

Article

Compositional Glass: A State with Inherent Chemical Disorder, Exemplified by Ti-rich $\text{Ni}_3(\text{Al,Ti})_1 \text{D}_{024}$ Phase

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Abstract: A compositional glass is a state with an unavoidable disorder in chemical compositions on each site, characterized by frustration and freezing of the compositional degrees of freedom at low temperature. From this state a full atomic long-range order is unachievable by a reasonable thermodynamic treatment. There is a similarity between a spin glass (a magnetic state with disorder in spin orientations) and a compositional glass (with disorder in site occupations by chemical elements): both have frustrated ground states and a frozen disorder at low temperatures $T < T_f$ (here T_f is called the freezing temperature). While it is possible to perform a ground-state search in a compositional glass, the resulting set of the fully ordered structures does not adequately represent the real solid with an inherent atomic disorder. Compositional glasses constitute a class of materials, which is insufficiently understood, but is of high industrial importance. Some of the phases in the precipitated alloys (including steels, high-entropy alloys, and superalloys) might be compositional glasses, and their better understanding would facilitate materials design. Due to their strength at high operating temperatures, superalloys are used in combustion engines and particularly in jet turbine engines. Precipitation strengthening of nickel superalloys is an area of active research. Local phase transformations inside Ni_3Al -based precipitates are of particular interest due to their impact on creep strength. In the $\text{Ni}_3(\text{Al}_{1-x}\text{Ti}_x)_1$ ternary system, the competing phases are Ni_3Al -type L_{12} (γ') and Ni_3Ti -type D_{024} (η), while D_{019} (χ) is higher in energy. These three phases differ by the stacking of atomic layers: locally, the last two look like the internal and external stacking faults in L_{12} . We compute enthalpies of disordered and ordered $\text{Ni}_3(\text{Al}_{1-x}\text{Ti}_x)_1$ ternary structures, examine phase stability, investigate the ground states and competing structures, and predict that the Ti-rich $\text{Ni}_3(\text{Al}_{1-x}\text{Ti}_x)_1 \text{D}_{024}$ phase is a compositional glass with the atomic disorder on the Al/Ti sublattice. To resolve apparent contradictions among the previous experiments and to confirm our prediction, we perform X-ray diffraction and scanning electron microscopy analysis of the cast $\text{Ni}_3(\text{Ti}_{0.917}\text{Al}_{0.083})_1$ sample. Our measurements appear to confirm the ab initio computed results. Our results elucidate properties of compositional glasses and provide a better understanding of precipitation strengthening mechanisms in Ni superalloys.

Keywords: compositional glass; disorder; atomic ordering; precipitation; superalloys; $\text{Ni}_3(\text{Al+Ti})_1$



Citation: Zarkevich, N.A.; Smith, T.M.; Baum, E.N.; Lawson, J.W. Compositional Glass: A State with Inherent Chemical Disorder, Exemplified by Ti-rich $\text{Ni}_3(\text{Al,Ti})_1 \text{D}_{024}$ Phase. *Crystals* **2022**, *12*, 1049. <https://doi.org/10.3390/cryst12081049>

Academic Editors: Andrew Kao, Dmitri Alexandrov, Liubov V. Toropova, Catherine Tonry and Jagdish K. Vij

Received: 8 July 2022

Accepted: 25 July 2022

Published: 28 July 2022

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1. Introduction

The efficiency of heat engines increases with temperature T of a heater if an environment is used as a cooler. Thus, higher-efficiency engines require appropriate materials suitable for use at higher operating temperatures. Due to their strength at elevated T , superalloys are used for critical high- T applications in energy, automotive, and aerospace industries. In particular, nickel-based superalloys are used in jet engine turbine disks [1]. These alloys are strengthened by Ni_3Al γ' precipitates [2], grain boundary strengtheners (e.g., carbon or boron) [3], and solid-solution strengtheners [4]: refractory elements (W ,

Re, Ta, Mo, Nb) [5] and rare earth elements (La, Ce, etc.) [6]. Local phase transformations inside Ni_3Al -based precipitates result in additional strengthening and improved creep of Ni superalloys [7–11].

Here we focus on the atomic ordering and phase stability in the $\text{Ni}_3(\text{Al}_{1-x}\text{Ti}_x)_1$ ternary system. The competing phases in $\text{Ni}_3(\text{Al}_{1-x}\text{Ti}_x)_1$ are L_{12} (γ')—the ground state (GS) of Ni_3Al , and D_{024} (η)—the ground state of Ni_3Ti . We find that D_{019} (χ) phase is higher in energy and less thermodynamically relevant. L_{12} , D_{019} , and D_{024} phases differ by the stacking of atomic layers, see Figure 1. The last two phases locally look like stacking faults in L_{12} [7].

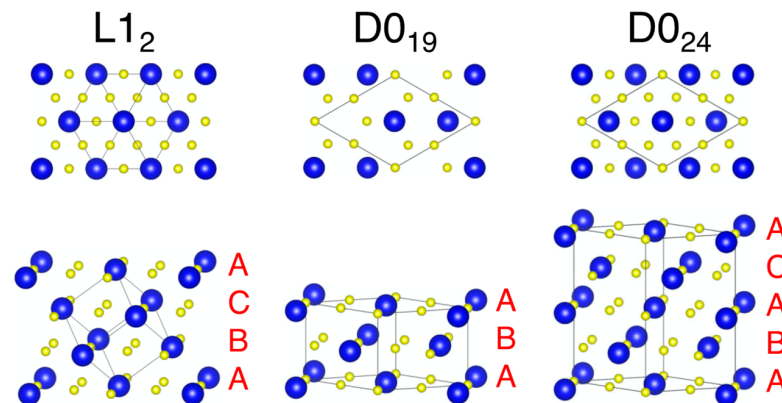


Figure 1. Atomic structures of L_{12} (γ'), D_{019} (χ), and D_{024} (η) phases, shown for the fully relaxed Ni_3Ti . The upper panel shows cubic (111) and hexagonal (0001) projections. The lower panel compares stacking of the 2D layers. Ti (Al) atoms are dark blue; Ni atoms are small yellow.

