Exploring Structural Properties of the Al-Mn-Ni based φ Phase

Avner A. White[1], Victor Zenou[2], David Fuks[1], Yatir Sadia[3], Louisa Meshi[1]

1 Department of Materials Engineering, Ben Gurion University of the Negev, Beer Sheva, Israel

2 Nuclear Research Center of the Negev, Beer Sheva, Israel

3 Faculty of Engineering, Bar Ilan University, Ramat Gan, Israel

whitea@post.bgu.ac.il

Understanding the relationship between crystal structure and physical properties is central to the study of complex intermetallic compounds, particularly those structurally related to quasicrystalline approximants. The φ phase (*$P6_3/mmc$*; *a*=7.601Å, *c*=7.819Å) is an approximant of a decagonal quasicrystal found in the ternary Al-Mn-Ni system. In this ternary system the φ phase exists over a wide range of compositions [1,2]. Aluminides isostructural to φ phase were reported to exist in many ternary systems such as the Al-Mn-Co [3] and the Al-Mn-Fe systems [4]. As a function of stoichiometry (i.e. the ratio between Al and (Mn+Ni/Co/Fe)), the φ phase can be considered as isostructural to either Al_5Co_2 or $Al_{10}Mn_3$ previously reported structure types, where the difference between them is in the occupancy of the *2d* site. In a work by Takeuchi et al. [5], unique thermoelectric properties of each structure type were reported. Despite sharing identical symmetry and closely related atomic frameworks, these phases are commonly treated as distinct structure types. This raises a fundamental crystallographic question: does the φ phase represent two discrete structure types, or a single structure accommodating compositional variation through partial site occupancy?

In this work, we investigate crystallographic and physical properties of the φ phase across a range of compositions in the Al–Mn–Ni ternary system, with particular emphasis on quantitative determination of site occupancy and unit cell parameters using Rietveld refinement method applied on powder X-ray diffraction data. Alloys were synthesized by arc melting followed by long-term heat treatment to stabilize the φ phase over different compositions (representing different ratios of Al/transition metal). Microstructure investigation and chemical analysis was performed using electron microscopy including both Scanning electron microscopy (SEM) and Transmission electron microscopy (TEM), equipped with Wavelength Dispersive Spectroscopy (WDS) and Energy Dispersive X-ray Spectroscopy (EDS). Thermal diffusivity values, measured over a wide range of temperatures, were determined for each alloy using a NETZSCH 457 Laser Flash Analysis system. Diffraction data was collected using a Bruker D2 Phaser diffractometer and analysed using GSAS-II [6].

The experimental results are complemented by first-principles density functional theory calculations, incorporated in the WIEN2K software [7], evaluating the energetic stability of structural variants corresponding to different stoichiometries. *Systematic trends in lattice parameters, c/a ratio and thermoelectric properties are correlated with composition and refined occupancy values*. *The combined experimental and theoretical analysis provides insight into whether structural changes occur discontinuously between Al_5Co_2 type and $Al_{10}Mn_3$ type configurations, or continuously through vacancy-mediated site occupation*.

[1] Balanetskyy S, et al (2011) J Alloys and Compds, 509, 3795-3805.
[2] Balanetskyy S, Meisterernts G, Feuerbacher M (2011) J Alloys and Compds, 509, 3787-3794.
[3] Grushko B, Pavlyuchkov D, Mi S.B., Balanetsky S (2016) J Alloys and Compds, 677, 148-162.
[4] Balanetsky S, Pavlyuchkov D, Velikanova T, Grushko B (2015) J Alloys and Compds, 619, 211-220.
[5] Takeuchi T, et al (2010) J. Electronic Materials 39 (9), 1433-1438.
[6] Toby B, Von Dreele R (2013) J. Appl. Cryst. (2013). 46, 544–549.
[7] Schwarz K, Blaha P, Madsen G.K (2002) Compt. Phys. Comm, 147, 71-76.