Corrosion Science xxx (xxxx) xxx–xxx

Contents lists available at ScienceDirect

Corrosion Science

journal homepage: www.elsevier.com/locate/corsci

Microstructure and corrosion properties of the low-density single-phase compositionally complex alloy AlTiVCr

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ARTICLE INFO

Keywords:
High entropy alloy
Compositionally complex alloy
TEM
Polarisation
XPS

ABSTRACT

Compositionally complex alloys (CCAs) possess unique microstructures and passive films, which need to be studied to contribute to fundamental understanding of corrosion in such alloys. Herein, we report the corrosion characteristics of a single phase CCA, AlTiVCr, designed to have a low-density ($5.06\ \mathrm{g\,cm^{-3}}$) relative to other CCAs. AlTiVCr was found to exhibit excellent corrosion resistance in 0.6 M NaCl (with $E_{pit} > 1.27\ V_{SCE}$). A passive layer comprising of mixed metallic oxides interspersed with un-oxidised metal species was detected upon this CCA using X-ray photoelectron spectroscopy, which was hypothesised to contribute to excellent corrosion resistance.

1. Introduction

High entropy alloys (HEAs) are defined as alloy systems comprising of five or more principle elements in more or less equi-atomic ratios, forming solid solution phases [1]. Some HEAs possess complex microstructures owing to the formation of secondary phases or intermetallic phases [2–4] within the matrix, which may lead to the brittleness of such HEAs. Such microstructural heterogeneity in HEAs could result in their localised corrosion during exposure to aqueous environments, as evidenced by reports on the corrosion of HEAs by several researchers [5–7]. For example, in copper (Cu)-containing HEAs [5], Cu tends to segregate out of the matrix due to a positive binary enthalpy of mixing of Cu with other constitutional elements such as Co, Cr, Fe, Ni. The Cu-rich phase suffers from micro-galvanic driven dissolution as it is electrochemically less noble compared to the alloy matrix. However, in many other HEAs [8–13], face-centred cubic (FCC), body-centred cubic (BCC) or even hexagonal close packed (HCP) solid solution phases form without secondary intermetallic phases. Such microstructures are concomitant with superior corrosion resistance [14,15] and thermal stability [16]. It is worthwhile to note that a high entropy of mixing of itself does not ensure the formation of a solely solid solution alloy, and intermetallic phases may also form within the matrix − as reported in many so-called HEAs. As a result, alloy systems that contain second (third, or more) phases are better termed as 'compositionally complex alloys' (CCAs) [17,18].

There remains an ever-present demand for structural materials with low densities and high specific strengths, as they may lower the energy consumption (by light-weighting). In this context, low-density HEAs are being explored and they nominally contain elements like Mg, forming either an amorphous phase [19] or a multiple-phase structure with secondary intermetallic phases [20,21]. Recently, Youssef et al. [11] developed a novel low-density ($2.67\ \mathrm{g\,cm^{-3}}$) $AlLiMg_{0.5}ScTi_{1.5}$ HEA. This particular alloy comprised of reactive metals such as lithium (Li) and was prepared by mechanical alloying. However, of practical interest, the preparation of HEAs is ideally carried out by preparing alloys employing a process closer to equilibrium than mechanical alloying. The $AlLiMg_{0.5}ScTi_{1.5}$ alloy had a single-phase FCC structure following ball milling, and transformed to a single HCP phase after annealing at 500 °C for 1 h. The as-milled and annealed alloys were both found to have high mechanical hardness values of 5.9 GPa and 4.9 GPa, respectively. A literature survey revealed that only a limited number of low-density CCAs have been reported [11] and therefore, it is of significant interest to the HEA community to develop and explore low-density HEAs.

The development of CCAs/HEAs requires alloy design in terms of predicting elemental combinations which could result in the formation of purely solid solution phases [22–31]. The design of CCAs/HEAs is complicated by the fact that existing thermodynamic databases and phases diagrams, do not account for such complex blends (which have not previously been empirically tested). In fact, an empirical rule was previously established using parameters including the entropy of mixing (ΔS_{mix}), the enthalpy of mixing (ΔH_{mix}) and the so-called atomic

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https://doi.org/10.1016/j.corsci.2018.01.035
Received 18 October 2017; Received in revised form 21 January 2018; Accepted 28 January 2018

Please cite this article as: Qiu, Y., Corrosion Science (2018), https://doi.org/10.1016/j.corsci.2018.01.035

size parameter (δ). It has been proposed that, in order to form solid solution, HEAs should have small atomic size differences, near-zero values of the absolute enthalpy of mixing and a high entropy of mixing [23]. Yang and Zhang [27] also proposed a parameter Ω that indicates the solid solution formability according to:

$$\Omega = \frac{T_m \Delta S_{mix}}{|\Delta H_{mix}|} \tag{1}$$

where, T_m is the melting temperature of an n-element HEA and can be calculated from a the rule of mixtures,

$$T_m = \sum_{i=1}^{n} c_i (T_m)_i \tag{2}$$

where $(T_m)_i$ is the melting temperature of the i^{th} element. When $\Omega > 1$, the so-called HEAs are more likely to be a solid solution. However, these rules are empirical and only serve as a guideline to assist in alloy design.

