

Epitaxial B2–NiAl Layers Formed by Nanosecond Laser Irradiation of Thin Al/Ni Bilayers

V. G. Myagkov^{a,*}, L. E. Bykova^a, and G. N. Bondarenko^b

^a Kirensky Institute of Physics, Siberian Division, Russian Academy of Sciences, Krasnoyarsk, Russia

^b Institute of Chemistry and Chemical Technology, Siberian Division, Russian Academy of Sciences, Krasnoyarsk, Russia

* e-mail: miagkov@iph.krasn.ru

Received April 19, 2006

Abstract—The results of experiments on the synthesis of epitaxial B2–NiAl layers by means of nanosecond laser irradiation of sequentially deposited thin nickel and aluminum layers (Al/Ni bilayers) on a MgO(001) substrate surface are presented. Features of the phase formation under the laser action and during the combustion wave initiation are considered. The rapid formation of an epitaxial B2–NiAl layer is explained in terms of a martensitic-like mechanism of the transfer of reacting atoms via a layer of reaction products. It is suggested that this mechanism can compete with diffusion via grain boundaries and dislocation, thus explaining the ultrafast transfer of reacting atoms via a layer of reaction products for various methods of initiation of the solid-state synthesis.

PACS numbers: 68.35.Rh, 69.55.Ac, 75.50.Bb

DOI: 10.1134/S1063785006100026

The action of femtosecond laser pulses can lead to ultrafast structural transformations during athermal melting of semiconductors [1], amorphous-to-crystalline phase transition in GeSb films [2], structural transformations in silicon [3], and metal–insulator phase transition in VO₂ [4]. Assuming that such structural transformations are made possible by atomic displacements on the order of 0.1 nm occurring within 100 fs–100 ps, the average rate of atomic shear can be estimated at 1–1000 m/s. Ultrafast phase transitions in shock waves can also proceed at high rates, which are comparable with the velocity of sound [5].

Solid-state reactions, including those proceeding in thin films and multilayers, involve three sequential stages: (1) rupture of chemical bonds, (2) transfer of reacting atoms via a layer of reaction products, and (3) atomic rearrangement and formation of new chemical bonds. Stage 2 is absent in the case of structural phase transitions, but it is the main, rate-controlling step in solid-state synthesis. Nevertheless, solid-state reactions initiated by nanosecond laser pulses in thin bilayer Fe/Si [6], Ti/Si [7], and Au/Cd [8] systems proceed at anomalously high rates. Indeed, for the typical thickness of a reaction product layer (5–50 nm) and the usual irradiation time (50–100 ns), the reacting atoms must be transferred via the product layer at a velocity of 0.5–0.05 m/s.

Recently, it was shown [9] that the temperatures of initiation T_0 of solid-state reactions in thin bi- and multilayers coincide with the temperatures of phase transitions in the corresponding binary systems. In particular,

the solid-state synthesis in Ni/Ti, Au/Cd, and Ni/Al bilayers is initiated at temperatures coinciding with the start temperatures A_S of the reverse martensite transformation in NiTi, AuCd, and NiAl alloys, respectively: $T_0(\text{Ni/Ti}) = A_S(\text{NiTi}) = 400$ K, $T_0(\text{Au/Cd}) = A_S(\text{AuCd}) = 340$ K, $T_0(\text{Ni/Al}) = A_S(\text{NiAl}) = 500$ K. Based on these experimental data, we formulated the following rule of the first phase formation at the interface of condensed films in the course of annealing at an increased temperature [9]:

(i) The first phase formed at the interface of a thin bilayer condensate is that possessing the minimum temperature of a structural phase transition (according to the phase equilibrium diagram of the corresponding binary system), provided that the reaction initiation temperature T_0 coincides with the temperature T_K of the onset of this phase transition ($T_0 = T_K$).

