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Fabrication and characterization of aluminum - magnetic shape memory alloy composites

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ABSTRACT

Keywords: Aluminum composites Metal matrix composites Magnetic shape memory alloys Structural health monitoring Martensitic transformation Smart composites, manufactured with embedded functional materials, hold the potential for a new type of structural health monitoring systems. The work herein focuses on how embedding Ni₄₃Co₇Mn₃₉Sn₁₁ metamagnetic shape memory alloy (MMSMA) sensory particles into pure aluminum matrix modifies the chemical constitution and mechanical properties of both materials. Martensitically transforming particles in pure Al or Al alloys can interact with crack tip stress fields and undergo stress-induced martensitic transformation. This process emits acoustic signals and changes the magnetic state of the particles, which can then be exploited using acoustic monitors and/or magnetic sensors to determine the crack locations. Fabrication of these composites consisted of consolidation of homogeneously mixed powder precursors containing 10 vol% of Ni₄₃Co₇Mn₃₉Sn₁₁ MMSMA particles. Elemental composition, hardness, and elastic modulus of the embedded particles and resulting diffusion region between the particles and the matrix were determined using wavelength dispersive spectrometry and instrumented nanoindentation. Elastic constants of the sintered bulk composites were also experimentally determined using resonant ultrasonic spectroscopy (RUS). Compositional analysis revealed that the diffusion region contained a diverse group of intermetallics. Nanoindentation results demonstrated that the diffusion region exhibits a high hardness value of 10.0 ± 0.3 GPa and an elastic modulus of 163 ± 5 GPa, as compared to the embedded particles having a hardness of 4.5 \pm 0.4 GPa, and elastic modulus of 127 \pm 6 GPa. Poisson's ratio and the stiffness tensor components (C11, C12, and C44) were found to be 0.34, 214 GPa, 111 GPa, and 52 GPa, respectively, through RUS. The important material properties determined in the present study, especially the interface properties, can be used to model the composite system to optimize the particle size, distribution, and the size of the interfaces for desired bulk mechanical properties and damage sensing ability.

1. Introduction

Long term structural health monitoring (SHM) is an essential component for the design of structures in space and extended life flight platforms. The most applicable method for long term SHM is through acoustic methods; either via an active measurement by propagating ultrasonic waves through a system, or through passive monitoring of the acoustic pulses that occur during cracking or fracture [1–4]. While effective, this method is hindered by two major flaws. The first is that, while the energy input is minimal, power failure shuts down the system's ability to monitor damage, even if the power failure is temporary. Second, the sensors themselves must possess a robust construction with guaranteed extended lifetimes. If a sensor fails, the monitoring system is blind to damage in the area of the failed sensor. Therefore, a secondary

system needs to be implemented to act as backup should the primary system fail. Once a failed sensor has been found, sensor replacement must be expedited and done with care to ensure no change in the monitoring capabilities. These requirements are expensive, and if the system is not properly maintained, service dates are too far apart, or improper training reduces the effectiveness of the monitoring system, critical events such as fatigue cracking, fracture, sensor failure, power loss, or a critical signal being overwhelmed by environmental noise could be life threatening.

A more robust alternative would be to embed a sensory material into the structure that is able to passively monitor and detect damage in the structure by interacting with an intrinsic aspect of the structural damage, such as stress concentrations at crack tips [5–9]. Shape memory alloys (SMAs) [10–12], and more specifically magnetic SMAs [13–37],

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are excellent candidate materials for this purpose due to their unique property relations between stress, strain, and magnetization [38-41]. In particular, a sub-class of magnetic SMAs, called metamagnetic SMAs (MMSMAs) exhibit simultaneous martensitic phase transformation and magnetic phase transition and feature massive change in magnetization levels upon martensitic transformation [13,28]. However, successful development of this sensory composite requires the characterization of the interface properties between the (magnetic) shape memory particles and the matrix. To accomplish this, we selected the Ni₄₃Mn₃₉Co₇Sn₁₁ metamagnetic SMA as it demonstrates great potential to meet the aforementioned sensory material needs. The Ni-Mn metamagnetic SMA family demonstrates the largest change in magnetization upon martensitic transformation [17,22,24,32,42-45]; the addition of cobalt shifts the Curie temperature to higher temperatures allowing for greater magnetization levels before transformation (further magnifying the change in magnetization between the martensite and austenite phases), and addition of Sn versus elements like Ga or In significantly reduces production costs; and Ni43Mn39Co7Sn11 possesses transformation temperatures near room temperature that are largely unaffected by secondary heat treatments [46-49].

For the matrix phase, as the ultimate use is intended for aerospace structures, selection of an aerospace grade alloy would seem the sensible choice for a host matrix, e.g. Al7075. However, the additional elements in the aluminum alloy may cause unnecessary difficulties in characterization of the interface between matrix and particle. As diffusion between the magnetic SMA and the matrix is an expected requirement for an effective composite in order to ensure sufficient load transfer across the interface upon loading [40,50], reducing the number of elements in the system simplifies identification of diffusion products that will occur during composite processing. Therefore, pure aluminum was selected as the host matrix material. It is easily acquirable, not sensitive to processing conditions, any diffusion products observed would likely be present in the case of the aerospace grade aluminum matrices, and limiting the complexity of the system to five elements simplifies analysis.

For effective monitoring, the sensory material would ideally be on the order of a few tens of microns [6,40]. Therefore, any mechanical testing or compositional analysis would need to be effective at the micron scale. We have chosen to perform quantitative elemental analysis with a wavelength dispersive spectrometer equipped electron probe micro-analyzer (WDS-EPMA). WDS-EPMA is widely used to determine elemental concentrations and locations in highly chemically complex specimens [51–56]. It is more precise in determining elemental concentrations than EDS. As the ultimate microstructure is unknown, and will likely be on the order of 10 μ m, high resolution and high accuracy are required.

For mechanical testing, we have chosen to use nanoindentation. This offers the ability to directly probe the mechanical properties of the $Ni_{43}Mn_{39}Co_7Sn_{11}$ particles as well as the diffusion zone between the particles and matrix [54,57–69]. Additionally, it will permit better correlation of the determined properties to the observed microstructural features. As the success of the smart composites with embedded sensory particles depends on the efficient load transfer and compatible deformation across the interface between the particle and the matrix, it is necessary to determine the fundamental mechanical properties of various interfaces that may form during the fabrication of the composites. This will help better design the matrix-sensory particle interface with proper selection of the fabrication parameters.

Finally, the mechanical properties of single crystal and oligocrystalline $Ni_{43}Mn_{39}Co_7Sn_{11}$ are largely unknown due to its wellknown inability to be grown into large scale singe crystals. Therefore, mechanical properties of the magnetic SMA, e.g. Young's Modulus, will be confirmed through resonant ultrasonic spectroscopy (RUS) of a polycrystalline specimen manufactured via sintering the $Ni_{43}Mn_{39}$. Co_7Sn_{11} powder used as the sensory material. RUS uses wave propagation through a material to determine the vibrational modes for well-known sample geometries, across a frequency spectrum, fit a mathematical model to the observed peaks, and subsequently determine elastic material properties in a number of materials including magnetic SMAs [70–82].

2. Materials and experimental methods

2.1. Material fabrication and specimen preparation

2.1.1. Powder consolidation

High purity aluminum powder (99.9% aluminum by metals basis), sieved to -325 mesh particle size, with an average particle size ranging from 7 to 15 µm was purchased from Alfa Aesar (item number 11067). Ni₄₃Co₇Mn₃₉Sn₁₁ pre-alloyed powders were fabricated using gas atomization, then sieved to between 27 and 63 µm. The magnetic SMA powder was sealed under an ultra-high purity argon atmosphere in a quartz tube and heat treated at 900 °C for 12 h to chemically homogenize the powder. A small amount of sintering occurred during the heat treatment, however, the powder state was recovered through very gentle grinding with a mortar and pestle.

Two powder compacts were manufactured through the consolidation of the above powders via spark plasma sintering (SPS, SPS25–10, Thermal Technologies, CA). Appropriate amounts of the powders were taken in a ratio of 90 vol% aluminum and 10 vol% Ni₄₃Mn₃₉Co₇Sn₁₁, to yield a final compact with nominal dimensions of 40 mm in diameter and 8 mm thick (based on 100% theoretical density). To ensure homogenous mixing of the powders, low energy ball milling was employed with a ball to powder ratio of 1:1 (using 20 of 6.3 mm and 80 of 3.11 mm stainless steel balls) in a polypropylene jar under an inert atmosphere at a rotational speed of 85 rpm. The stainless steel balls were extracted via sieve and the powder mixture was poured into a 40 mm graphite SPS die.