In the $\text{Ni}_3(\text{Al}_{1-x}\text{Ti}_x)_1$ ternary system the terminal binary L_{12} Ni_3Al and D_{024} Ni_3Ti structures differ. We investigate the phase stability of $\text{Ni}_3(\text{Al}_{1-x}\text{Ti}_x)_1$ with a homogeneous atomic disorder on the $(\text{Al}_{1-x}\text{Ti}_x)$ sublattice, consider energy gain due to the atomic ordering, and construct the ground-state hull. We predict the existence of the fully ordered ground-state structures at intermediate compositions—in addition to the known binary L_{12} Ni_3Al and D_{024} Ni_3Ti structures. A subset of the predicted ground-state structures is shown in Figure 2. The computed energies are plotted in Figure 3.

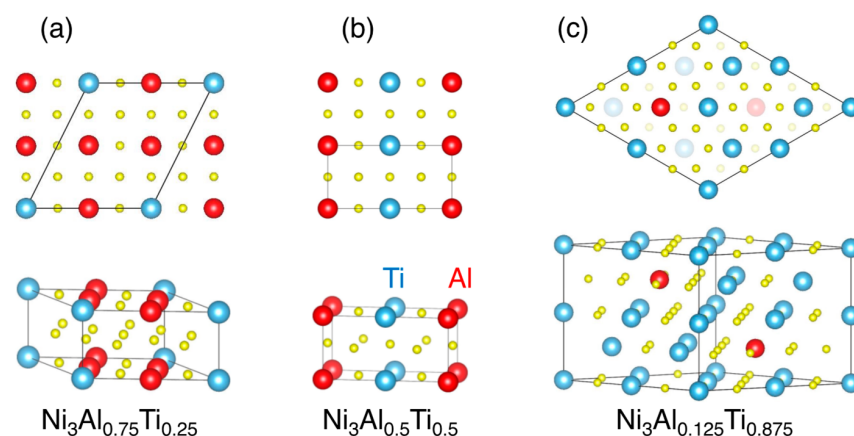


Figure 2. The ground-state candidates: L_{12} -based orthorhombic structures at (a) $x = 1/4$ and (b) $x = 1/2$; (c) D_{024} -based hexagonal structure at $x = 7/8$. Ti is light blue; Al is red; Ni is small yellow. There are multiple structures with well-spaced Al solute on the GS hull at $x > 0.875$, see text.

Interestingly, the energy decrease due to atomic ordering in the Ti-rich D_{024} phase is very small (see Figure 3); hence, we do not expect development of a long-range order (LRO) on the Al/Ti sublattice in experimental samples at these compositions, while a weak

short-range order (SRO) is expected due to the repulsion between the solute Al atoms. This phase is an example of a compositional glass, generic properties of which we discuss.

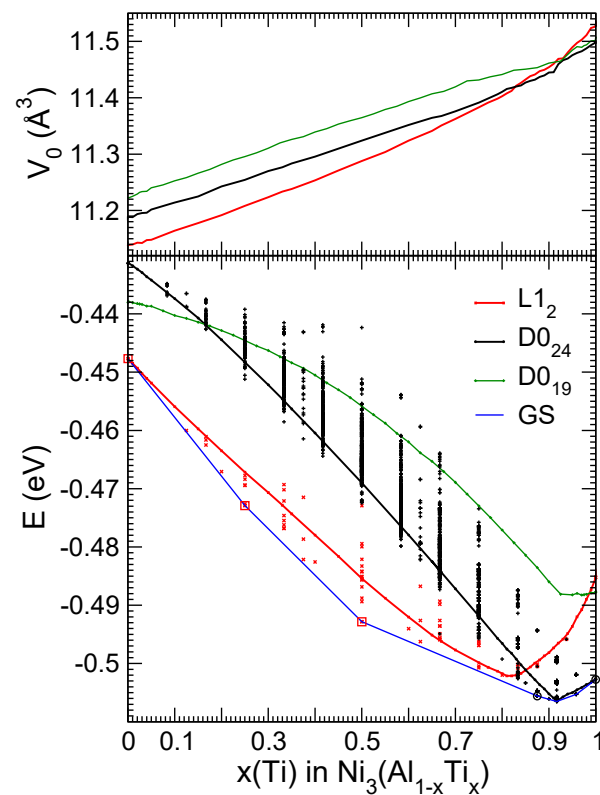


Figure 3. Equilibrium volumes V_0 [$\text{\AA}^3/\text{atom}$] and formation energies E [eV/atom] of $\text{Ni}_3(\text{Al}_{1-x}\text{Ti}_x)_1$ fully ordered structures (points) and phases with a homogeneous disorder on the Al/Ti sublattice (lines), based on $L1_2$ (red), $D0_{24}$ (black), and $D0_{19}$ (green) lattices. The ground-state (GS) hull is shown by the blue line, with marked $L1_2$ -based (red squares) and terminal $D0_{24}$ -based (black circles at $x = 0.875$ and 1) ground states. There are multiple GS candidates with spaced Al solute at $0.875 < x < 1$.

In addition to the structural phase transition between $L1_2$ and $D0_{24}$ phases, there is a magnetic transition in the $\text{Ni}_3(\text{Al}_{1-x}\text{Ti}_x)_1$ ternary system. Dependence of atomic magnetic moments on composition is given in Figure 4.

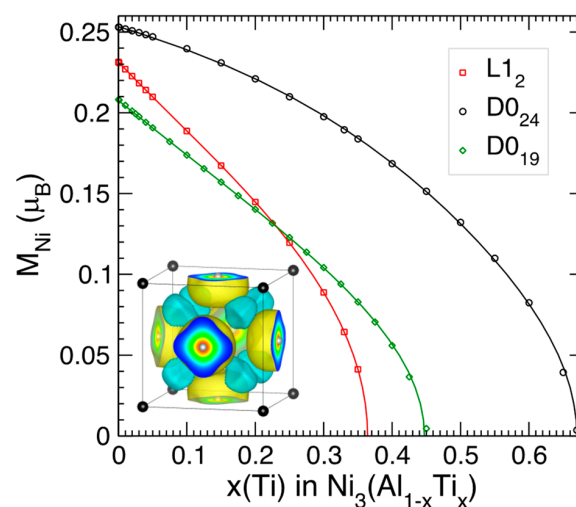


Figure 4. Ni atomic magnetic moment (Bohr magnetons, μ_B/atom) versus Ti concentration x in three phases of $\text{Ni}_3(\text{Al}_{1-x}\text{Ti}_x)_1$ alloys with a homogeneous atomic disorder on the Al/Ti sublattice. Lines

are 6th degree $x(M_{\text{Ni}})$ polynomials with even powers, fitted to DFT data points. Inset: $0.0005 e^-/\text{\AA}^3$ iso-surfaces of electronic spin density in cubic $L1_2$ Ni_3Al unit cell with Ni (grey) and Al (black) atoms.