(ii) If the system features a martensite transformation, which occurs at a minimum temperature as compared to the other phase transitions, the solid-state reaction in thin films is initiated at a temperature T_0 equal to the reverse martensite transformation start temperature A_S ($T_0 = A_S$), and the reaction products contain both austenite and martensite phases.

The relation between solid-state synthesis and martensitic-like (ML) mechanism of the transfer of reacting atoms via a layer of reaction products [8, 9]. In contrast to the diffusion mechanism based on the random walk of atoms via grain boundaries and dislocations, the ML

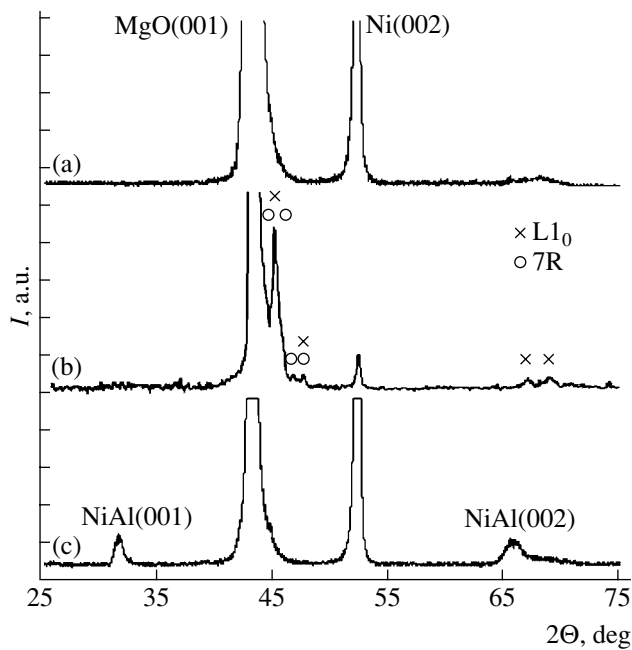


Fig. 1. X-Ray diffraction patterns of thin-film Al/Ni/MgO(001) system: (a) in the initial state; (b) upon SHS wave propagation; (c) after irradiation with ten laser pulses.

mechanism implies directed cooperative motion of reacting atoms via the layer of reaction products along the planes and directions coinciding with those of the martensitic shear. The directed motion of atoms of one reactant in a single-crystal layer of another reactant must lead to oriented growth of the reaction products. Therefore, the ML mechanism stipulates the epitaxial growth of reaction products at the contact surface even in the case of ultrafast transfer of the reacting atoms [9].

The aim of this study was to verify the possibility of obtaining epitaxial B2-NiAl layers on Ni(001) by means of nanosecond ($\tau = 10$ ns) laser irradiation of a thin-film Al/Ni(001)/MgO(001) structure. The possible scenario of synthesis according to the proposed ML mechanism is discussed.

Solid-state synthesis in thin Al/Ni bilayers is initiated at a temperature T_0 that coincides with the start temperature A_S of the reverse martensite transformation in NiAl alloy: $T_0(\text{Ni/Al}) = A_S(\text{NiAl}) = 500$ K [9]. Based on the above rule of the first phase formation, we can expect that B2-NiAl austenite, as well as $L1_0(3R)$ and 7R(14M) martensite and their modifications, will be first formed at the Ni-Al interface during solid-state synthesis of various kinds. The validity of this conclusion is confirmed by the formation of a B2-NiAl phase during shock-wave synthesis [10], self-propagating high-temperature synthesis (SHS) [11], and mechano-activated synthesis [12], and by the shape memory effect in Ni/Al bilayers upon solid-state reaction [9].

The initial Al/Ni bilayers were prepared by sequential vacuum ($\sim 10^{-4}$ Pa) deposition of thin nickel and

aluminum layers of approximately equal thickness (50–100 nm) onto a MgO(001) substrate surface. First, a single-crystal Ni(001) layer was deposited at 500–520 K. In order to avoid premature interaction, the subsequent deposition of aluminum was performed at room temperature. The results of measurements of the X-ray diffraction (Fig. 1a) and the first constant of the crystallographic magnetic anisotropy showed evidence for the following orientation relation between Ni(001) layer and MgO(001) substrate: (001)[100]Ni || (001)[100]MgO. The absence of reflections from aluminum implied that this metal formed a finely dispersed layer on the Ni(001) surface.

