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High-Speed Electron Microscopy of Nanocrystallization in Al–Ni Films by Nanosecond Laser Pulses

By

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Dedicated to Professor Dr. JOHANNES HEYDENREICH on the occasion of his 65. birthday

Nanocrystallization of 3 Al : 1 Ni and Al_3Ni films is realized with short laser pulses (7 and 20 ns), and traced by high-speed transmission electron microscopy on the nanosecond time scale. Composite films melt within the laser pulse above a threshold fluence, and solidify to a mixture of nanocrystalline Al, Al_3Ni, and Al_3Ni_2 at cooling rates of $\approx 10^8$ K/s. Al_3Ni crystals are amorphized by a laser pulse within 5 ns above a threshold temperature and with negligible absorbed latent heat. A nanophase composed of Al, Al_3Ni, Al_3Ni_2 is quenched, as in composites. The reported effects should occur in all intermetallic compounds having a complex lattice like Al_3Ni, and composites of equal overall composition.

3 Al : 1 Ni und Al_3Ni-Schichten wurden mit Laserpulsen (7 und 20 ns) erstmalig nanokristallisiert und die Umwandlungen mit der Hochgeschwindigkeits-Transmissionselektronenmikroskopie verfolgt. Misch-Schichten werden durch einen Laserpuls oberhalb einer Grenzfluenz während des Pulses geschmolzen. Sie erstarren zu einem Gefüge aus nanokristallinem Al, Al_3Ni, Al_3Ni_2 bei Abkühlraten von $\approx 10^8$ K/s. Al_3Ni Kristalle amorphisieren innerhalb von 5 ns oberhalb einer Grenztemperatur und mit vernachlässigbarer latenter Wärme. Auch bei Al_3Ni wird ein Gemisch aus Al-, Al_3Ni-, Al_3Ni_2-Nanokristallen eingefroren. Diese Effekte sollten bei allen intermetallischen Verbindungen mit komplizierten Gittern wie Al_3Ni auftreten sowie bei Elementgemischen der gleichen Zusammensetzung.

1. Introduction

Aluminides of transition metals are currently studied because of their importance as reaction products of barrier layers and Al metallization in Si-based integrated circuits [1], as light weight alloys with potential application at high temperatures and as protective layers with increased resistance against wear and oxidation [2]. The Al–Ni system attracted particular interest, and the phase formation occurring in very different treatments has been studied.

Steady state thermal annealing up to 1000 K of Al–Ni multilayers resulted in solid state diffusion-controlled growth of intermetallic compounds with Al_3Ni appearing first [1 to 5]. A self-sustaining, 'explosive' reaction was observed to produce the intermetallic compound $AlNi_3$ or a mixture of Al_3Ni and Al_3Ni_2 in pulse-heated multilayers [4] and ball-milled [6] and shock-loaded [7] elemental powders of the overall composition 1 Al : 3 Ni or 3 Al : 1 Ni, respectively. The compounds were assumed to crystallize from a transient melt generated by the liberated heat of reaction.

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Quenching of Al–Ni systems from highly non-equilibrium states produces intermetallic compounds in the case of Ni-ion implantation at elevated temperatures [8], or chemical disordering and amorphization in the case of inert gas ion irradiation at lower temperatures [9 to 12]. Quenching of Al–Ni vapors and liquids by sputter deposition [13, 14] and melt-spinning [15] results in disordered f.c.c. and amorphous solids.

When surfaces of bulk aluminium or nickel covered with Ni or Al powder, respectively, are remolten by continuous or millisecond pulse laser radiation [16 to 19] a hard cladding is grown, which consists of Al_3Ni, Al_3Ni_2 crystals and a disordered f.c.c. solid solution.

Combined high heating/quenching rates as are achieved with nanosecond laser pulses have been so far applied only to Ni-rich alloy films. Pulse-molten films solidify by heterogeneous nucleation and thermal diffusion-controlled growth of disordered f.c.c. and $AlNi_3$ crystals [20, 21]. A quite different phase formation was expected on the Al-rich side of the Al–Ni system for kinetic reasons, as the Al-rich intermetallic compounds have complicated lattices and a eutectic is present there [22]. This paper reports the observed phase transitions induced by nanosecond laser pulses in 3 Al : 1 Ni and Al_3Ni films which completely differ from those in 1 Al : 3 Ni films. Thin films were chosen as specimens, since the phase transitions can be followed here with a high space/time resolution by high-speed transmission electron microscopy [23].