The kink in the energy versus composition dependence (see Figure 3), present in all three phases, is caused by a rapid change of the electronic density of states (DOS) at the Fermi level E_F , which is in the pseudo-gap in the Ti-rich structures, see Figure 5.

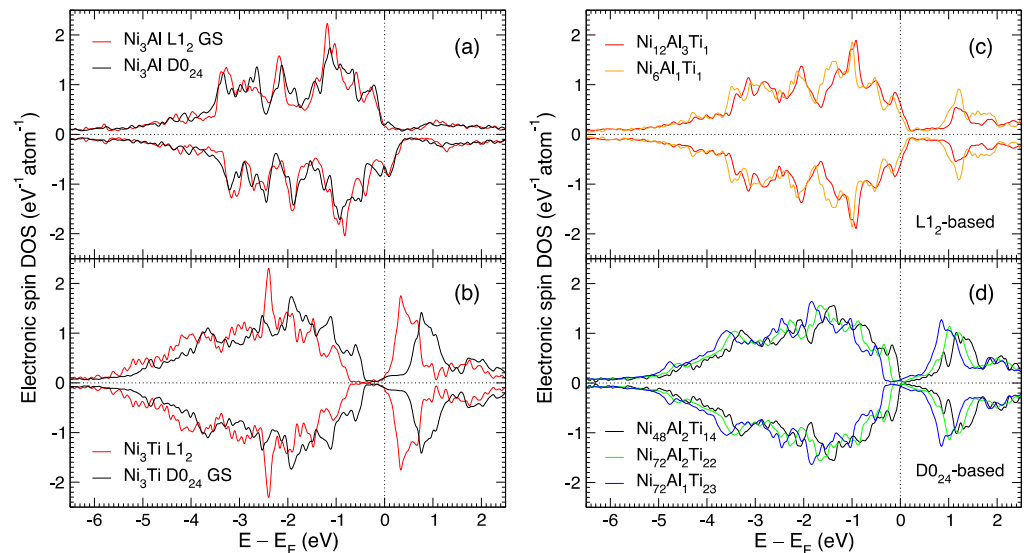


Figure 5. Electronic density of states (states/eV·spin·atom) of magnetic Ni_3Al (a) and non-magnetic Ni_3Ti (b) in $L1_2$ (red) and $D0_{24}$ (black) phases is compared to that of the $L1_2$ -based GS at $x = 1/4$ and $1/2$ (c) and $D0_{24}$ -based GS at $x = 7/8$, $11/12$, and $23/24$ (d).

This article is organized as follows. Methods and materials are described in Section 2. Results in Section 3 clarify phase stability and atomic ordering in the $\text{Ni}_3(\text{Al}_{1-x}\text{Ti}_x)_1$ ternary system, while our experiment confirms our theoretical predictions. Discussion and summary are in Sections 4 and 5, respectively.

2. Methods and Materials

2.1. Theory

Physically different systems can be described by similar mathematical equations. Hamiltonian formalisms are equivalent for a magnetic system composed of interacting particles with spins (moments with a quantized projection on the chosen axis) and for an alloy with a variable composition on each site, occupied by one of the available chemical elements. On an occupied site an atom can be displaced from the ideal crystallographic position [12]; a vacancy can be treated as another atomic type with zero nuclear charge. A magnetic quantum system can be described in terms of the spin variables s_i . For spins $s = 1/2$ (here we omit the reduced Plank constant $\hbar$), on each site i there are only 2 possible values of $s_i = \pm \frac{1}{2}$, corresponding to either up or down spin orientations. The same spin-like variables s_i can describe occupation of each site i in a binary alloy, which is composed of only 2 chemical elements (for example, Al and Ti). One can extend this formalism to describe either spin or atomic disorder on a particular sublattice, if all the other sublattices are fully ordered. One can use the spin-like variables with a larger amplitude and more projections, for example, $\{-1, 0, 1\}$ for a spin 1 magnetic system or for a ternary alloy. Next, there is a one-to-one correspondence between descriptions of an alloy in terms of the spin-like (s_i) and occupational variables $x_i(X)$, where X is a particular chemical element (e.g., Ti). The values of $x_i(X)$ are between zero and one: $x_i(\text{Ti}) = 1$ if the site i is occupied by Ti and 0 otherwise. For a binary alloy, composed by Al and Ti only, at each site i there is a constraint $x_i(\text{Al}) + x_i(\text{Ti}) = 1$, due to which one can exclude one variable $x_i(\text{Al}) = (1 - x_i)$

and keep only $x_i(\text{Ti}) \equiv x_i$. The equation $s_i = (x_i - \frac{1}{2})$ connects the occupational and spin variables, in which $s_i = -\frac{1}{2}$ for Al and $+\frac{1}{2}$ for Ti.

Historically, the Ising model [13] and its generalizations [14] described spin ordering in magnetic systems, while the cluster expansion [15,16] described atomic ordering in multicomponent systems. Hamiltonian formalisms for both are mathematically equivalent. In both cases, such systems can be frustrated. A spin glass [17] is an inherently disordered state of a frustrated magnetic system, and in the compositional space we expect the existence of a similar state, which we call a compositional glass. As a formality, below are two definitions.

A spin glass is a magnetic state, in which magnetic moments have orientational disorder due to frustration, caused by a balance between attractive and repulsive interactions. A spin glass [17] is characterized by randomness in orientations of spins and freezing of spin dynamics below the freezing temperature T_f .