For each consolidation process, the following sintering procedure was repeated: the graphite die filled with the powder mixture was placed in the SPS chamber and a stress of 5 MPa was applied to the powder (the lowest stress the SPS is able to register). High vacuum atmosphere was then applied on the SPS chamber $(10^{-5}$ Torr). The die and powder were heated with pulsed DC current (20V, 100A; 20/2 ms on/off cycles) at a rate of 100 °C/min to the target sintering temperature, and was maintained until the consolidation was completed. After achieving the target sintering temperature, stress was increased on the die to the sintering pressure of 100 MPa, and was maintained until the ram of the SPS registered zero change in position for 60 s (except for the 400 °C consolidation). Table 1 summarizes the main processing parameters used.

In the case of the 400 °C consolidation, the load was held for 10 min in an attempt to allow time for the matrix to sinter as much as possible. Previous attempts (not shown here) at consolidating the mixed powders yielded a composite with no diffusion between the Ni₄₃Mn₃₉Co₇Sn₁₁ particles and the aluminum matrix at this temperature, and it was thought that adding additional time might allow the matrix to achieve full density and notable diffusion zone. Each compact was allowed to cool in the die to a temperature between 50 and 80 °C before extraction from the SPS chamber and graphite die.

The loading rates for each consolidation differed due to initial attempts (not shown here) at consolidating the mixed powders under 100 MPa/min fracturing the graphite die; due to the expansion of the die, the loading rate was reduced by a factor of five for the 560 °C consolidation of the mixed powders, and then increased by a factor of 2.5 for the 400 °C of the mixed powder when the 560 °C consolidation demonstrated success. We do not anticipate that the different loading rates had significant effect on the final compacts.

A third powder compact was made containing only the $Ni_{43}C$ o₇Mn₃₉Sn₁₁ pre-alloyed powder. Sufficient powder was used to fabricate a compact that had the dimensions of 40 mm diameter and 8 mm, and followed the same sintering procedure stated previously, except that the

Table 1

Summary of the main sintering parameters used to fabricate two powder compacts of Al/Ni 43Co7Mn39Sn11 using spark plasma sintering (SPS).

Powder Mixture (Matrix/Additive)	Sintering Temperature (°C)	Sintering Pressure (MPa)	Loading Rate (MPa/min)	Sintering Starting Atmosphere
Al/Ni ₄₃ Co ₇ Mn ₃₉ Sn ₁₁ 90/10 vol%	560	100	20	Vacuum (~10 ⁻⁵ Torr)
Al/Ni ₄₃ Co ₇ Mn ₃₉ Sn ₁₁ 90/10 vol%	400	100	50	

sintering pressure was held for 20 min to promote diffusion and densification. The compact was then allowed to cool in the die until 50 °C before extraction from the SPS chamber and graphite die. Table 2 summarizes the main processing parameters used for the $Ni_{43}Mn_{39}$. Co₇Sn₁₁ consolidation.

2.1.2. Specimen preparation

Two specimens for quantitative compositional analysis using WDS-EPMA were sectioned from the Al - $Ni_{43}Mn_{39}Co_7Sn_{11}$ composite consolidated at 400 °C with a diamond saw rotating at 150 rpm. These specimens were wrapped in tantalum foil and sealed in separate quartz tubes under ultra-high purity argon. One specimen was heat treated at 550 °C for 20 min, while the other was heat treated at 550 °C for 60 min. Both specimens were "air quenched" (removed from the furnace and allowed to cool to room temperature on a heat resistant surface) before extraction from the quartz tubes. The specimens were mounted in bakelite and mechanically polished using various steps starting from 600 grit silicon carbide paper down to 0.10 μ m diamond suspension at the platen speed of 150 rpm. The specimens were then vibratory polished in 50 nm colloidal silica solution for 12 h. A final polish on a polishing media free felt cloth and DI water was used to remove polishing media still adhered to the surface of the specimens.

One specimen for nanoindentation was sectioned from the Al - Ni₄₃Mn₃₉Co₇Sn₁₁ composite material consolidated at 560 °C with a diamond saw rotating at 150 rpm with dimensions of 8.75 × 7.25 × 3 mm. This specimen was then subject to the same polishing treatments, except the specimen was adhered to an appropriate mount for auto polishing and a Buehler Ecomet 3 Variable Speed Grinder-Polisher with an AutoMet2000 Power Head was used to auto polish the specimen for the steps preceding vibratory polishing. After polishing, the specimen was removed from the auto polishing mount before nanoindentation was performed.

One specimen for (RUS) with dimensions $12 \times 14 \times 2$ mm, was wire electrical discharge machined (EDM) from the compact containing only Ni₄₃Mn₃₉Co₇Sn₁₁ consolidated at 950 °C. The specimen was wrapped in tantalum foil, sealed in a quartz tube under ultra-high purity argon atmosphere, heat treated for 28 h at 950 °C, and "air quenched" as previously stated. Both large planar surfaces were then mechanically auto polished using various steps starting from 600 grit silicon carbide paper down to 0.10 µm diamond suspension at the platen speed of 150 rpm, then the specimen was vibratory polished for 12 h in a solution of colloidal silica. The edges of the specimen were gently and carefully polished with a high rpm, hand held abrasive polisher to remove EDM residue and as much surface roughness as possible without significantly changing the dimensions of the specimen (final dimensions of specimen were within 100 µm of original dimensions).

2.2. Characterization techniques

2.2.1. Quantitative elemental and diffusion analysis

EPMA X-ray elemental maps were obtain using Cameca SXFive electron microprobe equipped with five (5) detectors and calibrated with pure elemental standards for the following X-ray elemental energies: Al (K α), Ni (K α), Mn (K α), Co (K α), and Sn (L α). Some overlap in the Co (K α) and Sn (L α) energies is not significant enough to have a detrimental impact on the results. All collected maps were 670 × 503 pixels (dwell time: 40 ms), and 428 × 569 pixels (dwell time: 50 ms) in size with a step size of 0.1 µm. Maps show elemental distributions as atomic percentages (at.%). A back scatter electron (BSE) image of the location is given for reference.

Thermodynamic equilibrium calculations were conducted using the CALPHAD approach [83,84] as implemented in the Thermo-Calc software [85]. Aluminum was assumed to diffuse into Ni₄₃Co₇Mn₃₉Sn₁₁, and the considered concentrations ranged from 0 to 10 at.% solubility of aluminum in Ni₄₃Co₇Mn₃₉Sn₁₁, in increments of 0.1 at.% (in the case of aluminum substituting for cobalt, the range was set to 0–7 at.%). These calculations demonstrated no change in the Ni₄₃Co₇Mn₃₉Sn₁₁ alloy, nor any impurity phases, for any concentration of aluminum. As this was contradictory to the observed experimental results, this indicated that diffusion did not occur from aluminum matrix to Ni₄₃Co₇Mn₃₉Sn₁₁, but rather from the Ni₄₃Co₇Mn₃₉Sn₁₁ particle to the aluminum matrix. Given the more complex state of interaction an alternative approach was applied.

The flux of elemental species in a multicomponent alloy, based on unreduced diffusion coefficients, D_{ik} in an isothermal, and isobaric state is expressed as [86,87]:

$$J_i = -\sum_k D_{ik} \frac{\partial c_k}{\partial x} = -D_{ii} \frac{\partial c_i}{\partial x} - \sum_S D_{iS} \frac{\partial c_S}{\partial x}$$
(1)

where J_i is the flux of species *i* with respect to the local lattice plane and the summation over *k* is over all atom species in the crystal, and *c* is the concentration of species. It should be noted that the cross terms can have an appreciable effect on the atomic fluxes. The unreduced diffusivities are related to thermodynamic, and kinetic factors, and are expressed as [87]:

$$D_{ik} = -\sum_{i=1}^{n} L'_{ik} \frac{\partial \mu_i}{\partial c_k}$$
⁽²⁾

where L'_{ik} , is the proportionality factor and μ_i is the chemical potential. Diffusion coefficients for nickel, manganese, and cobalt were extracted from the MOBFE2 database within the DICTRA package [85,88,89]. For simplicity, only the coefficients in the aluminum-based binary systems were considered. The diffusion coefficient of tin in aluminum was obtained from Refs. [90]. The extracted diffusion coefficient values for the nickel, manganese, cobalt, and tin diffusing in aluminum are reported in Table 3.