2. Experimental Procedure

Composite and sandwich Al–Ni films with an overall composition 3 Al :1 Ni and a thickness of 90 to 110 nm were evaporated in a cryotrapped vacuum at 10^{-4} Pa onto formvar-covered glass slides. They were stripped-off in chloroform by dissolving the formvar and mounted on electron microscope grids. These free-standing films consisted of Ni and Al crystallites with sizes of 10 to 30 nm. They were transferred into a high-speed transmission electron microscope, modified for real time investigations down to the nanosecond range [23]. Large ordered Al_3Ni crystals were grown in the electron microscope by intense electron beam irradiation of the film.

Phase transitions in the thin film specimen were triggered by a focused Gaussian pulse from an attached Q-switched and frequency-doubled Nd : YAG laser. Two different pulse widths, 7 ns and 20 ns FWHM, were used. The diameter of the laser spot on the specimen was 15 μm FWHM.

The kinetics of the laser pulse induced phase transitions were traced either by recording the intensity of a selected region within the bright-field electron image with photomultiplier and storage oscilloscope, or by short exposure time imaging. In this mode of microscopy the specimen was illuminated with an intense electron pulse from a laser pulse driven electron gun for 20 ns. The short exposure image was recorded by an intensified CCD-camera and stored in a memory.

3. Experimental Results and Discussion

3.1 *Composite and sandwich 3 Al : 1 Ni films*

If the peak fluence of a nanosecond laser pulse exceeds a threshold the following scenario has been observed for all hitherto studied metals (Al, Ni, Au, Fe, Ti, 1 Al : 3 Ni). The film is completely molten within a central zone of the laser spot during the laser pulse. The melt is surrounded by a 'slush' zone, where the volume fraction of the liquid continuously drops

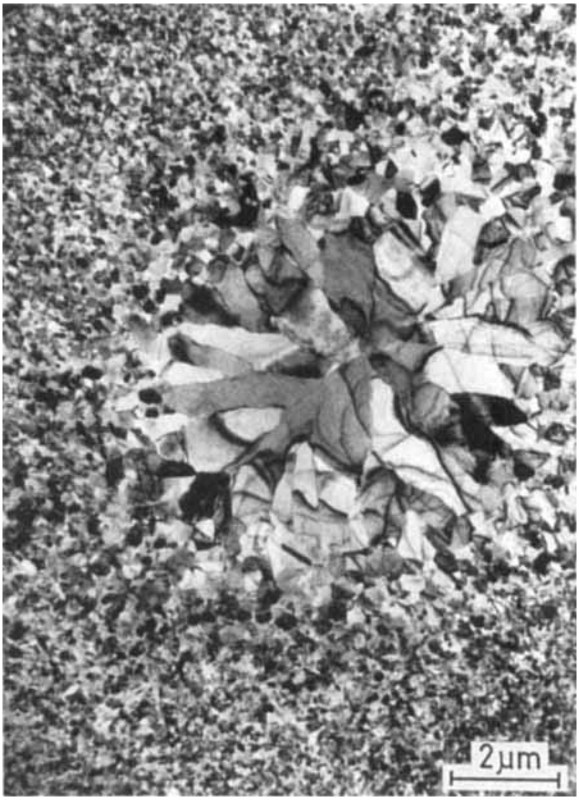

Fig. 1. Ordered and disordered $AlNi_3$ crystal plates which typically grow in laser pulse molten 1 Al : 3 Ni films within 4 µs (laser pulse 20 ns FWHM, ≈ 1 µJ)

with increasing distance from the center. Solidification starts by heterogeneous nucleation in the 'slush' zone. It continues by inward growth of crystal plates with velocities 1 to 5 m/s, signalizing a supercooling of about 10 K at the phase boundary [21]. Crystallization is completed within 4 µs after the laser pulse and a texture is produced as shown in Fig. 1. The original 'slush' ring-shaped zone is characterized by equiaxed crystals and has a width of 0.5 to 1 µm.