A compositional glass is a state with an inherent chemical disorder, characterized by a randomness in the local chemical compositions on a set of sites (each site is occupied by one of the constituting chemical elements), and freezing of disorder below temperature T_f , at which atomic diffusion stops. A compositional glass is an analogue of a spin glass: both systems are described by similar equations, have comparable properties of mathematical solutions, but differ by a physical interpretation of mathematical symbols.

An example of a compositional glass will be considered in Section 3.

2.2. Computations

Density functional theory (DFT) is used to address fully ordered and partially disordered periodic atomic structures [18]. Two DFT codes are used: the all-electron Green's function-based KKR-CPA [19,20] code MECCA [21] and the full-potential pseudo-potential VASP [22,23]. We use the same PBEsol exchange correlation functional [24] in both codes.

The Korringa–Kohn–Rostocker (KKR) approach [19,20] was combined with the coherent potential approximation (CPA) [25] to consider a homogeneous substitutional chemical disorder on the Al/Ti sublattice [21]. The truncated basis set with the maximal orbital angular momentum quantum number $l_{\max} = 3$ included s , p , d , and f orbitals. We used the atomic spheres approximation (ASA) [26] with the periodic boundary corrections [27]. The ideal c/a ratio of the lattice constants was used for the close-packed hexagonal phases in KKR-CPA.

The Murnaghan equation of state (EoS) [28] was fitted to the $E(V)$ data with at least 5 DFT points (with a step from 1% to 1.5% in the lattice constant, with an energy minimum near V_0) to find the equilibrium volume V_0 at each composition for the phases with a homogeneous disorder on the Al/Ti sublattice, see Figure 3. New DFT calculations were performed at the equilibrium volume to find atomic magnetic moments in Figure 4. We checked that the EoS energy at V_0 (shown in Figure 3) and the directly computed DFT energy E at V_0 agree within the DFT error bar at each composition.

The Thermodynamic Tool Kit (TTK) [29] was used to generate a set of periodic structures with various decorations of atoms on the Al/Ti sublattice in $L1_2$ and $D0_{24}$ phases. An iterative method described in Section 3.4 was used to add more ground state candidates into DFT consideration.

The VASP code [22,23] with PAW pseudopotentials [30] was used to compute energies of the fully ordered structures, which were fully relaxed at zero pressure. The plane-wave energy cutoff was increased to $\text{ENCUT} = 650$ eV. During relaxation we used the Gaussian smearing ($\text{ISMEAR} = 0$) with $\text{SIGMA} = 0.043$ eV, corresponding to $k_B T$ at $T = 500$ K. For the fully relaxed structures we also used the tetrahedron method with Blöchl corrections ($\text{ISMEAR} = -5$). We used the Γ -centered Monkhorst–Pack k -mesh [31] with at least 50 points per inverse ångström. The spin-polarized calculations were performed for magnetic systems. For consistency, full-potential corrections (assumed to be linear versus composition) were applied to the KKR-CPA results using VASP energies at the terminal compositions.

2.3. Experimental Sample Preparation and Characterization

A 30 g ingot composed of 79.24 wt.% Ni, 19.75 wt.% Ti, and 1.01 wt.% Al was produced using vacuum induction melting (VIM) at the NASA Glenn Research Center Materials Processing Laboratory. The 30 g button was then cut, mounted in polyfast epoxy, and polished. The microstructural $\text{Ni}_3(\text{Ti},\text{Al})$ sample was polished using SiC grit paper followed by 0.5 μm suspension and a final 0.05 μm colloidal silica finish. Scanning electron microscopy of the sample was performed using a Tescan MAIA3 at 15 kV of acceleration using a secondary electron detector. Chemical maps were performed using an Oxford Ultim Max Silicon Drift Detector and Aztec Software. Phase identification of the button sample was performed using both a Panalytical Empyrean X-ray diffractometer with a position sensitive detector (Galipix) in scanning 1D mode utilizing Mo- $\text{K}\alpha$ radiation and Bruker D8 Discover (area detector) X-ray diffractometer utilizing Cu- $\text{K}\alpha$ radiation. Ten separate SEM images were obtained, each containing a surface area of 0.02 mm [2]. The micrographs were then cropped and transformed into 8-bit images. They were then segmented using the adaptive threshold plug-in within the image processing software ImageJ [32]. The threshold plug-in segments the image using the gray-scale contrast between the darker γ' precipitates and lighter D0_{24} matrix. The software determines a gray-scale cut-off and a minimum size of a precipitate. Hence, any pixel that is determined “dark” enough to be considered a γ' precipitate must also have a minimum number of connecting “dark” pixels for it to be considered a precipitate and included in the segmentation step. Otherwise, the plug-in will consider that pixel as noise and exclude it. After the segmentation, the segmented images were transformed into binary images and the segmented phases were analyzed to determine their area fractions.

3. Results

3.1. Relevant Phases

The L1_2 (cP4, Cu_3Au -type, cubic $Pm\bar{3}m$ space group no. 221), D0_{19} (hP8, Ni_3Sn -type), and D0_{24} (hP16, Ni_3Ti -type, hexagonal $P6_3/mmc$ space group no. 194) atomic structures are shown in Figure 1. They differ by the stacking of 2-dimensional (2D) atomic layers along the cubic (111) direction in L1_2 or the hexagonal (0001) direction in D0_{19} and D0_{24} structures, as well as by c_1/a_1 ratio, where c_1 is the lattice constant along the stacking direction, divided by the number of layers, and a_1 is the interatomic distance between the nearest periodic Al/Ti sites within the 2D layers. The periodic stacking of the 2D layers is [ABC] in L1_2 , [AB] in D0_{19} , and [ABAC] in D0_{24} . The Al/Ti sublattice is simple cubic (sc) in L1_2 , hexagonal close-packed (hcp) in D0_{19} , and double hexagonal close-packed (dhcp) in D0_{24} , see Figure 1. In all three phases, the 3D Al/Ti sublattice is composed by the stacked 2D triangular lattices.