2.2.2. Nanoindentation

Two sets of nanoindentation experiments were performed on the Aluminum-Ni₄₃Mn₃₉Co₇Sn₁₁ composite material consolidated at 560 °C. The first experiment was a set of $20-7 \times 7$ indentation grids with an indent spacing of 9 µm, loading at 500 µNs⁻¹, hold for 10 s, and unloading at 2500 µNs⁻¹, with a diamond Berkovich tip on a Hysitron TI 950 Triboindenter. The depth-area relationship was fit based upon a six

Table 2

Summary of the main sintering parameters used to fabricate the compact of Ni $_{43}Co_7Mn_{39}Sn_{11}$ using SPS.

Powder Mixture (Matrix/Additive)	Sintering Temperature (°C)	Sintering Pressure (MPa)	Loading Rate (MPa/min)	Sintering Starting Atmosphere	
Ni ₄₃ Co ₇ Mn ₃₉ Sn ₁₁	950	100	100	Vacuum ($\sim 10^{-5}$ Torr)	

Table 3

Calculated diffusivities for each element in the $Ni_{43}Mn_{39}Co_7Sn_{11}$ within an aluminum matrix at 560 °C.

Temperature (°C)	Nickel Diffusivity (m^2s^{-1})	Manganese Diffusivity (m^2s^{-1})	Cobalt Diffusivity (m^2s^{-1})	Tin Diffusivity (m^2s^{-1})	Matrix Element
560	$3.12452 \times \ 10^{-13}$	5.77008×10^{-16}	5.07776×10^{-13}	1.6512×10^{-12}	Aluminum

term fit over depths ranging between 50 and 300 nm in fused silica. Elastic analysis followed the universal stiffness equation, which relates the contact stiffness, S, to the elastic modulus, E [57,60,65]:

$$S = \beta \frac{2}{\sqrt{\pi}} E_r \sqrt{A} \tag{3}$$

where β is a geometric constant that depends on the indenter geometry (taken as 1 in this work), and A is the contact area. The reduced modulus, E_r , is given as follows:

$$E_r = \left(\frac{1-\nu_i}{E_i} + \frac{1-\nu}{E}\right)^{-1} \tag{4}$$

where E_i and ν_i represent the elastic modulus and Poisson's ratio of the indenter, whereas E and ν represent the elastic modulus and Poisson's ratio of the indented sample.

The hardness was estimated from the contact area using the relation

$$H = \frac{P_{max}}{A} \tag{5}$$

where P_{max} is the maximum load achieved during indentation, and A is the contact area. Both the frame stiffness and the depth-area relationship were empirically determined based upon the indentation response of a fused silica standard sample. Optical microscopy images were taken of the indentation grids to correlate indentation position with the forcedisplacement response.

The second experiment was a series of selective, singular indents on specific regions of the Aluminum-Ni₄₃Mn₃₉Co₇Sn₁₁ composite material consolidated at 560 °C (same specimen as used in Hysitron experiments). The selective indents were performed using a Nanomechanics iMicro nanoindenter with an InForce 1000 actuator (maximum load capability of 1 N) and a diamond Berkovich tip with a constant loading rate over load ($\frac{\dot{p}}{p}$) of 0.2 s⁻¹. In addition to recording force and displacement, continuous stiffness measurements were also made at a target frequency of 110Hz and a RMS dynamic displacement of 2 nm [62,63,65,68]. The use of continuous stiffness measurement allows observation of the depth-dependency of the measured properties. Elastic analysis, frame stiffness, and the depth-area relationship were determined using methods previously stated. The depth-area relationship was fit based upon a five term fit over depths ranging between 150 and 1000 nm in fused silica.

2.2.3. Resonant ultrasound spectroscopy (RUS)

To confirm the Young's modulus measurements acquired during nanoindentation, resonant ultrasound spectroscopy was performed on a parallelepiped specimen of sintered $Ni_{43}Co_7Mn_{39}Sn_{11}$ powder. Measurements were taken using a custom-made high temperature resonant ultrasound spectroscope (HT-RUS) utilizing a commercially available RUS system (Magnaflux Quasar, Albuquerque, NM). The device was modified for high temperature measurements by using large single crystal sapphire extension rods to transmit ultrasound waves between heated sample and transducers thereby protecting the transducers from the high temperature environment. The parallelepiped specimen was supported by three extension rods attached to piezoelectric transducers, and high purity argon was used to purge and maintain an inert atmosphere to hinder specimen oxidation at elevated temperatures.

The specimen was heated at 10°Cmin⁻¹ and held isothermally for 5 min at each desired temperature before the device swept a 10–500 kHz frequency range to cover the first 40 eigenfrequencies [71,75,77,78,80,

82]. Calculations for elastic constants and elastic moduli were determined from RUS spectra using a multidimensional algorithm (Magnaflux Quasar, Albuquerque, NM) that minimizes root-mean-square error between measured and calculated resonant peaks. Initial inputs were sample dimensions, mass, and estimated C_{11} and C_{44} elastic constants.

3. Results

3.1. Starting aluminum and Ni₄₃Co₇Mn₃₉Sn₁₁ powders

Fig. 1 depicts the morphologies of the starting aluminum and Ni₄₃Mn₃₉Co₇Sn₁₁, as well as the solution heat treated powder. The particle sizes observed for the aluminum powder are in agreement with the stated powder ranges given by Alfa Aesar, and demonstrated both spherical and elongated structures. The larger particles in the size range appeared to consist of engorged, oblong globules, while the finer particle sizes maintained the expected sphere shape. The as received Ni₄₃Mn₃₉₋ Co₇Sn₁₁ powders exhibited significantly rounder geometries in addition to other elongated ellipsoidal forms. The internal microstructure revealed a highly dendritic structure in good agreement with the images shown of similar powder by Ito et al. [91]. Post solution heat treatment, the Ni₄₃Mn₃₉Co₇Sn₁₁ particles maintained the largely spherical geometries and demonstrated small divots on the surface of each particle. This was likely due to sintering that occurred during the solution heat treatment process and subsequently broken during grinding with the mortar and pestle. The images also depicted very few fractured or broken particles, which indicate that using a mortar and pestle to regain the powder form of the solution heat treated material was satisfactorily gentle enough not to expect much change in the material response of the powder. The internal microstructure of the solution heat treated Ni₄₃Mn₃₉Co₇Sn₁₁ revealed a uniform structure with no apparent dendrites. Additionally, a significant number of the particles investigated with SEM demonstrated typically less than four grain boundaries (sometimes no grain boundaries were observed) within the 2D microstructural cross sections of the particles. This indicated that the solution heat treatment was successful in homogenizing the powders, and the material was expected to demonstrate uniform material responses.

3.2. Composites consolidated at 400 °C and 560 °C

Fig. 2 displays the microstructures for the composites consolidated at 400 °C (a-b) and at 560 °C (c-d). The micrographs in (a-b) (400 °C sintering temperature) demonstrated no diffusion occurred between the Ni₄₃Mn₃₉Co₇Sn₁₁ particle and the aluminum matrix. The highly porous nature of the matrix was likely due to the lower sintering temperature which did not permit full densification of the aluminum matrix powder. The micrographs for the composite sintered at 560 °C revealed a highly dense matrix with the occasionally observed pore. Additionally, a diffusion zone was observed between the Ni43Mn39Co7Sn11 particle and the aluminum matrix consisting of two distinct regions (as seen by contrast differences in the BSE images). As contrast is affected by differences in atomic number, this indicated a segregation of species within the interface between the particles and matrix. Given the elements present in the system, the brighter inner diffusion region likely possessed a higher concentration of tin, while the darker outer diffusion region likely consisted of aluminum, nickel, manganese, and cobalt. Further inspection of the outer diffusion region revealed minute second phases that demonstrated a slight difference in contrast, and suggested the diffusion region may not be homogeneous in composition and



Fig. 1. Scanning electron microscopy (SEM) images of the as received pure aluminum (a-c) powders, as received, gas atomized Ni43Co7Mn39Sn11 (d-f) powder, and the gas atomized, solution heat treated in inert atmosphere, Ni₄₃Co₇Mn₃₉Sn₁₁ (g-i) powders. Partial sintering of particles not broken during grinding of the Ni₄₃C-07Mn39Sn11powder after solution heat treatment are indicated with red arrows in image (g). (For interpretation of the references to color in this figure legend, the reader is referred to the Web version of this article.)

microstructure.

Fig. 3 shows the elemental locations for aluminum, nickel, manganese, cobalt, and tin in the composite that was consolidated at 560 °C acquired through EDS. Each map was taken simultaneously and at the same location as the BSE image given in the top left. Elemental labels are given at the top left of each map, and changes in color intensity indicate changes in concentration of the element. Aluminum was detected only in the matrix and outer most portion of the diffusion zone, in conjunction with nickel, cobalt and manganese. Tin was only observed in the core Ni43Mn39Co7Sn11 material and a highly concentrated region at the boundary with the diffusion region demonstrating the presence of aluminum. Nickel, cobalt, and manganese were noted in the core Ni₄₃Mn₃₉Co₇Sn₁₁ material and every region of the diffusion zones. Nickel surprisingly revealed a depleted ring at the junction of the inner and outer diffusion regions, while it was unknown whether the variability demonstrated by manganese was due to compositional differences or resolution of the map.