Now, 3 Al : 1 Ni films, which are treated by a laser pulse with a fluence exceeding a certain threshold, also melt during the laser pulse (Fig. 2), as Ni-rich films do. That the 'amorphization' is actually a liquefaction and is not a solid state reaction, is proved by the fast material transport occurring within the laser pulsed region (Fig. 3). But contrary to Ni-rich melts, this 3 Al : 1 Ni melt does not solidify by growth of large crystal plates. Instead, a nanocrystalline phase is quenched at the center of the laser spot, composed of Al, Al_3Ni, and Al_3Ni_2. Fairly large Al_3Ni and Al_3Ni_2 crystals are produced at the boundary of the melt (Fig. 2). Very probably they heterogeneously nucleated on those Ni crystals, which were not molten in this colder region.

Obviously, growth of large crystals of the equilibrium intermetallic compound Al_3Ni, having a complicated lattice, is impossible for kinetic reasons if the cooling rate is in the order of 10^8 K/s (Fig. 4).

If the laser pulse energy is below the threshold to melt the Ni crystals of the 3 Al : 1 Ni composite film completely, these crystals are alloyed by the liquid Al. A nanocrystalline

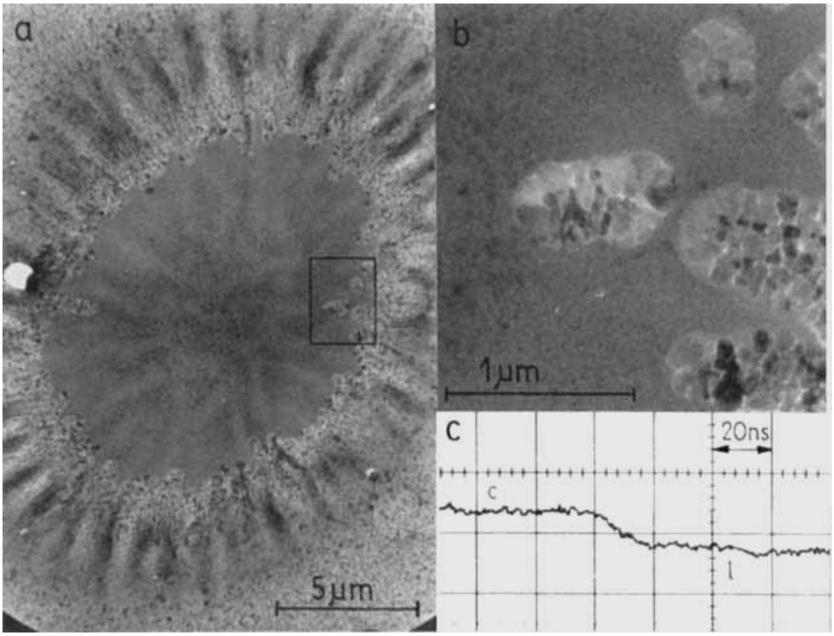

Fig. 2. Melting of a 3 Al : 1 Ni composite film by a laser pulse and quenched nanophase (laser pulse 20 ns FWHM, ≈2 µJ). a) Final texture; b) marked region in a) at an increased scale, showing large Al_3Ni and Al_3Ni_2 crystals grown in the cooler boundary of the melt some 10 µs or later after the laser pulse; c) image intensity within the molten region in a) during the melting process (c original crystalline solid, l liquid)