3.2. Ground-State Candidates

The known ground states at the terminal binary compositions are L1_2 Ni_3Al and D0_{24} Ni_3Ti . The lowest-energy structures at three selected $\text{Ni}_3(\text{Al}_{1-x}\text{Ti}_x)$ ternary compositions are shown in Figure 2. The exhaustive set of L1_2 -based ground states includes the three structures at $x = 0, 0.25$, and 0.5 (see Figure 3). In contrast, the D0_{24} -based ground states include many structures with well-spaced Al solute at $0.875 \leq x \leq 1$; one of them at $x = 0.875$ is shown in Figure 2c. This $\text{Ni}_3\text{Al}_{1/8}\text{Ti}_{7/8}$ structure is hexagonal, with the maximally spaced Al solute; the Al sublattice forms a close-packed structure (hcp with AB stacking in Figure 2c); the competing structures differ by a stacking of the close-packed Al sublattice (other possibilities include [ABC] for fcc or [ABAC] for dhcp, see Figure 1). Due to the repulsion between Al atoms at a short distance, all D0_{24} -based ground states have a well-spaced Al solute and prefer mixing for the atomic ordering on the Al/Ti sublattice. However, at small Al concentrations at $x(\text{Ti}) \rightarrow 1$, there are many competing structures with well-spaced Al solute and similar energies; the energy differences between those are within the DFT error. In addition, the energy difference ΔE_d between the states with a homogeneous disorder on the Al/Ti sublattice and the ordered ground

states with the well-spaced Al solute is small and constitutes only 2.37 meV/atom or 9.48 meV per $\text{Ni}_3\text{Al}_{1/8}\text{Ti}_{7/8}$ formula unit (f.u.) at $x = 0.875$; it reduces to 1.42 meV per $\text{Ni}_3\text{Al}_{1/12}\text{Ti}_{11/12}$ at $x = 11/12$; 2.85 meV per $\text{Ni}_3\text{Al}_{1/24}\text{Ti}_{23/24}$ at $x = 23/24$; and 0 meV/ Ni_3Ti at $x = 1$. At $x = 7/8$, chemical entropy of the Al/Ti homogeneous atomic disorder is $S_d = k_B(x \ln(x) + (1-x) \ln(1-x)) = 3.247 \cdot 10^{-5}$ eV/K per $\text{Ni}_3\text{Al}_{1/8}\text{Ti}_{7/8}$ f.u. (here k_B is the Boltzmann constant) and is zero for the fully ordered structure; the expected ordering phase transition temperature is below $\Delta E_d/S_d = 292$ K, while the experimental atomic diffusion is negligible below 500 K. Hence, due to the insufficient energy gain from forming the long-range order at $0.875 < x < 1$ (see Figure 3), experimental Ti-rich D0_{24} -based $\text{Ni}_3(\text{Al}_{1-x}\text{Ti}_x)$ samples are expected to have only short-range order on the Al/Ti sublattice. This prediction makes it unnecessary to point at the fully ordered ground states, which differ from the actual state with an inherent atomic disorder at $0.875 < x < 1$. We expect that $\text{Ni}_3(\text{Al}_{1-x}\text{Ti}_x)$ alloys at $0.875 < x < 1$ will remain in D0_{24} phase and have a disorder (no LRO) on the Al/Ti sublattice, while SRO [33] will be caused by a repulsion between Al solute atoms. An alloy with an inherent occupational disorder behaves as an analogue of a spin glass in occupational variables, with a corresponding similarity between magnetic (spin) [13] and occupational degrees of freedom. Such a state of matter is called a compositional glass.

3.3. Relative Energies of Disordered Structures

The computed energies $E_{dis}(x)$ of the relevant phases of $\text{Ni}_3(\text{Al}_{1-x}\text{Ti}_x)_1$ with a homogeneous atomic disorder on the Al/Ti sublattice are compared with the energies of the fully ordered structures in Figure 3. For the Al/Ti disorder, we find a mixing tendency (indicated by a positive curvature of the convex $E_{dis}(x)$ curve) in L1_2 phase at all compositions x , while a mixing tendency in both D0_{19} and D0_{24} phases is present only at large Ti concentrations. Negative mixing energies (relative to the terminal Ni_3Al L1_2 and Ni_3Ti D0_{24}) indicate that Al and Ti atoms prefer to mix (and not to segregate) on the Al/Ti sublattice. If mixing with a homogeneous disorder is already energetically favorable, then further relaxation of compositional degrees of freedom with a formation of SRO or LRO on the Al/Ti sublattice is expected to lower energy. This leads to an expectation of existence of ordered structures (some of which are the ground states) with lower energies than those of disordered states. Indeed, Figure 3 shows the computed ground-state hull, which is below the $E_{dis}(x)$ curves for both L1_2 and D0_{24} phases. As discussed in Sections 3.2 and 4, small differences ΔE_d indicate that the actual state is a compositional glass.

3.4. Energies of Fully Ordered Structures and the Ground-State Hull

Using the Thermodynamic Tool Kit (TTK) [34], for both D0_{19} and D0_{24} phases we generated a hierarchical set of ordered structures (smallest first) with atoms at the ideal lattice positions and used density functional theory (DFT) to compute energies of the fully relaxed structures. Next, energies and correlation functions for a set of structures [35] were used in the structural inversion to construct a cluster expansion (CE) [29]. The CE Hamiltonian was used to predict the CE energies of a very large number of structures and to find new ground state candidates [36]. Energies of those were computed directly in DFT. With energies and correlation functions of those additional structures, another CE was constructed and another search for additional ground states was performed. This iterative procedure was stopped (with 68 L1_2 -based and 2650 D0_{24} -based structures) when no new lower-energy (within the DFT accuracy) ground state candidate structures were suggested by the CE and confirmed by DFT.

A CE Hamiltonian provides a polynomial energy versus composition dependence for the structures with a homogeneous disorder on the Al/Ti sublattice. A low-degree polynomial does not reproduce the kink near $x = 0.915$ on the $E_{dis}(x)$ curve for D0_{24} phase in Figure 3. Hence, any CE with a finite cutoff for the multi-body interactions (we considered m -body clusters with $m \leq 7$) does not accurately reproduce the $E_{dis}(x)$ curve for this phase, although a CE is useful during an iterative search for new GS candidate structures.