3.3. EPMA-WDS of diffusion regions formed in 400 $^{\circ}C$ composite subjected to secondary heat treatments

Fig. 4 displays the EPMA-WDS maps for a Ni₄₃Mn₃₉Co₇Sn₁₁ particle in the aluminum matrix taken from the composite sintered at 400 °C and subjected to a secondary heat treatment at 550 °C for 20 min. Each elemental map was taken at the same location as the BSE image, and a diagonal shift in position as compared to the BSE image was noted. This shift was due to a minor error in the mechanism for positioning the stage from saved coordinates. The colored scale bars depict increasing concentration in atomic percent from black (bottom) to white (top). Note that each scale bar was optimized to show the greatest change in concentration for each of their respective elements; therefore, aluminum has a concentration range from 0 to 100 at.%, while cobalt has a concentration range from 0 to 10.5 at.%. While this slowed direct comparison between each elemental map, it provided means by which finer and more distinct concentration changes over smaller regions were observed. The concentrations of each element within the core $Ni_{43}Mn_{39}Co_7Sn_{11}$ particles were homogeneous and in excellent agreement with the expected nominal concentration of the powder. This indicated no internal diffusion occurred within the particle during the secondary heat treatment to grow the diffusion region, maintaining the original composition.

The shape of the diffusion region was noted to be comprised of flares, or fins, radiating away from the core $Ni_{43}Mn_{39}Co_7Sn_{11}$ particle. It was uncertain whether this was caused by the highly porous nature of the aluminum matrix restricting the directional diffusion of the elements in the system, or if this was an effect of rapid diffusion of singular elements in a narrow cone.

Four distinct regions were observed in these maps, and are summarized with regions, phases, compositions, and predicted phases in Table 4. The first region, the matrix, contained 100 at.% aluminum; the second, the outer diffusion zone, contained 70–75 at.% aluminum, 4–24 at.% nickel, 8–24 at.% manganese, 1–3 at.% cobalt, while no tin was observed in this region; more specifically, three distinct phases were observed in the outer diffusion region. Phase I: 75 at.% aluminum, 13 at. % manganese, 10 at.% nickel, and 2 at.% cobalt; Phase II: 70 at.% aluminum, 22 at.% nickel, 5 at.% manganese, and 2.5 at.% cobalt; and Phase III: 71 at.% aluminum, 14 at.% nickel, 12 at.% manganese, and 3 at.% cobalt.

In the third region, the inner diffusion region, we observed concentrations were 24–29 at.% manganese, 5.25 at.% cobalt, and 15.5–21 at. % tin, and 0–20 at.% aluminum; specifically, two distinct phases were observed. Phase IV: 29 at.% nickel, 29 at.% manganese, 23 at.% tin, 14 at.% aluminum, and 5.25 at.% cobalt; and Phase V: 42 at.% nickel, 36 at. % manganese, 16 at.% tin, and 6 at.% cobalt. Finally, the fourth region,



Fig. 2. Scanning electron micrographs of the composites sintered from the starting powders at 400 $^{\circ}$ C (a,b) and 560 $^{\circ}$ C (c,d). Image type (back scatter and secondary electron) is indicated at the bottom left of each image. Note the relatively high porosity of the aluminum matrix and apparent lack of diffusion in the 400 $^{\circ}$ C case, and the highly dense aluminum matrix with a diffusion zone divided into two regions for the 560 $^{\circ}$ C case.



Fig. 3. EDS maps showing the location and relative concentrations of the elements in the system for the $Al-Ni_{43}Mn_{39}Co_7Sn_{11}$ composite consolidated at 560 °C. Each element is indicated in the upper left hand corner of each map. Changes in color intensity represent relative changes in concentration. Black indicates no presence of the element was detected. (For interpretation of the references to color in this figure legend, the reader is referred to the Web version of this article.)

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Fig. 4. EPMA-WDS elemental concentration maps for a $Ni_{43}Mn_{39}Co_7Sn_{11}$ particle from the composite consolidated at 400 °C then heat treated at 550 °C for 20 min. The color bar to the right of each map has been optimized separately for each element. Elemental labels are given in the top right of each map. For reference and comparison, a back scatter electron image has been provided of the same region in which the maps were taken. (For interpretation of the references to color in this figure legend, the reader is referred to the Web version of this article.)

Table 4

Table summarizing the phases, compositions, and identifications for the composite sample subjected to post processing heat treatment of 550 °C for 20 min.

Secondary Heat T	reatment 550°C-20 min	Al (at%)	Ni (at%)	Mn (at%)	Co (at%)	Sn (at%)	Indicated (Phase Diagram)	Modeled (Phase Stability Calculations)
Region 1	Matrix	100	-	-	-	-	Aluminum	-
Outer Diffusion	Phase I	75	10	13	2	_	Mn _{53.3} Al _{230.8}	Confirmed
	Phase II	70	22	5	2.5	-	NiAl ₃ solid solution	Confirmed
	Phase III	71	14	12	3	_	Al ₃₁ Mn ₆ Ni ₂ (unconfirmed)	Predicted
Inner Diffusion	Phase IV	14	29	29	5.25	23	NiMnCoSnAl solid solution	Not Predicted
	Phase V	_	42	36	6	16	NiMnCo-Sn Solid solution	Predicted (BCC_B2)
Region 4	Particle	-	43	39	7	11	Ni43Mn39C07Sn11	-

the Ni₄₃Mn₃₉Co₇Sn₁₁ particle, comprised of 43 at.% nickel, 39 at.% manganese, 11 at.% tin, and 7 at.% cobalt. Additionally, for the portions of the Ni₄₃Mn₃₉Co₇Sn₁₁ particle not in contact with the aluminum matrix, changes in concentration were only observed for the very edges of the particle, likely caused by edge effects and diffraction of the electron beam, and interactions with the voids between materials. It was not expected this was due to actual changes in composition of the material.

Fig. 5 displays the EPMA-WDS elemental maps for a $Ni_{43}Mn_{39}$. Co₇Sn₁₁ particle in the aluminum matrix from the composite consolidated at 400 °C and subjected to a secondary heat treatment at 550 °C for 60 min. As before, each elemental map was taken in the same location as the BSE image and a diagonal shift in position was noted for the maps as compared to the BSE image; this was due to the minor positioning error as previously stated.

The maps here demonstrated the same four regions of general elemental segregation, but further delineation was observed within those regions. Table 5 summarizes these results. The matrix and core $Ni_{43}Mn_{39}Co_7Sn_{11}$ materials maintained the same concentrations as observed for Fig. 4, but the inner and outer diffusion regions revealed a richer diversity of diffusional products than previously observed. The outer diffusion region displayed aluminum concentrations of 75–80 at.% at the outer most edge of the diffusion region, while closer to the inner diffusion region a distinct shift to 50–65 at.% was noted. According to the elemental maps, the sudden drop in aluminum concentration was countered by a sudden increase in nickel, manganese, cobalt. What was surprising is that regions replete in nickel and cobalt appeared to be

manganese poor, with the opposite being true as well.

Specifically, four distinct phases were observed in the outer diffusion region. Phase VI: 75 at.% aluminum, 13 at.% nickel, 9 at.% manganese, and 2.75 at.% cobalt; and Phase VII: 75 at.% aluminum, 13 at.% manganese, 10 at.% nickel, and 1.5 at.% cobalt; Phase VIII: 63 at.% aluminum, 25 at.% nickel, 8 at.% manganese, and 4 at.% cobalt. In particular, the right side of the outer diffusion region shows a region containing 65 at.% aluminum, 20–22 at.% nickel, 4–4.5 at.% cobalt, and only 8–10 at.% manganese; and Phase IX: 59 at.% aluminum, 26 at.% manganese rich regions were notably similar to the flare and fin shapes observed in the sample heat treated at 550 °C for 20 min. The regions rich in nickel and cobalt displayed forms more akin to fans and delta formations, which indicated longer diffusion times (which was expected).