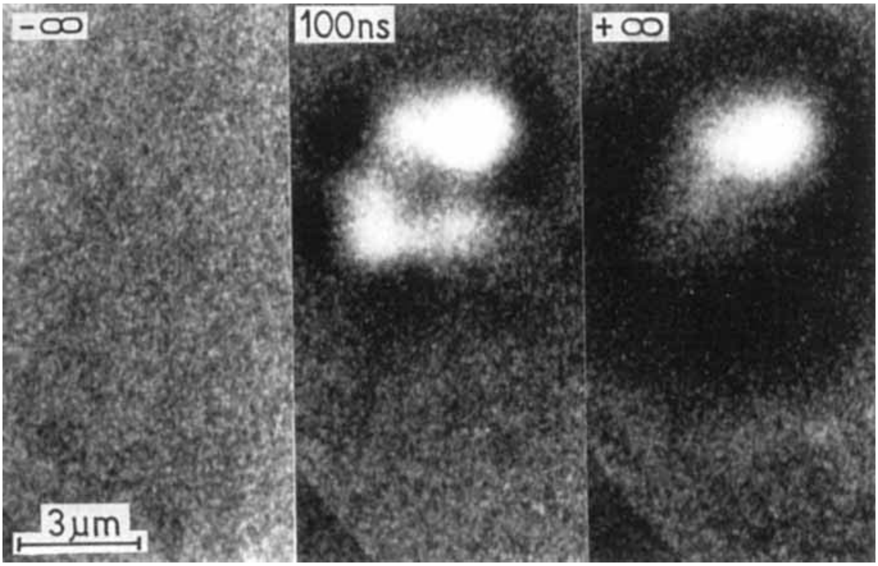

Fig. 3. Short exposure time images of a 3 Al : 1 Ni film showing motion of a laser-produced melt. Before the laser pulse '$-\infty$', 100 ns after the maximum of a 20 ns FWHM laser pulse, final image '$+\infty$' with nanocrystalline region (dark). Note the fast variation of the local film thickness 100 ns after the pulse, proving that the strongly scattering region has been molten (electron exposure time 20 ns, laser pulse energy 500 nJ)

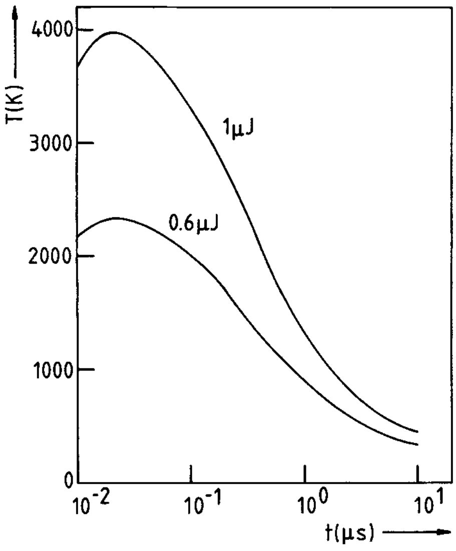

Fig. 4. Computed temperature T at the center of a laser pulsed 3 Al : 1 Ni film as function of time t after the maximum of the laser pulse (pulse width 20 ns FWHM, pulse energy 0.6 and 1 μJ). (By courtesy of V. Yu. Balandin)

phase is quenched with larger crystals dispersed within. They have a lower melting temperature than Ni as a purely nanocrystalline phase is quenched after a second laser pulse with equal, low energy.

3.2 Ordered Al_3Ni crystals

If Al_3Ni crystals are heated by a short laser pulse they are amorphized during the laser pulse within 5 ns (Fig. 5), and a nanocrystalline phase is quenched wherever the absorbed laser fluence exceeded a threshold. It is composed of Al, Al_3Ni, and Al_3Ni_2 as in 3 Al : 1 Ni composite and sandwich films.

The boundaries of the nanophase regions are surprisingly sharp. These regions end quite abruptly within a single crystal without any trace of a 'slush' zone (Fig. 5c). This means that amorphization must set in at a definite transition temperature T_a, and that any absorbed latent heat (per atom) must be much smaller than the heat content $\approx 3\,kT_a$ per atom at the transition point (k Boltzmann constant). Accordingly, the pulse-induced amorphization of Al_3Ni is a process quite different from ordinary melting, where a latent heat is absorbed by the melting solid, which actually is in the order of its heat content.

The very small or zero latent heat absorbed in the fast amorphization of Al_3Ni crystals cannot be understood from the equilibrium Al–Ni phase diagram. On slow heating, 1 mol of Al_3Ni decomposes into 0.32 mol of crystalline Al_3Ni_2 and 2.4 mol of liquid $Al_{0.85}Ni_{0.15}$ at $T_0 = 1127$ K [24]. The liberated heat of formation of Al_3Ni_2 (57 kJ/mol [25]) cannot compensate the absorbed heats of formation of Al_3Ni (38 kJ/mol [25]) and of the Al-rich liquid (about $RT_0 \approx 9.4$ kJ/mol [26], R gas constant). Perhaps, a chemical disordering occurs during the laser pulse heating, which destabilizes the Al_3Ni lattice and enables a direct transition to an amorphous state as in ion induced amorphization [9]. This state relaxes to the observed nanocrystalline phase during cool down after the laser pulse.