The solid-state reaction in thin-film Al/Ni(001)/MgO(001) structures in an autowave (SHS) regime proceeded at a heating rate above 20 K/s and did not lead to the formation of single-crystal products. Completely reacted Al/Ni(001)/MgO(001) samples became nonferromagnetic; their X-ray diffraction patterns showed the absence of pure Ni and exhibited only reflections corresponding to the interplanar spacings $d_1 = 0.203$ nm and $d_2 = 0.176$ nm. Initially, it was suggested that these reflections belong to the Al_3Ni_2 phase [9], which is frequently considered to represent the B2-NiAl austenite phase with an ordered arrangement of defects. In order to reveal weak reflections, the X-ray diffraction measurements were performed in a regime of signal accumulation. As a result, weak additional reflections with $d_3 = 0.1955$ nm, $d_4 = 0.1938$ nm, $d_5 = 0.1912$ nm, $d_6 = 0.154$ nm, and $d_7 = 0.138$ nm were found (Fig. 1b), which could belong to $L1_0$ and 7R martensite phases. Thus, we can suggest that the solid-state synthesis in thin-film Al/Ni(001)/MgO(001) structures begins with the formation of a B2-NiAl austenite phase at $T \sim 500$ K), which exhibits a martensite transition with decreasing temperature. The lattice mismatch and low symmetry do not allow the oriented growth of $L1_0(3R)$ and 7R(14M) phases and their modifications on the Ni(001) surface.

The laser synthesis was performed in vacuum at a residual pressure of $\sim 10^{-4}$ Pa using an LTI-207 laser, which operated in a Q -switched regime at $\lambda = 1.06$ μm and produced pulses with a duration of $\tau = 10$ ns, a repetition rate sufficient for sample cooling, and an intensity of $E = 44 \times 10^3$ J/m². The samples for X-ray diffraction measurements were prepared by scanning the 1.7-mm-diameter laser beam over a ~ 1 cm² surface area. The results of magnetic measurements showed that the solid-state reaction involved only about 30–50% of the Ni film volume, which corresponded to the formation of a ~ 30 -nm-thick layer of reaction products.

Figure 1c shows the X-ray diffraction pattern of a thin-film Al/Ni(001)/MgO(001) sample upon tenfold pulsed laser action. As can be seen, only the (001)B2-NiAl, (002)B2-NiAl, and (002)Ni reflections are present, this pattern being indicative of the formation of an epitaxial B2-NiAl layer on the Ni(001) surface with the orientation relation (001)B2-NiAl || (001)Ni. Since

the epitaxy of B2–NiAl proceeds only on a single-crystal nickel film, we can suggest that the solid-state synthesis in Al/Ni(001)/MgO(001) samples proceeds predominantly by means of the directed migration of aluminum atoms in the nickel lattice. According to modern notions about solid-state synthesis, a significant time is required for atoms at the interface to rearrange and occupy stable equilibrium positions determined by atoms of the single-crystal substrate. An important factor of epitaxial growth is the matching of lattice parameters of the substrate and the growing oriented layer. It was reported that an optimum growth regime is provided by the deposition rate corresponding to the formation of one atomic monolayer per second [13]. However, this value is 10^8 times as small as the velocity of epitaxial growth observed in our experiments.