The suggested ground-state structures are shown in Figure 2. DFT energies of the fully ordered structures (including the ground states) are in Figure 3. Importantly, in $D0_{24}$ phase there are many GS candidates at $0.875 < x < 1$, and at each composition there are many competing structures with similar energies (within the DFT accuracy), which differ by the longer-ranged atomic correlations at larger interatomic distances. In other words, at $x \rightarrow 1$ the $D0_{24}$ -based ground states are the structures with a well-spaced Al solute, and each ground state is accompanied by multiple competing structures with similar energies, see Figure 3.

3.5. Magnetism

Ni_3Al and Al-rich $Ni_3(Al_{1-x}Ti_x)$ alloys are magnetic [37], with the ferromagnetic (FM) spin ordering of Ni magnetic moments M_{Ni} , while the induced atomic magnetic moments of Al and Ti are small (and oriented oppositely to Ni). Ni_3Ti is non-magnetic, with zero atomic magnetic moments. At larger x , atomic magnetic moments and the total magnetization in each phase of $Ni_3(Al_{1-x}Ti_x)_1$ become smaller and disappear, see Figure 4. Although at small x $D0_{24}$ phase has higher moments M_{Ni} than $L1_2$, all $D0_{24}$ -based ground states at $x \geq 0.875$ are non-magnetic. Disappearance of M_{Ni} is a magnetic phase transition, which happens near $x = 0.364$; 0.447 ; and 0.67 in $L1_2$, $D0_{19}$, and $D0_{24}$ phases, respectively.

3.6. Electronic Structure

Considering the electronic density of states (DOS) $n(E)$, we find that the $L1_2$ -based GS at $x=0$ (Ni_3Al), 0.25 , and 0.5 have a pseudo-gap above the Fermi energy E_F . In contrast, $D0_{24}$ -based GS at $x \geq 0.875$ (including Ni_3Ti at $x = 1$) have the pseudo-gap at or below E_F , see Figure 5. Considering $n(E_F)$ versus composition, we find an electronic transition from the states with higher $n(E_F)$ at $x(Ti) < 0.875$ to the states with low $n(E_F)$ and the Fermi energy in the pseudo-gap at $x \geq 0.875$. In practice, this electronic transition coincides with the structural transition between $L1_2$ (at smaller x) and $D0_{24}$ phases (at $x \geq 0.875$).

The valence electron charge density in real space in the selected ground states is shown in Figure 6. Locally, the neighborhoods of each Al and Ti atom in $Ni_{48}Al_2Ti_{14}$ (Figure 6b) resemble those in $L1_2$ Ni_3Al (Figure 6a) and $D0_{24}$ Ni_3Ti (Figure 6c), respectively. This is also true for the other $D0_{24}$ -based ground states at $x \geq 0.875$, which differ from $D0_{24}$ Ni_3Ti by a substitution of a fraction of Ti atoms by Al solute, with Al-Al spacing distance not shorter than $7.1 \text{ \AA}$ in $Ni_{48}Al_2Ti_{14}$ (Figure 2c).

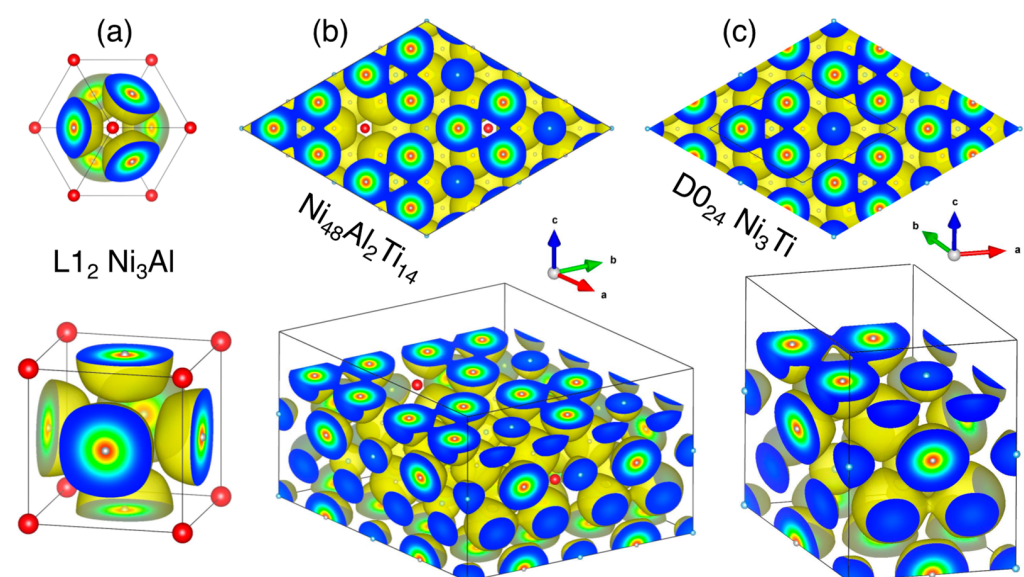


Figure 6. $0.05 e^-/\text{\AA}^3$ iso-surfaces of valence electron density in (a) cubic $L1_2$ Ni_3Al at $x=0$, (b) hexagonal $Ni_{48}Al_2Ti_{14}$ (see Figure 2c) at $x = 7/8$, and (c) $D0_{24}$ Ni_3Ti at $x=1$, with Ni (grey), Al (red), and Ti (blue) atoms. The upper panel shows cubic 111 (a) and hexagonal 0001 (b,c) projections.