According to the above results it should be possible to produce nanocrystalline claddings on Al, Ni and their alloys by using nano- instead of millisecond or scanned cw laser radiation

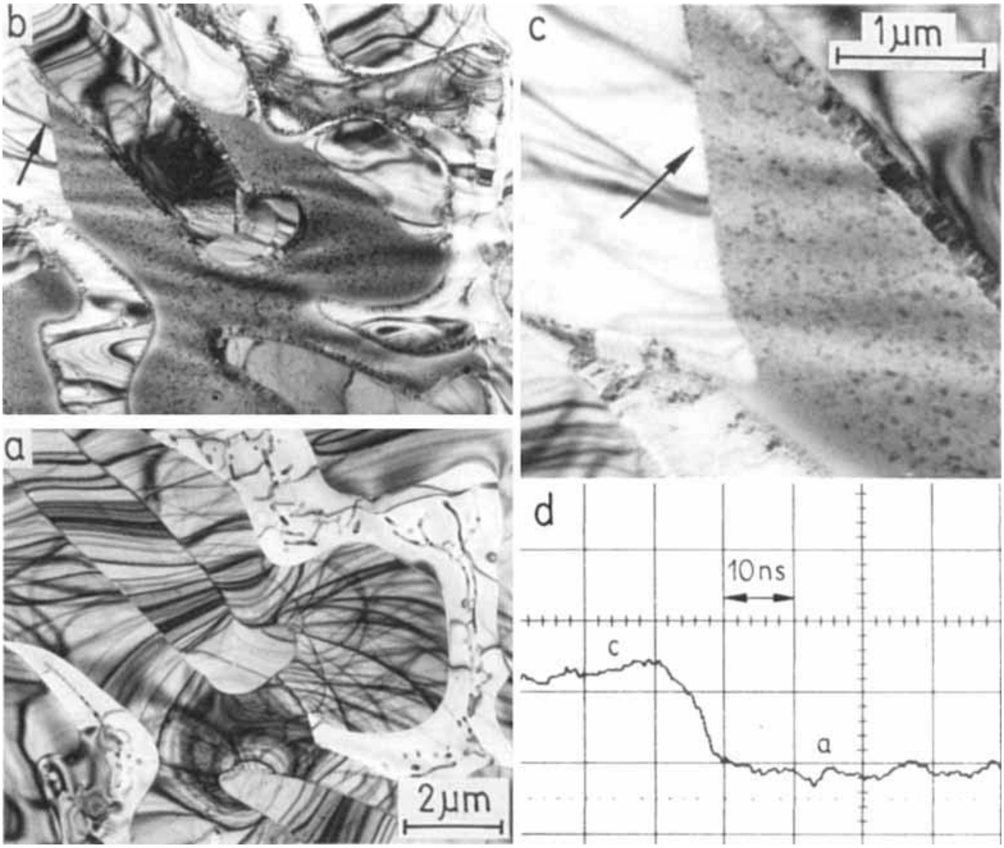

Fig. 5. Nanocrystallization of Al_3Ni crystals by a laser pulse (7 ns FWHM, 250 nJ). a) Crystals before laser pulse; b) region a) after laser pulse, showing partial nanocrystallization (grey parts); c) boundary between nanocrystallized material and a survived crystal (arrow in b). Note the sharp transition, signalizing that no 'slush' was formed; d) typical fast change of image intensity of an area of 1 μm diameter during the amorphization of a crystal (c crystalline, a amorphized)

[16 to 19] with their small heating/cooling rates. Nanophase claddings promise mechanical properties far superior to those of polycrystalline or even glassy material (see e.g. [27]). Nanocrystallization by nanosecond laser pulse quenching is expected to occur in any intermetallic compound having a complex crystal lattice or in an elemental composite with an equivalent overall composition.

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