In the absence of heat exchange with the environment, the change in the temperature of the laser-beam-affected zone can be evaluated as $D_T = (1 - R)E/lc_p\rho$, where R is the reflection coefficient, c_p is the heat capacity, ρ is the density, and $l = 2(D_T\tau)^{1/2}$ is the temperature diffusion length, and D_T is the thermal diffusivity [14]. Assuming for the uppermost layer of aluminum $R = 0.95$, $D_T = 87.2 \times 10^{-6}$ m²/s, $c_p = 0.9 \times 10^3$ J/(kg K), and $\rho = 2.69 \times 10^3$ kg/m³, we can estimate the change in the film temperature as $\Delta T \sim 500$ K (relative to the initial temperature $T_0 = 300$ K). The coefficient of diffusion for Al atoms in a nickel single crystal at $T = T_0 + \Delta T \sim 800$ K is $D_{Al} = 1.9 \times 10^{-19}$ m²/s [15]. This value indicates that normal diffusion can provide mass transfer only within a diffusion length of $d = 2(D_{Al}\tau)^{1/2} \sim 10^{-4}$ nm, which is $\sim 10^5$ times shorter than the thickness of the epitaxial B2–NiAl layer formed due to the action of a 10-ns laser pulse. These estimates show that considerable difficulties are encountered in the attempts to explain the ultrafast mass transfer during nanosecond-laser-induced solid-state synthesis.

Taking into account the nanosecond time scale of the process, we propose the following ML mechanism to explain the scenario of a solid-state reaction between a fine-crystalline aluminum layer and the single-crystal nickel film, which leads eventually to the formation of an epitaxial B2–NiAl layer based on the Ni(001) film structure. According to this mechanism, Al atoms move via octahedral positions in the [001]Ni direction (i.e., along the normal to the surface) inward the film and displace atoms situated at the centers of the fcc lattice faces. The resulting tetragonal bcc lattice, with the parameters $a = b = 0.2492$ nm and $c = 0.3524$ nm, exhibits insignificant deformation and transforms into a B2–NiAl lattice with the parameter $a = 0.28869$ nm. This scenario leads to the orientation relation (001)[110]B2–NiAl \parallel (001)[100]Ni that corresponds to a lattice mismatch of 13.6%. In contrast to the case of solid-state synthesis in Al/Ni(001)/MgO(001) samples in the SHS regime, nanosecond laser synthesis does not involve the B2–NiAl phase transition to martensite

phases. Retardation of the phase transition can be related to significant stresses developed at the grain boundaries of the B2–NiAl phase formed in the course of ultrafast growth.

The possibility of ultrafast structural transformations in the solid state cannot be explained by a mechanism involving slow diffusion and requires expansion of the possible mechanisms of atomic transport. In particular, a nondiffusion martensitic shear of one lattice into another was used to explain the ultrafast character of the structural transformations induced by shock waves [5]. In the past two decades, a more complicated ML mechanism has been developed in geophysics and mineralogy in order to explain the structural transformation of olivine [α -(Mg,Fe)₂SiO₄] into wadsleyite [β -(Mg, Fe)₂SiO₄] and ringwoodite [γ -(Mg,Fe)₂SiO₄]. It was suggested that shear instabilities in the Earth's upper mantle initiate ultrafast $\alpha \rightarrow \beta$ and $\alpha \rightarrow \gamma$ transformations, which can lead to deep earthquakes and explain an increase in the velocity of seismic waves at a depth of ~ 410 km. One possible mechanism of the $\alpha \rightarrow \beta$ and $\alpha \rightarrow \gamma$ phase transitions is the incoherent nucleation and subsequent diffusion growth of β and γ phases at the boundaries of olivine (α phase) grains. An alternative is offered by the ML mechanism, according to which dislocations with [001] Burgers vector exhibit slippage along the (100) _{α} plane and decompose into four partial dislocations: $1/12[013]$ and $1/12[0\bar{1}3]$. These dislocations create stacking faults in the (100) _{α} plane and obey the following dislocation reaction: $[001] \rightarrow 1/12[013] + 1/12[0\bar{1}3] + 1/12[013] + 1/12[0\bar{1}3]$. This dislocation mechanism transforms the orthorhombic lattice of olivine (α phase) into the cubic spinel lattice of ringwoodite (γ phase) with the orientation relation (100) _{α} \parallel {111} _{γ} . The experimental observation of this relation for the $\alpha \rightarrow \gamma$ transformation in olivine and its analogs at high temperatures ($>1000^\circ\text{C}$) and pressures (up to 20 GPa) is considered evidence in favor of the ML mechanism [16, 17]. Nanosecond laser radiation pulses can also produce significant heating and induce shock waves in thin films. The formation of epitaxial B2–NiAl layers under nanosecond laser irradiation of thin Ni/Al bilayers provides additional evidence for the ML mechanism of synthesis. This result agrees with the conclusions made in [18], where a nondiffusion cooperative mechanism of chemical synthesis under the action of shock waves was admitted for the first time.