Three distinct phases were observed in the inner diffusion region. Phase X: 50 at.% manganese, 38 at.% tin, 10 at.% nickel, and 2 at.% cobalt; Phase XI: 40 at.% manganese, 29 at.% nickel 27 at.% tin, 4 at.% cobalt; Phases XII: 39 at.% nickel, 31 at.% manganese, 23 at.% tin, 7.25 at.% cobalt; and finally the fourth region, the Ni₄₃Mn₃₉Co₇Sn₁₁ particle, demonstrated the same concentrations of nickel, manganese, cobalt, and tin seen previously.

The greater diversity in diffusional products within both the inner and outer diffusion regions for the extended time at 550 °C suggested the system had not achieved thermodynamic equilibrium after 60 min.



Fig. 5. EPMA-WDS elemental concentration maps for a $Ni_{43}Mn_{39}Co_7Sn_{11}$ particle from the composite consolidated at 400 °C then heat treated at 550 °C for 60 min. The color bar to the right of each map has been optimized separately for each element. Elemental labels are given in the top right of each map. For reference and comparison, a back scatter electron image has been provided of the same region in which the maps were taken. (For interpretation of the references to color in this figure legend, the reader is referred to the Web version of this article.)

3.4. Structure and phase stability analysis

A phase diagram based on the equilibria between Ni₄₃Co₇Mn₅₀ and Al is calculated and illustrated in Fig. 6. Ni₄₃Co₇Mn₅₀ system is taken as an approximation for the Heusler particle in this study. The studied system is 1 mol, and confined to have 0.5 mol Ni₄₃Co₇Mn₅₀, and 0.5 mol Al. We neglected the presence of Sn due to lack of sufficient data. It is worthwhile to point out that Sn does not form any compound with Al according to the binary Al-Sn phase diagram, however ternary compounds may form in combination with other elements. Considering the isothermal state of 560 °C, the diffusion path between Ni₄₃Co₇Mn₅₀ and Al passes through different one-, two-, and three-phase regions in which the intermetallic phases, BCC_B2(2), FCC_L12, Cub-A13, Al₃Ni₂, Al₈Mn₅, Al₁₃Co₄, Al₁₁Mn₄ (LT: Low Temperature), Al₉Co₂, and Al₃₁Mn₆Ni₂ are thermodynamically stable. For instance, when x is Al = 0.5, and T = $560^{\circ}C$, the single point phase equilibria calculations indicate that only Al₃Ni₂, Al₈Mn₅, and BCC_B2(2) phases are present, and the mole fraction of these co-existing phases are 0.01324, 0.30332, and 0.68334 respectively.

Here, we limit the discussion to the phases that appear across the isothermal diffusion line at 560°*C*. Both BCC_B2, FCC_L12 are suffixes that are used to identify ordered BCC, and FCC phase structures with a three sublattice configuration, AmBnCo. The site fraction configuration of BCC_B2 phase is m = 0.5, n = 0.5, and o = 3, and the site fraction of

FCC_L12 phase is m = 0.75, n = 0.25, and o = 1. Since there are several possible composition sets for these phases, the number in between the parenthesis in front of the suffixes differentiates between these possible states in the phase diagram. CUB_A13 is a Mn-based disordered structure with a two sublattice configuration, AmBn where m = 1, and n = 1 are the site fractions. Al₃Ni₂ is a three sublattice structure with m = 3, n = 2, and o = 1 as side fractions. In this configuration, Al always resides in the first sublattice, Al and Ni both can reside in the second sublattice, and Ni and vacancy interchange roles in the third sublattice. Al₈Mn₅ is a three sublattice structure with m = 12, n = 5, and o = 9 as side fractions. Al₁₁Mn₄ (LT), Al₁₃Co₄, Al₁₁Mn₄ (LT), and Al₉Co₂ are two sublattice structures with site fractions as indicated by their suffixes. Al₃₁Mn₆Ni₂ is an orthorhombic fixed stoichiometry ternary compound.

Sn-based thermodynamic data are investigated separately. While limited data is available for Sn-based systems, such as Co–Ni–Sn ($25^{\circ}C$) [92], and Sn–Ni–Al ($25^{\circ}C$) [93], their respective binary phase diagrams indicated Ni₃Sn and/or Ni₃Sn₄ were likely to form. To rigorously define which phases are likely to appear during the evolution of the microstructure other factors such as driving force for nucleation, and kinetic contributions (rate of Al diffusion in NiCoMnSn particle, and/or rate of impurity diffusion in Al) should be carefully investigated. Table 3 summarizes the calculated diffusivities for each of the elements in the Ni₄₃Mn₃₉Co₇Sn₁₁ particle within a hosting aluminum matrix. The fastest diffusive elements are tin, cobalt, nickel, and manganese, respectively.

Table 5

Table summarizing the phases, compositions, and identifications for the composite sample subjected to post processing heat treatment of 550 °C for 60 min.

Secondary Heat T	reatment 550°C-60 min	Al (at%)	Ni (at%)	Mn (at%)	Co (at%)	Sn (at%)	Indicated (Phase Diagram)	Modeled (Phase Stability Calculations)
Region 1	Matrix	100	-	-	-	-	Aluminum	_
Outer Diffusion	Phase VI	75	13	9	2.75	-	NiAl ₃ solid solution	Confirmed
	Phase VII	75	10	13	1.5	-	Mn _{53.3} Al _{230.8}	Confirmed
	Phase VIII	63	25	8	4	-	NiAl ₃	Confirmed
	Phase IX	59	10	26	5	-	Mn ₁₁ Al ₁₅ solid solution	Not Predicted
Inner Diffusion	Phase X	-	10	50	2	38	Mn ₃ Sn ₂	Not Predicted
	Phase XI	-	29	40	4	27	NiMnSn solid solution	Not Predicted
	Phase XII	-	39	31	7.25	23	NiMnCo-Sn Solid solution	Predicted (BCC_B2)
Region 4	Particle	-	43	39	7	11	Ni43Mn39Co7Sn11	-
0							10 05 7- 11	



Fig. 6. The calculated phase diagram for Ni₄₃Co₇Mn₅₀ – Al system. The isothermal line at 560 °*C* passes through different multiple phase regions that include Cubic-A13, BCC_B2(2), Al₃Ni, Al₃Ni₂, Al₈Mn₅, Al₁₃Co₄, Al₃₁Mn₆Ni₂, Al₉Co₂.

However, given the relatively low concentration of cobalt in the system, and immiscibility of Sn in Al, we inferred that the impurity phases containing Ni, and Mn are more likely to be observed in this case than those containing Co or Sn.

3.5. Micro-mechanical properties of $N_{143}Mn_{39}Co_7Sn_{11}$ and aluminum - $N_{143}Mn_{39}Co_7Sn_{11}$ interface through nanoindentation

3.5.1. Indents performed using the Hysitron nanoindenter

Fig. 7 displays a representative set of 7 \times 7 grid nanoindentations



Fig. 7. Optical image of a representative nanoindentation grid performed with the Hysitron nanoindenter, the corresponding force-displacement curves for indents seen in the optical image, and the combined force-displacement curves for the diffusion region and $Ni_{43}Mn_{39}Co_7Sn_{11}$ particles from all 20 sets of 7 × 7 indentation grids.

performed with the Hysitron nanoindentor (optical microscopy image on the left) on the composite sample consolidated at 560 °C. The corresponding force-displacement curves for each indent in the set are given on the right, with indents of the different regions (matrix, particle, diffusion zone) differentiated by color; orange for the indents performed on the diffusion region, teal for the Ni₄₃Mn₃₉Co₇Sn₁₁ sensory particle, and blue for the matrix. Indents marked in dark red indicate indents that occurred at boundary regions between the different phases and yielded mixed material responses which were not used in the analysis of the material properties.

Distinct clustering of material responses was observed in the nanoindentation results and indicated notably different moduli and hardness between the three major phases observed (particle, diffusion region, aluminum matrix). The diffusion region demonstrated the smallest indentation depth for the maximum load applied, and was expected given its composition and likely presence of intermetallic phases. Indent depth ranged from 100 nm to 140 nm at peak load. With such small indentation depths, compositional differences between inner and outer regions of the diffusion zone may contribute to the scatter in the corresponding load-depth curves gathered for grid indentation. Due to the quasistatic nature of these indents and lack of knowledge regarding thickness of the diffusion zone directly beneath each indent, the possibility of measurement being affected by the matrix or particle below the surface cannot be discarded for indents in the diffusion region. Inspection of the unloading portion of the curve for the diffusion region demonstrated a highly linear region with a small amount of elastic recovery and indicated a very brittle material with low ductility. This further confirmed the intermetallic nature of the diffusion region.

