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A new complex ternary phase in the Al-Cr-Sc push-pull alloy

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ABSTRACT

The purpose of this study is to find new ternary intermetallic compounds within the Al-Cr-Sc system, which is typical of a push-pull system in which two constituents (Cr and Sc) are immiscible, whilst they form compounds, respectively, with the third constituent (Al). By arc-melting of the three components aluminium (Al), chromium (Cr) and scandium (Sc) under inert atmosphere, a range of different alloys was produced. The microstructure was observed using scanning electron microscopy (SEM) and the phase compositions were analysed by electron dispersive X-ray spectroscopy (EDS). The samples were measured with X-ray diffraction (XRD) and transmission electron microscopy. The results were confirmed by Rietveld refinement. Three different phases were found in the microstructure of the samples, the two known binary phases $Al_{16}Cr_{10}$ and Al_3Sc and a new ternary phase coined ϕ-Al_8Cr_4Sc. ϕ-Al_8Cr_4Sc showed great similarities to other Al_8Cr_4RE compounds with tetragonal *I*4/*mmm* crystal structure. Starting from the structure of already known Al_8Cr_4RE crystals, *ab initio* calculations were performed to determine the crystallographic parameters of ϕ-Al_8Cr_4Sc and also to investigate its electronic structure, which identified the energy band factor as the key factor that determines the stability of this compound. The lattice parameters and atomic positions were found in good agreement with the ones obtained by Rietveld refinement. Experimental atomic resolution high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) image analysis of the ϕ-Al_8Cr_4Sc phase confirmed the predicted atomic model.

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1. Introduction

The application of aluminium alloys is widely spread, e.g. in aircraft, automotive and electronic industries, to name only a few. Advantages of aluminium are its light-weight, its reasonable ductility, and its resistance to corrosion, which can be further enhanced by alloying Al with other elements such as Cr, Mo, Ti and Zr [1–5]. Corrosion resistance is especially enhanced when a small amount of Cr is added to Al in spite of its low solid solubility [6,7]. At higher concentrations, the structure of the material evolves drastically, leading to the formation of a complex phase, the so-called γ-brass structure, which is found around the Al_8Cr_5 stoichiometry [8]. This compound is considered a good representative of the γ-brass family that is widely spread over many binary and multi-component metallic systems [9]. Good examples in the context of the present study are the cubic and rhombohedral γ-brass Al-Fe-Cr compounds that form in a narrow area around the $Al_{70}Cr_{21}Fe_9$ (at.%) composition and show definite crystallographic relationships with quasicrystals [10].

For improving the microstructures and mechanical properties, such as tensile strength, corrosion resistance, heat resistance, vibration resistance, and extrudability, small amounts of rare earth (RE) elements can be added to Al-alloys [5]. In this context, one of the rather unexplored systems is Al-Cr-Sc. According to Dubois et al. this system can be described as a push-pull alloy [11]. This term is used to refer to ternary alloy systems that form complex intermetallics, which exhibit crystalline compounds having more, or far more, atoms in their unit cell than their individual constituents. Complex metallic alloys (or CMAs for short), which were the

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focus of attention of a European Network of Excellence [12] few years ago include structurally complex alloy phases, namely quasicrystals and so-called approximants [13]. Such compounds yield several tens to an infinite number of atoms. Yet, compounds of intermediate size, with less atoms per unit cell, but more than in the constituent metal, also exist and are of interest. The concept of push-pull alloy unites the two points of view and draws attention to the rise of complexity in a metallic alloy more than to crystal structures.

A push-pull alloy (PPA) is basically a ternary alloy $A_xB_yC_z$ ($x + y + z = 100$ at.%) consisting of three binaries, where two of the binaries A-B (Al-Cr) and A-C (Al-Sc) yield defined compounds and therefore exhibit attractive interactions or equivalently, negative formation enthalpies. For the components B and C (Cr-Sc) on the other hand, the formation enthalpy is positive: the constituents are immiscible and no compounds are forming. These interactions are described as repulsive interactions, meaning that possible ternary compounds forming in the system are "pushed" away from the B-C binary part to the opposite corner in the system (Fig. 1). The balance between repulsive (push) and attractive (pull) pair interactions may lead to the occurrence of complex compounds, with some of them reaching the ultimate complexity of quasicrystals.

To this day, not much is known about the mechanisms supporting the formation of rare-earth (RE) containing complex compounds in PPAs. Various Al-Cr-RE systems have been reported before, where different complex compounds were discovered [14–21], but to the best of our knowledge, no ternary Al-Cr-Sc compound was reported so far.