In conclusion, it should be noted that ML shear probably not only underlies polymorphous transitions, but also determines the mass transfer in solid-state synthesis. It can also be suggested that the ML mechanism can compete with diffusion via grain boundaries and dislocation, thus explaining the ultrafast transfer of reacting atoms via reaction products for various methods of initiation of the solid-state synthesis.

Acknowledgments. The authors are grateful to A.I. Pozdnyakov and V.S. Zhigalov for their help in laser annealing of samples.

This study was supported in part by the MMK Company Foundation, "Ausferr" Center, and "Intels" Society (project no. 11F001C).

REFERENCES

1. A. Rousse, C. Rischel, S. Fourmaux, et al., *Nature* **410** (6824), 65 (2001).
2. J. P. Callan, A.-T. Kim, C. A. D. Roeser, et al., *Phys. Rev. Lett.* **86**, 3650 (2001).
3. S. I. Kudryashov and V. I. Emel'yanov, *Zh. Éksp. Teor. Fiz.* **121**, 113 (2002) [*JETP* **94**, 94 (2002)].
4. A. Cavalleri, S. Toth, C. W. Siders, et al., *Phys. Rev. Lett.* **87**, 3650 (2001).
5. *Shock Waves and Extremal States of Substances*, Ed. by V. E. Fortov, L. V. Al'tshuler, R. F. Trunin, and F. I. Funtikov (Nauka, Moscow, 2000) [in Russian].
6. S. Wagner, E. Carpane, P. Schaaf, and M. Weisheit, *Appl. Surf. Sci.* **186**, 156 (2002).
7. R. Larciprete, M. Danailov, A. Barinov, et al., *J. Appl. Phys.* **90**, 4361 (2001).
8. V. G. Myagkov, *Dokl. Akad. Nauk* **392**, 54 (2003) [*Dokl. Phys.* **48**, 495 (2003)].
9. L. E. Bykova, V. G. Myagkov, and G. N. Bondarenko, *Khim. Interes. Ustoich. Razvit.* **13**, 137 (2005).
10. E. Dunbar, N. N. Thadhani, and R. A. Graham, *J. Mater. Sci.* **28**, 2903 (1993).
11. A. Biswas, S. K. Roy, K. R. Gurumurthy, et al., *Acta Mater.* **50**, 757 (2002).
12. M. Atzmon, *Phys. Rev. Lett.* **64**, 487 (1990).
13. P. Finnie and Y. Homma, *Surf. Sci.* **500**, 437 (2002).
14. H. Y. Zheng, Q. Chen, X. C. Wang, et al., *Surf. Rev. Lett.* **11**, 305 (2004).
15. L. N. Larikov and V. I. Isaichev, *Diffusion in Metals and Alloys* (Naukova Dumka, Kiev, 1987) [in Russian].
16. L. Kerschhofer, T. Sharp, and D. C. Rubie, *Science* **274**, 79 (1996).
17. P. C. Burnley, *Am. Mineral.* **90**, 1315 (2005).
18. N. N. Thadhani, R. A. Graham, T. Royal, et al., *J. Appl. Phys.* **82**, 1113 (1997).

Translated by P. Pozdeev