Indentations on the Ni₄₃Mn₃₉Co₇Sn₁₁ particles yielded a tighter cluster of material responses and indicated a uniform material response within the particle. This further supported the observation of the homogenous nature for the solution heat treated particles, and confirmed that significant diffusion within the core regions of the Ni₄₃Mn₃₉Co₇Sn₁₁ particles did not occur during processing. Indentation depths ranged from 160 nm to 180 nm at peak load, and analysis of the unloading curve demonstrated a highly linear response, with a slight increase in the amount of elastic recovery as compared to the diffusion region.

Indents performed on the aluminum matrix yielded a broad range of indentation depths spanning 540 nm–640 nm. Analysis of the unloading portion demonstrated almost no elastic recovery and indicated a soft, highly ductile material (expected of pure aluminum). The broad range in indentation depths was believed to be largely influenced by the distance between indents in the matrix. In an effort to acquire as much information about the mechanical properties of the diffusion region and the Ni₄₃Mn₃₉Co₇Sn₁₁ particles, the indentation spacing within the grid was reduced; the cost for this was indents in the matrix being too close



Fig. 8. SEM images of representative indentations made on the $Ni_{43}Mn_{39}Co_7Sn_{11}$ particles and their subsequent Force-displacement curves. White dashed circles indicate the indent relating to the dark line in the force-displacement curve, and the insert depicts the hardness and modulus as a function of depth for the same indent.

together for their size. Furthermore, closer inspection of the indents themselves displayed "pile up" along the outer edges of the indents; this caused further over estimation of material response as the device was not properly calculating contact area with respect to depth. For these reasons, analysis of the indents for the aluminum matrix were not performed for the results from the Hysitron nanoindenter.

3.5.2. Micro-mechanical material response of $Ni_{43}Mn_{39}Co_7Sn_{11}$ and the diffusion region using iMicro nanoindenter

Fig. 8 displays representative scanning electron microscopy images of nanoindentations performed on the $Ni_{43}Mn_{39}Co_7Sn_{11}$ particles embedded within the aluminum matrix for the composite consolidated at 560 °C using the iMicro nanoindenter. The type of image, secondary versus back scatter electron, is indicated in the lower left hand corner of the images. The corresponding force-displacement curves for the four observed indentations are given directly below the micrographs. The inset within the force-displacement plot indicates the hardness and modulus as a function of depth for the curve indicated in black. This same indent (black curve) is highlighted in the micrographs with a white dashed line. Image analysis of the SEM micrographs confirmed indentation spacing to be greater than or equal to the commonly recommended 2.5 times indentation width.

Indentation depths reached 500 nm (2.5 times the depth for Hysitron data) and peak loads of 22,000 μ N (4.4 times that for indents with the Hysitron). The force-displacement curves demonstrated similar shapes

to those observed with the Hysitron, largely the highly linear unloading portion with some elastic recovery at the end. All four indents demonstrate acceptable uniformity in the loading and unloading portion of the force-displacement curve, with dissimilarities likely due to indents performed on martensite versus austenite within the particle. The inset plotting hardness and modulus as a function of depth revealed stable material response after a depth of 210 nm was achieved, and the micrographs of the indents do not reveal pile up at the indentation site. The variation of observed material properties is within the expected range for differences between austenite and martensite. Due to the minor differences in material responses between the phases and to simplify the discussion in this paper, analysis of the material properties for the Ni₄₃Mn₃₉Co₇Sn₁₁ particles will treat each phase (austenite and martensite) as the same rather than differentiating between them.

Fig. 9 shows the SEM images for the indentations performed on the diffusion region observed in the composite consolidated at 560 °C. The image type is indicated in the lower right of each image with the forcedisplacement curves for the observed indentations given directly below the micrographs. As before, the inset within the force-displacement plot gives modulus and hardness as functions of indentation depth for the indent marked with a black line (force-displacement plot), with the actual indent highlighted with a white dashed line in the micrograph. Image analysis of the SEM micrographs confirmed the spacing between indents to be greater than or equal to the recommended 2.5 times the indentation width. After the indentation reaches depths in the range of



Fig. 9. SEM images of the indentations made on the diffusion region. White dashed circles indicate the indent for which the dark line of the force-displacement curves corresponds to. The insert depicts the modulus and hardness as a function of depth for the same indent.

100–200 nm, the stress field reaches self-similarity. Should a substrate effect contaminate the data, the elastic modulus would decrease or increase as a function of depth. However, because the elastic modulus is constant as a function of depth once elastic-plastic contact has developed, the measurements in the diffusion region do not indicate any contamination from the Ni₄₃Mn₃₉Co₇Sn₁₁ or the aluminum matrix.

Comparison of the BSE images in Figs. 5 and 9 indicated the majority of the indents performed here were on in the region predominately containing aluminum-nickel-cobalt and aluminum-manganese phases. Indentations achieved a depth of 350 nm and peak loads 20,000 to 22,000 μ N, and the inset of the force-displacement curves showed a stable material response at a minimum depth of 110 nm. The portions of the force-displacement curves that indicated loading and unloading displayed high uniformity, with the unloading portion indicated a highly linear response with a small degree of elastic recovery at the end. All eleven indents demonstrated high uniformity in material response despite the dissimilarities observed in the microstructure of the region. While no indents were performed within the inner diffusion region (which demonstrated a significant shift in composition), the mean values for hardness and modulus for the diffusion region were determined using this data.

Indentation on the aluminum matrix resulted in residual indent impressions with significant pile up. Using a Keyence VH-Z500 microscope at 5000x magnification, the ultimate contact area at 2 µm indentation depth was measured optically. This ultimate contact area was used for the calculation of both modulus and hardness. For a set of nine indents, the measured elastic modulus and hardness of the Al matrix were 67.16 \pm 0.98 and 402 \pm 20 MPa, respectively. This elastic modulus value agrees well with the values from literature (67 GPa). Pure aluminum samples in literature have yield strengths near 10–20 MPa, or hardnesses near 30–50 MPa (assuming a Tabor constraint factor of 2.8) [94,95]. However, these hardness values have been observed to increase to 300–400 MPa with cold working [96,97].

Table 6 summarizes the material properties determined from the nanoindentation performed by the Hysitron and the iMicro nanoindenters. Comparison of the results from both devices demonstrated that the calculated values lay within a standard deviation of each other. This indicated the observed material properties for the $Ni_{43}Mn_{39}Co_7Sn_{11}$ particles and diffusion region were accurate. It should be noted that the majority of indents occurred in the outer diffusion region of the diffusion zone, and the mechanical properties reported are indicative of only that region. Further work would need to be done to specifically probe the inner diffusion region and determine if the mechanical properties were similar to that of the outer diffusion region, given that the two demonstrated significantly different compositions.

3.6. Microstructure and resonant ultrasonic spectroscopy of sintered $Ni_{43}Mn_{39}Co_7Sn_{11}$

Fig. 10 exhibits the microstructure of the $Ni_{43}Mn_{39}Co_7Sn_{11}$ powder sintered at 950 °C and solution heat treated for 28 h at 950 °C. Surface deformations were observed, likely remnants form the polishing process, but the general microstructure appeared homogeneous. A few pores and some martensite was noted in a few of the grains and grain boundaries, however no phase separation or secondary phases were observed. This indicated the material was highly dense and uniform after the sintering and heat treatment processes. Thus it was expected the derived material properties from the RUS experiments would yield material properties for the polycrystalline pure Ni₄₃Mn₃₉Co₇Sn₁₁.

Fig. 11 exhibits the cooling and heating thermograms acquired from the differential scanning calorimetry performed on a portion of the Ni₄₃Mn₃₉Co₇Sn₁₁ powder sintered at 950 °C and heat treat for 28 h at 950 °C. Transformation temperatures are indicated at the intersection of the tangents, and are summarized in the inset table. The colored circles overlaid on the heating curve indicate the temperatures at which the RUS experiments were performed. The martensite finish and austenite start temperatures presented some difficulty in their determination as the transformation region was extended and diffuse.

Table 7 summarizes the material constants determined for the sintered $Ni_{43}Mn_{39}Co_7Sn_{11}$ powder used in the RUS experiment. The colored cells in the left hand column of the table correlate with the same colored circles overlaid on the heating DSC thermogram of Fig. 10. Very little change is noted in the material constants across the temperature range tested. The RMS error, presented in the last column on the right, was consistently less than 0.5% which indicated excellent fit of the peak positions of the sonogram, and indicated good fit between the model and peak position within the spectra.