Scandium is by the definition of N.G. Connelly et al. [22] a rare-earth element, even though it is not part of the group of the lanthanoids. Since other rare-earth elements form compounds with aluminium, on the one hand, and scandium is highly immiscible with chromium, on the other hand, it is expected that complex compounds can be found in the Al-Cr-Sc system. Hence, the purpose of this study is to find new ternary intermetallic compounds within the Al-Cr-Sc system and to provide a basis for further experiments concerning the properties of these compounds such as possible magnetic and electronic properties. Al-Cr-Sc alloys on the Cr-Sc-rich side are of little interest because of the broad miscibility gap forming already in the liquid state. Therefore, we had to restrict ourselves to a limited number of compositions located in the Al-rich corner of the system. To select specific compositions, we assumed that complexity shows up when the average electronic concentration e/a (number of valence electrons per atom) is similar to the one known in already studied quasicrystalline compounds such as Al-Cu-Fe [23] and Al-Pd-Mn [24]. A possible mechanism that explains why Nature selects one specific phase at a given e/a ratio is based on the Hume-Rothery rule [25], which was recently revisited in great detail by Mizutani and Sato [26,27]. The optimal value of e/a that favours complexity in metallic systems falls between 2.0 and 2.2 electrons per atom (el/at) [28–30], which is different from the value initially considered by Tsai to find out quasicrystals [31], but is placed on a more secure theoretical basis thanks to electronic band calculations [26]. For simplicity, we shall take it equal to e/a = 2.1 el/at. Contributions to the valence band brought by the individual elements were taken from the work of Mizutani et al. [32,33], namely: $e/a_{(Al)} = 3.01$ el/at, $e/a_{(Cr)} = 0.92$ el/at and $e/a_{(Sc)} = 1.3$ el/at. This valence of 1.3 el/at for Sc is in contrast with the usually accepted value of 3 el/at, but has to be taken into account when the Sc atom is placed in a metallic environment [30]. With this in mind, the compositions $Al_{100-y-z}Cr_ySc_z$ (at.%) that fulfil the constraint e/a = 2.1 el/at must satisfy the following balance equation:

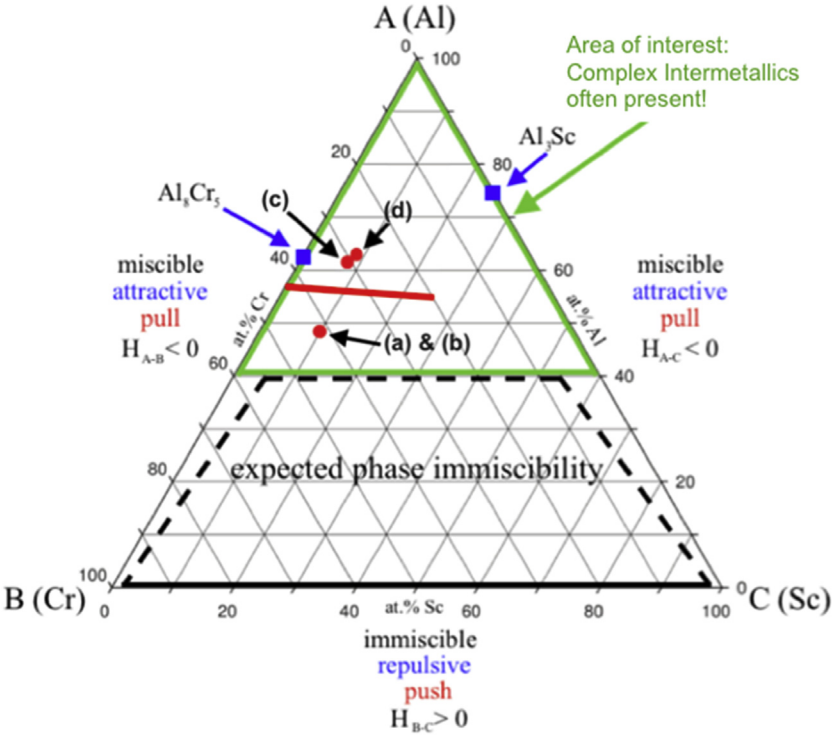

Fig. 1. Schematic diagram of the Al-Cr-Sc ternary system displaying the area of interest where complex intermetallics are most likely to form and the region where they are least likely to form (expected phase immiscibility). Al-Cr and Al-Sc function as "attractive" binaries forming several intermetallic compounds, whereas the Cr-Sc binary is acting as "repulsive" binary due to the immiscibility of Cr and Sc. Points (a), (b), (c) and (d) show the positions of the compositions in which a ternary phase was formed. The solid line represents Eq. (2) in this region of the phase diagram.

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