3.7. Comparison to the Previous Experiments

Fully ordered $\text{Ni}_3(\text{Al}_{1-x}\text{Ti}_x)_1$ at $T = 0$ K should segregate between the L_{12} -based $\text{Ni}_3(\text{Al}_{0.5}\text{Ti}_{0.5})$ and D_{024} -based $\text{Ni}_3(\text{Al}_{0.125}\text{Ti}_{0.875})$ ground states at $0.5 \leq x \leq 0.875$. However, from a small energy difference between ordered and disordered states, we expect that experimental $\text{Ni}_3(\text{Al}_{1-x}\text{Ti}_x)_1$ samples will not form LRO on the $(\text{Al}_{1-x}\text{Ti}_x)$ sublattice. $\text{Ni}_3(\text{Al}_{1-x}\text{Ti}_x)_1$ samples with disorder (only SRO) on the Al/Ti sublattice will be in D_{024} phase at $x \geq 0.915$ and predominantly in L_{12} phase at $x < 0.8$, with a phase-segregated region between. Currently, there is no consensus among the previous experimental assessments of the phase boundaries of D_{024} and L_{12} phases in $\text{Ni}_3(\text{Al}_{1-x}\text{Ti}_x)_1$ alloys, see Table 1. Due to disagreement among the previous experimental data [38–45], a new measurement is desirable.

Table 1. Phase boundaries of L_{12} and D_{024} phases in $\text{Ni}_3(\text{Al}_{1-x}\text{Ti}_x)_1$ from our theory, our experiment, and literature. Here x (at.%Ti) is titanium atomic percent on the Al/Ti sublattice.

Temperature		$x_{\text{max}}(\text{L}_{12})$	$x_{\text{min}}(\text{D}_{024})$	Year	Ref.
Order	0 K	50	87.5	This	Theory
Disorder	∞	≈ 80	91.5	This	Theory
RT	300 K		≤ 91.68	This	Expt.
900 °C	1173 K	70	82	2016	[39]
900 °C	1173 K	67	83	2001	[40]
800 °C	1073 K	73	88	1999	[41]
1200 °C	1473 K	65	83	1999	[41]
850 °C	1123 K	64	96	1993	[42]
1250 °C	1523 K	62	90	1993	[42]
800 °C	1073 K	67	100	2005	[43]
800 °C	1073 K	63	100	1991	[44]
800 °C	1073 K	47	95	1965	[45]

3.8. Experiment

3.8.1. X-ray Diffraction

XRD analysis using the $\text{Cu-K}\alpha$ data of the cast $\text{Ni}_3(\text{Ti}_{0.917}\text{Al}_{0.083})_1$ sample is revealed in Figure 7. The graph shows that all the peaks, except for $36.5^\circ 2\theta$, match the expected peak positions for the D_{024} crystal structure associated with Ni_3Ti . The $36.5^\circ 2\theta$ is most likely associated with the Ni_3Al L_{12} phase. Quantification of the phase weight percent was not performed due to significant peak intensity discrepancies between the $\text{Cu-K}\alpha$ and $\text{Mo-K}\alpha$ scans. It was determined that this discrepancy was due to poor sampling statistics associated with the large grains found in the sample. Still, from the XRD analysis it is clear that this sample formed primarily the D_{024} crystal structure, while the scanning electron microscopy (SEM) analysis was performed to validate the 79.24 wt.% Ni, 19.75 wt.% Ti, and 1.01 wt.% Al composition, corresponding to 0.7500 at.% Ni, 0.2292 at.% Ti, and 0.0208 at.% Al in $\text{Ni}_3(\text{Ti}_{0.9168}\text{Al}_{0.0832})_1$ at $x = 0.9168$.

3.8.2. Scanning Electron Microscopy

To validate the XRD results, scanning electron microscopy of the cast ingot was performed. A SEM image of the sample is shown in Figure 8a and the corresponding chemical maps of the area are revealed in Figure 8b. The chemical maps agree with the XRD result in that the majority of the cast $\text{Ni}_3(\text{Ti}, \text{Al})$ utilizes the D_{024} crystal structure. There are small thin areas of material that appear to be composed of Ni_3Al -type L_{12} phase due to the increase in Al content and the corresponding L_{12} peaks found in the XRD analysis. The Al chemical map also reveals that the Al content is not uniform in the D_{024} phase in the as-cast state where areas that surround the L_{12} phase are richer in Al. Figure 8 also shows the presence of smaller dark phases which are most likely Al- and Ti- rich oxides. Multiple SEM micrographs were taken of the $\text{Ni}_3(\text{Ti}, \text{Al})$ sample in the as-cast state to quantify the area fractions for the two present phases— D_{024} and L_{12} . Since the two phases appear in

different contrast when imaged with a secondary detector, they can be separated, and their corresponding area fractions quantified. From this analysis, the $L1_2$ phase corresponded to only $0.86\% \pm 0.12\%$ of the total area, while the rest was composed of the $D0_{24}$ phase and oxides. This result appears to confirm the calculations performed on this ternary system.

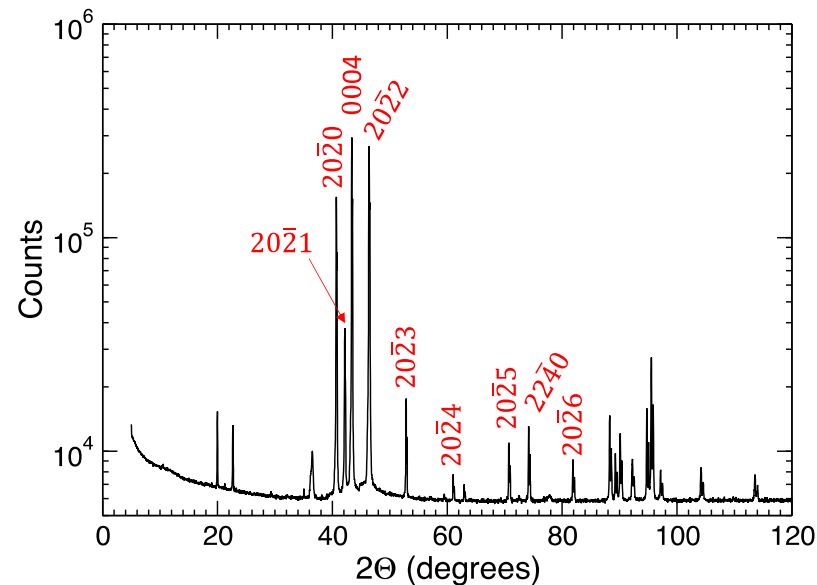


Figure 7. X-ray diffraction peaks of the of 79.24 wt.% Ni, 19.75 wt.% Ti, and 1.01 wt.% Al ingot suggesting the formation of the $D0_{24}$ Ni_3Ti phase. No evidence of LRO on the Al/Ti sublattice.