4. Discussion of the results

Consolidation of the pure aluminum and Ni₄₃Mn₃₉Co₇Sn₁₁ powders at 400 °C yielded a composite with a highly porous matrix and no diffusion occurred between the two materials (as desired). This meant that controlled growth of a diffusion region between the Ni₄₃Mn₃₉. Co₇Sn₁₁ and pure aluminum could be achieved with secondary heat treatments, and permitted observation of the diffusional products at different time intervals. This was important to better understand how the diffusion region grows and develop at higher temperatures. As the intended use of these Ni₄₃Mn₃₉Co₇Sn₁₁ particles focused on embedding them in aluminum based alloys, the evolution of the diffusion products here would lend insight into the expected phases to be observed in the diffusion region between the Ni₄₃Mn₃₉Co₇Sn₁₁ particles and the aerospace grade aluminum.

4.1. Effect of consolidation temperature and secondary heat treatments on the microstructure of resulting composites

As predicted by the diffusion modeling from DICTRA, atoms from the $Ni_{43}Mn_{39}Co_7Sn_{11}$ particle were observed to migrate into the aluminum matrix as demonstrated by the concentration gradient seen in the WDS maps for nickel and manganese of Fig. 5. Furthermore, the insolubility of tin in aluminum caused tin to diffuse toward the center of the $Ni_{43}Mn_{39}Co_7Sn_{11}$ particle, and created a tin rich ring at the boundary of the particle.

4.1.1. 400 °C consolidated composite exposed to secondary heat treatments

Exposing the sample consolidated at 400 $^{\circ}$ C–550 $^{\circ}$ C for 20 min yielded three distinct phases in the outer diffusion region, and two in the inner. Comparison of the atomic percentages of aluminum, nickel, and manganese to the phases present in their ternary phase diagram (600 $^{\circ}$ C) [98] indicated the presence of NiAl₃, Mn_{53.3}Al_{230.8} and Al₃₁Mn₆Ni₂. These compounds are also among the suggested stable phases by our

Table 6

Table summarizing the calculated material properties for $Ni_{43}Mn_{39}Co_7Sn_{11}$ and the diffusion interface with aluminum through nanoindentation.

Device	Region Tested	Number of Indents	Modulus (Mean) (GPa $\pm \sigma$)	Hardness (Mean) (GPa $\pm\sigma)$
Hysitron	Ni7Mn39C07Sn11	81	129 ± 11	$\textbf{4.9} \pm \textbf{0.7}$
	Diffusion Region	219	175 ± 15	9.4 ± 1.4
iMicro	Ni ₇ Mn ₃₉ Co ₇ Sn ₁₁	13	127 ± 6	4.5 ± 0.4
	Diffusion Region	11	163 ± 5	10.0 ± 0.3



Fig. 10. Scanning electron micrographs of the Ni₄₃Mn₃₉Co₇Sn₁₁ powder compact sintered at 950 °C.



Fig. 11. Differential scanning calorimetry thermogram for SPS sintered $Ni_{43}Mn_{39}Co_7Sn_{11}$ material. The inset table summarizes the transformation temperatures determined by intersecting tangent method (denoted by black dashed lines). The colored circles overlaid on the heating curve correlate to the colors and temperatures given in Table 7.

calculated phase diagram. Further comparison of the binary Ni-Al and Ni–Mn [99,100] phases via the concentrations determined by WDS confirmed the presence of NiAl₃ (Phase II), as it is also shown as an stable phase in the calculated phase diagram. $MnAl_6$ is yet another likely candidate which was both indicated by the phase-diagram and WDS results, and given the similarity in atomic sizes between cobalt and manganese, and noting the comparatively low concentration of cobalt, it

was likely the cobalt substituted for the manganese rather than forming a new phase. Adding the atomic percentage of cobalt to that of manganese yielded a proportional concentration only 0.5 at.% greater than the concentration determined for the line compound $Mn_{53.3}Al_{230.8}$. Therefore, we believe the more likely phase present was $Mn_{53.3}Al_{230.8}$ (Phase I) as stated by the ternary phase diagram. Converting the molar concentrations of aluminum, manganese, and nickel in the $Al_{31}Mn_6Ni_2$ Table 7

Summary of material properties determined usi	g RUS on the sintered Ni ₄₃ Mn ₃₉ Co ₇ Sn ₁₁ materia
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Temperature (°C)	Bulk Modulus (GPa)	Shear Modulus (GPa)	Young's Modulus (GPa)	Poisson's Ratio	C _{11,22,33} (GPa)	C _{23,13,12} (GPa)	C _{44,55,66} (GPa)	RMS error (%)
30	144.34	52.20	139.75	0.34	213.94	109.54	52.20	0.386
36	145.34	52.15	139.73	0.34	214.87	110.57	52.15	0.346
40	145.73	52.00	139.43	0.34	215.07	111.06	52.00	0.400
45	146.00	51.89	139.18	0.34	215.19	111.41	51.89	0.384
50	145.58	51.88	139.11	0.34	214.75	110.10	51.88	0.378
60	144.58	51.79	138.80	0.34	213.63	110.05	51.79	0.380
70	145.29	51.58	138.36	0.34	214.06	110.91	51.58	0.370

compound, to atomic percentages yielded values of 79.50 at.% aluminum, 15.38 at.% manganese, and 5.13 at.% nickel. It was initially thought Phase III to be the Al₃₁Mn₆Ni₂, but the measured concentrations of nickel were significantly higher than was expected for the Al₃₁Mn₆Ni₂ compound. However, as the Al₃₁Mn₆Ni₂ is a solid solution, it is possible a supersaturated version containing extra nickel was present and lead to the precipitation of the NiAl₃ intermetallic; it is also possible that Phase III was merely the result of concentration gradients between the Al–Ni and Al–Mn intermetallics and the resolution of the map was not sufficiently fine to distinguish the small scale variations, subsequently showing the differences as a new phase. As no distinct regions with the appropriate concentrations of aluminum, nickel, and manganese for Al₃₁Mn₆Ni₂ solid solution were observed, its presence was not confirmed. However, given the other intermetallic species, its presence of the ternary solid solution was suggested.

Confirmation of the NiAl₃ intermetallic and the suggested presence of $Al_{31}Mn_6Ni_2$ was in agreement with the predictions made by the calculated phase-diagram. The obtained phase-diagram also predicted other intermetallic compounds depending on the Al enrichment in the diffusion zone. The presence of these other compounds was dependent on kinetic factors and, their stability with regard to other predicted phases, and was not confirmed by the WDS results.

Phase IV and Phase V of the inner diffusion region are more difficult to identify because of chemical complexity. As each of the five elements were in Phase IV, different scenarios were considered. As tin and aluminum are insoluble [101], it was not expected that intermetallics containing both tin and aluminum would form; this was confirmed through analysis of the ternary phase diagram for Al-Ni-Sn (25 °C) [93] which yielded possible phases as NiAl, Ni₃Sn₄ and elemental Sn (no phase diagram was available for Al-Mn-Sn). Analysis of the Mn-Ni-Sn ternary (400 °C) [102] for the measured atomic percentages suggested a three phase region consisting of Ni₃Sn₄, MnSn₂ and Sn. Noting the cobalt concentration of this phase was 5 at.%, consideration of the Ni-Mn-Co ternary diagram (25 °C) [103] shows a combination of two single phase regions: Ni-Mn solid solution, and a Ni-Mn-Co high temperature phase solid solution. Finally, the binary phase diagrams for Mn-Sn and Ni-Sn [104,105] both demonstrated solid solutions at 25 at.% tin, forming Mn₃Sn and Ni₃Sn solid solutions. As no evidence for liquid tin was observed in the microstructure, and both cobalt and aluminum are soluble in manganese and nickel, we believed that Phase IV was a solid solution of Ni-Mn-Co-Sn-Al, with very slight segregation between the aluminum and tin (aluminum preferring the nickel, and tin preferring the manganese).

Phase V was determined to be a Ni–Mn–Co–Sn solid solution, given the analysis of the appropriate phase diagrams previously stated. The intermetallic Co₃Sn₂, while suggested as a possible phase from the Co–Sn binary given the concentrations, no distinct phases with concentrations of cobalt higher than the parent Ni₄₃Mn₃₉Co₇Sn₁₁ were observed. Therefore, it was believed only the solid solution was present. Comparing the identified phases to the phases predicted by the thermodynamic stability analysis showed minor dissimilarity. This is likely due to the non-equilibrium condition of the physical system as is evidenced by the solid solution containing both tin and aluminum. The steep concentration gradients, and short diffusion times, likely provided sufficient driving force to stabilize the observed metastable regions.