Several researchers have investigated the corrosion characteristics of HEAs over the past decade [7,15,32–44], a recent summary provided by Qiu et al. [45]. Overall, some HEAs have superior corrosion resistance compared to that of the austenitic stainless steel, 304 SS [15,32,38,39]. Chen et al. [15] compared the electrochemical properties of a $Cu_{0.5}NiAlCoCrFeSi$ HEA with 304 SS and observed that over a wide range of NaCl and H_2SO_4 (sulphuric acid) concentrations, the general corrosion resistance of the CCAs/HEAs was superior to that of 304 SS. However, conversely, HEAs were found to be more susceptible to pitting corrosion than 304 SS in chloride-containing environments [14,15]. Titanium, a light metal, and some Ti-containing alloys CCAs such as $(TiAl)_{0.7}V_{0.15}Fe_{0.1}Ni_{0.05}$ and $Ti_{0.3}(CoCrFeNi)_{0.7}$ were reported to exhibit a higher resistance to pitting corrosion than 304 SS in 0.6 M NaCl, in spite of their heterogeneous microstructures [14]. Therefore, Ti may potentially be utilised in HEAs to promote corrosion resistance and herein, we report a low-density, single-phase Ti-containing CCA developed to be inclusive of only elements with a density lower than iron (Fe).

2. Material and methods

2.1. Material preparation

Arc melting was employed to produce the AlTiVCr CCA herein. Melting was carried out in a reduced argon atmosphere. CCA was melted on a water-cooled copper hearth with starting materials being pure (99.99%) metal chunks. The density of the alloy was measured using the standard Archimedes method using a balance with precision of 0.001 g.

2.2. X-ray powder diffraction

X-ray powder diffraction (XRD) was used to determine the phase composition of the as-cast AlTiVCr alloy. The alloy was cut into small pieces and ground using an agate mortar and pestle, followed by processing in a McCrone Micronsing mill for ~ 30 s to produce small particles for XRD. XRD data were collected on a PANalytical X'Pert PRO MPD using a Co target tube operated at 40 kV and 40 mA. The interplanar spacings (d-spacings) of CCAs are unique and not in available powder diffraction databases. Therefore, the d-spacings for individual peaks were calculated herein from the collected XRD patterns and were matched according to the relevant crystal structure.

2.3. Microstructural analysis

Specimens were investigated using an FEI Nova NanoSEM 450 scanning electron microscope (SEM). Samples for SEM analysis were prepared metallographically to a 1 µm diamond paste finish followed by final polishing using an oxide polishing suspension (0.05 µm), and then imaged using a FEI Nova NanoSEM 450 in secondary electron (SE) mode. Transmission electron microscopy (TEM) specimens were prepared by focused ion beam milling, using a FEI Quanta 3D FIB. A thin foil was milled from the bulk AlTiVCr specimen via Ga-ion milling, followed by 'lift-out' onto a Cu grid, and subsequent low energy ion beam thinning of the foil to ~100 nm thickness. Conventional TEM imaging was carried out using an FEI Tecnai G2 T20 and scanning-TEM (STEM) was carried using an FEI Tecnai G2 F20.

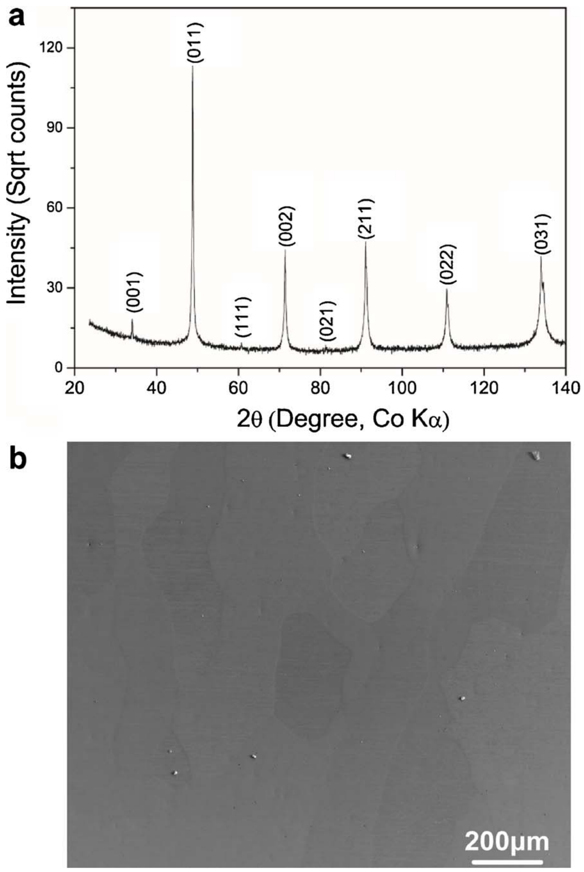

Fig. 1. (a) The XRD result of an as-cast AlTiVCr alloy and (b) a scanning electron micrograph of the as-cast AlTiVCr alloy.

2.4. Electrochemical testing

Potentiodynamic polarisation testing, cyclic polarisation testing and electrochemical impedance spectroscopy (EIS) were conducted in a typical three-electrode flat-cell (Princeton Applied Research, K-0235) with the test specimen as the working electrode, a saturated calomel reference electrode (SCE), and a platinum mesh counter electrode. The test solution used was quiescent 0.6 M NaCl, with the tests performed at 25 °C. The specimens were ground to 2000 grit finish (SiC paper) prior to electrochemical testing and at least four replicate tests were conducted for each alloy. The open circuit potential (OCP) was measured for 30 mins for CCA, 304 SS, and 20 mins for pure Al prior to polarisation testing to achieve an approximately stable potential. For the potentiodynamic polarisation testing, each specimen was scanned potentiodynamically at a rate of 1 mVs^{-1} from an initial potential of -150 mV_{SCE} versus OCP, to a final potential of 2.0 V_{SCE} using a VMP3 potentiostat (Biologic) under the control of EC-Lab 11.01 software. The potentiodynamic polarisation tests were automatically terminated when the anodic current reached a peak current of 1 mA or the applied potential reached 2 V_{SCE}. The corrosion potentials (E_{corr}), corrosion current densities (i_{corr}) and the pitting potential (E_{pit}) were deduced