The interesting result in this context is the changing ablation mechanism, in Al3Ni accompanied by a phase transition. Unfortunately, there are only very few experimental results available for these materials. Hopefully this study will encourage experiments for these materials.

First results on coatings of Ni by Al have been obtained. There alloying of a single layer system has been observed with a mixing gradient. Further studies of parallel and orthogonal multi-layer systems would be very interesting. The expected exothermal reaction of the nickel aluminate formation has not yet been studied in detail since the present results did not indicate an extraordinary behavior as expected from the shock wave studies.

Except for the weakly anisotropic orthorhombic Al3Ni all the structures studied here are isotropic due to the cubic symmetry. In Ref. [5] the MD+TTM model has been applied to strongly anisotropic Al13Co4 with orthorhombic crystal structure. Then the heat conductivity has to be treated as a diagonal tensor. However, it turned out that the ablation properties did only weakly depend on the crystal direction.
In conclusion, it was found that it is very involved to study complex materials with the combined MD+TTM model. It is difficult to obtain all the electronic and coupling parameters which for simplicity have been treated here as constant. In general the parameters should be a function of the electron temperature. The same is true for the atomic interactions which should also be electron-temperature dependent. First attempts to calculate such interactions exist, but only for pure metals.

From an experimental point of view there exists no obstacles to study other materials and compounds which might be more relevant. From an industrial point of view there is great interest to treat for example steel instead of pure iron. The major advantage of the MD+TTM method is the atomic resolution. Not only global observables like melting depths and ablation thresholds can be studied but also the ablation mechanisms, phase transformation, defect formation, and so on. Thus it is worth the effort.

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