Extending the heat treatment time to 60 min at 550 °C grew the diffusion region larger as compared to the sample exposed for only 20 min. In addition to the size, more distinct phases were observed within the inner and outer diffusion regions. In the outer diffusion region, 4 distinct phases were observed (Phases VI-IX), and three phases in the inner diffusion region (Phases X-XII). Comparison to the phase diagrams as above determined that Phase VI and Phase II were likely the same observed phase (Ni₃Al solid solution); Phase VII and Phase I were likely the same observed phase (Mn_{53 3}Al_{230 8}); Phase VIII was determined to be NiAl₃; Phase IX was determined to be Mn₁₁Al₁₅ solid solution; Phase X was determined to be Mn₃Sn₂. Given the relative concentrations of manganese, and tin, it was likely that the Mn₂Sn solid solution formed at 550 °C [104]. Upon cooling the majority of this material then transformed into the Mn₃Sn₂ intermetallic. Noting that the nickel concentration was not insignificant, analysis of the Mn-Sn and Ni-Sn [105] phase diagrams revealed that for 25 at.% Sn, manganese and nickel formed an intermetallic and solid solution, respectively, with identical crystal structures. Therefore, we believe the resulting intermetallic was based on the Mn₃Sn₂ crystal structure, but contained notable substitutions by cobalt and nickel. Phase XI was determined to most likely consist of a nickel-manganese-tin solid solution with minor substitutions by cobalt; and finally Phase XII was determined to be very similar to Phase V (nickel-manganese-cobalt solid solution with substitutions by tin). The core $Ni_{43}Mn_{39}Co_7Sn_{11}$ particle demonstrated no change in composition as compared to the nominal composition and the composition of the core $Ni_{43}Mn_{39}Co_7Sn_{11}$ particle after 20 min at 550 °C.

Some additional important points should be made about this system. First, despite the calculated diffusivity coefficient of manganese exhibiting a value three orders of magnitude smaller than the values for cobalt and nickel, manganese had a significant impact on the diffusional products of the system. Second, alternative approaches such as Density Functional theory for studying the mechanism of diffusion in the Heusler structure should be considered in future modeling. Third, the interaction between the five elements of the system provided more complex thermodynamic states and kinetic mechanisms than was expected, and emphasized that the simple assumptions for diffusion through aluminum were largely inaccurate. Fourth, given the diffusivity for tin being the highest of the system, intermetallics between tin, cobalt, manganese, or nickel were only observed for the extended time at 550 $^\circ$ C due to stability of Mn or Ni based compounds comparing to that of Sn compounds. And finally, it is worthwhile to point out that the thermodynamic state of the observed quaternary solid-solutions are not yet assessed.

Noting the differences between the calculated phases determined through the ThermoCalc calculations and those determined from the WDS maps also indicated that the Ni₄₃Mn₃₉Co₇Sn₁₁–Al system had not achieved equilibrium after 60 min at 550 °C, and that further times at elevated temperature would likely continue to evolve the system.

4.1.2. 560 °C consolidated composite and its similarity to the 400 °C + 550°C-60mins specimen

Comparing the BSE images of Fig. 2 to that of Fig. 5 demonstrated significant similarities in the diffusion regions. In the outer diffusion region of both, at least two distinct phases were observed (as seen by

contrast differences), and closer inspection of the BSE image in Fig. 8 showed almost identical features as seen in the BSE image of Fig. 5. Further comparison of the EDS maps shown in Fig. 3 to the WDS maps in Fig. 5 demonstrated remarkably similar segregation of the elements, including the nickel depleted ring at the boundary of the inner and outer diffusion regions. The similarities in the BSE images, the EDS maps and WDS maps, and the 10 °C difference in consolidation temperature (560 °C) and secondary heat treatment temperature (550 °C) for each compact respectively, we believe the diffusion regions observed in both composites to be reasonably similar. While the different phase fractions and sizes of the intermetallics would vary, we expected the diffusion regions to possess largely similar mechanical responses. Therefore, it was believed the mechanical properties determined through nanoindentation would be representative of the mechanical properties of the diffusion zone created by exposing the specimen from the 400 °C consolidated composite to 550 °C for 60 min.

4.2. Mechanical properties of the $Ni_{43}Mn_{39}Co_7Sn_{11}$ particles and their diffusion interface with the aluminum matrix—Nanoindentation

Comparison of the material properties determined through nanoindentation using two different devices showed that the Hysitron over estimated both the modulus and hardness of the diffusion region and $Ni_{43}Mn_{39}Co_7Sn_{11}$ particle. This was likely due to the depth to which the indents penetrated for the indents made in the Hysitron. While the iMicro demonstrated that a depth of 150 nm yielded a stable material response within the $Ni_{43}Mn_{39}Co_7Sn_{11}$ particle as seen by the modulus versus depth plot (with only three Hysitron indents that did not meet that criteria), only seven indents surpassed the depth of 200 nm. It seemed reasonable then the shallower indents would overestimate the modulus and hardness of the material.

The same trend was observed for the indents taken in the diffusion region. With a minimum depth of 125 nm being sufficient for stable material response, as seen in the modulus versus depth plot for the diffusion region indents of the iMicro, eight indents were insufficiently deep and only ten surpassed 160 nm (less than half of the maximum depth for the iMicro). Then as before it was sensible that the shallower indents made with the Hysitron overestimated the material properties. Despite these differences, however, reasonable agreement was achieved between the two different methods.

4.3. Material properties of sintered $Ni_{43}Mn_{39}Co_7Sn_{11}$ particles as determined by resonant ultrasonic spectroscopy and comparison to nanoindentation

The modulus values determined from the RUS analysis were in reasonable agreement with the values obtained in the mechanical nanoindentation tests. The small discrepancy was likely due to the grain size of the specimens tested. Review of the micrograph of the starting powders and embedded particles showed each particle typically containing 1–4 grains. As each particle then acts as a single or oligocrystalline material, orientation has a significant effect on mechanical properties. As the individual particles were not large enough to acquire a sufficient sample size of indents, multiple particles needed to be tested, sampling the various possible orientations each Ni₄₃Mn₃₉Co₇Sn₁₁ particle obtained. As polycrystalline FCC based materials (like Ni₄₃Mn₃₉. Co₇Sn₁₁) generally demonstrate mechanical properties closer to the <110> orientation, slightly higher or lower material properties would be expected until the sample population size (number of indents) achieved a minimum value.

5. Summary and conclusions

In the present work, the evolution of the diffusional products between $Ni_{43}Co_7Mn_{39}Sn_{11}$ and pure aluminum were investigated for two different temperatures. In both cases the diffusion region was segmented into two distinct parts, one rich in tin and poor in aluminum, while the other was rich in aluminum and devoid of tin. Further compositional analysis and thermodynamic modeling strongly suggested the presence of a diverse group of intermetallics, while nanoindentation revealed the region to be distinctly harder with a higher modulus of elasticity than either the Ni43Co7Mn39Sn11 particles or aluminum matrix, further confirming the presence of intermetallics. Elastic modulus determined through nanoindentation on the Ni₄₃Co₇Mn₃₉Sn₁₁ particles themselves were compared to values acquired with RUS on specimens fabricated by sintering the same powder to near full density and found to be within 10% of each other, signifying good agreement. In addition to confirming the elastic modulus acquired with nanoindentation, RUS analysis for the first time yielded shear, bulk, and elastic modulus values, as well as Poisson's ratio and elastic constants for the sintered, polycrystalline Ni43Co7Mn39Sn11 material. Overall, the present work yielded greater insight into the interaction between Ni43Co7Mn39Sn11 and aluminum and suggested that manufacturing methods that permitted consolidation of the starting powders into a highly dense material at temperatures low enough to halt reaction between the Ni₄₃Co₇Mn₃₉Sn₁₁ and aluminum possessed the greatest chance of success for a viable sensory material. Furthermore, the high data obtained through RUS on the bulk Ni43C-07Mn39Sn11 material will be greatly beneficial to attempts at modeling this system to determine optimum particle size, distribution, and thickness of diffusion region for proper load transfer across the interface for using these sensory particles in structural health monitoring of aerospace grade aluminum alloys.

Data availability statement

The data that support the findings of this study are available from the corresponding author, [IK], upon reasonable request.

CRediT authorship contribution statement

N.E. Barta: Conceptualization, Methodology, Formal analysis, Investigation, Data curation, Writing - original draft, Visualization, Project administration. C. Fincher: Validation, Investigation, Data curation, Writing - review & editing. A.M. Bolon: Validation, Investigation, Formal analysis, Investigation, Data curation, Writing - review & editing. V. Attari: Methodology, Data curation, Writing - review & editing. R. Arroyave: Methodology, Resources, Writing - review & editing. M. Radovic: Formal analysis, Resources, Writing - review & editing. G.M. Pharr: Validation, Resources, Writing - review & editing. I. Karaman: Conceptualization, Methodology, Resources, Writing - review & editing, Supervision, Project administration, Funding acquisition.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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