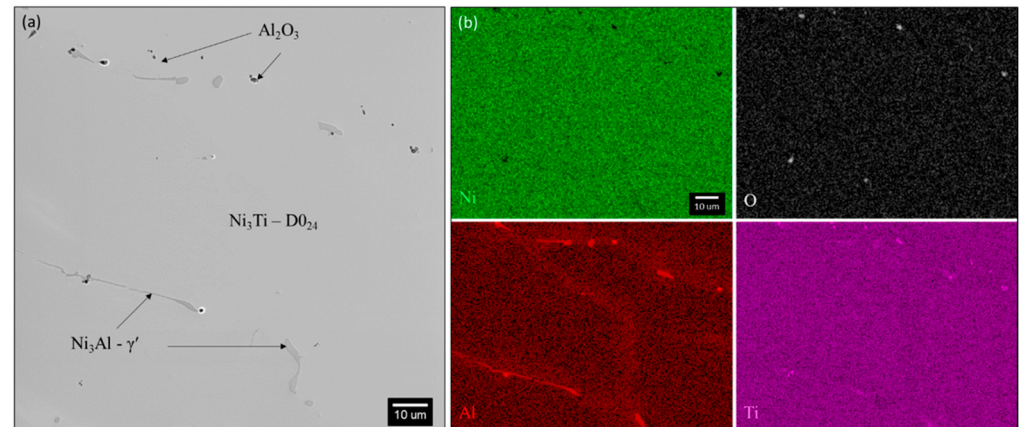


Figure 8. (a) SEM micrograph of the cast 79.24 wt.% Ni, 19.75 wt.% Ti, and 1.01 wt.% Al ingot and associated (b) chemical maps.

4. Discussion

Compositional glasses constitute a class of materials with inherent chemical disorder. If ordering enthalpy is small compared to diffusion activation energy, then atomic LRO on each sublattice is unachievable by a reasonable thermodynamic treatment. At low temperatures atomic diffusion becomes negligible and atomic order (or disorder) is frozen. Thus, a compositional glass does not transform to a fully ordered state [46] upon cooling.

Ground-state search algorithms [36] are applicable to both conventional crystals and compositional glasses. For thermodynamic predictions it is necessary to consider not only the ground states, but also competing structures [35], which might be ordered or partially disordered. Ordering enthalpy ΔE_d is defined as the enthalpy difference between the state with a homogeneous disorder on a particular sublattice and the ground-state hull at the same composition. Diffusion activation energy E_A can be either computed from

the first principles [47] or assessed from experimental data. According to the Arrhenius equation [48], diffusion rate D is proportional to $\exp(-E_A/k_B T)$; it becomes negligible below the freezing temperature T_f if the activation energy E_A is much higher than $k_B T_f$, where k_B is the Boltzmann constant. In Ni superalloys $T_f > 500$ K and $k_B T_f > 43$ meV, while $\Delta E_d < 10$ meV in the Ti-rich $\text{Ni}_3(\text{Al}_{1-x}\text{Ti}_x)_1$ D0₂₄ phase: $\Delta E_d(x)$ changes from 9.48 meV per $\text{Ni}_3\text{Al}_{1/8}\text{Ti}_{7/8}$ at $x = 0.875$ to zero at $x = 1$. Thus, $\Delta E_d < k_B T_f \ll E_A$ at any $x \geq 0.875$, and this phase is a compositional glass.

This example illustrates that in multi-phase materials (such as composites or precipitated alloys, superalloys, and steels) some of the phases can be compositional glasses; a better understanding of their fundamental properties is beneficial for materials design.

5. Summary

Compositional glass is a solid state with an inherent atomic disorder. An example of a compositional glass is Ti-rich $\text{Ni}_3(\text{Al}_{1-x}\text{Ti}_x)_1$ D0₂₄ phase, which is relevant to precipitation strengthening in Ni superalloys—multi-phase materials of high industrial importance.

We analyzed the phase stability and atomic order in $\text{Ni}_3(\text{Al}_{1-x}\text{Ti}_x)_1$ ternary system and identified the ground states and competing structures. We found multiple D0₂₄-based ground state candidates with a spaced Al solute at $x \geq 0.875$ and confirmed 3 L1₂-based GS at $x = 0, 0.25$, and 0.5 . We considered electronic, magnetic, and structural phase transitions. From the small enthalpy difference between the states with order and homogeneous disorder on the Al/Ti sublattice we anticipated that experimental samples at $x \geq 0.875$ would not develop LRO on this sublattice. We predicted that Ti-rich $\text{Ni}_3(\text{Al}_{1-x}\text{Ti}_x)_1$ alloy at $x > 0.915$ should be a compositional glass in D0₂₄ phase. Considering the previous experiments, we found no consensus in the literature regarding the boundaries of L1₂ and D0₂₄ phases. To resolve this contradiction, we conducted a new experiment at $x = 0.9168$, which appears to confirm our first-principles predictions.

Author Contributions: N.A.Z. provided the TTK code and advising to E.N.B., performed all DFT calculations, and wrote the manuscript. E.N.B. used the TTK code, performed data processing, and iteratively generated two sets of structures for L1₂ and D0₂₄ phases. T.M.S. performed experiment. J.W.L. participated in funding acquisition. All the authors participated in discussion and editing. All authors have read and agreed to the published version of the manuscript.

Funding: We acknowledge funding by NASA's Aeronautics Research Mission Directorate (ARMD) via Transformational Tools and Technologies (TTT) Project. The NASA internship of E.N.B. was funded by the NASA Minority University Research and Education Project (MUREP).

Data Availability Statement: Data is available from the authors upon a reasonable request.

Acknowledgments: We thank Smirnov, A.V. and Johnson, D.D. for the KKR-CPA code, Noebe, R. for the experimental sample creation, Leary, A. and Rogers, R. for XRD help, Mendelev, M.I. and Scalettar, R.T. for discussion.

Conflicts of Interest: The authors declare no conflict of interest.

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