Scripta Materialia 157 (2018) 67–71

Contents lists available at ScienceDirect

Scripta Materialia

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

Regular article

Engineering an ultrafine intermetallic eutectic ternary alloy for high strength and high temperature applications

Chandra Sekhar Tiwary [a,b,*], Ankush Kashiwar [a,1], Sanjit Bhowmick [c], K.C. Hari Kumar [d], Kamanio Chattopadhyay [a,**], Dipankar Banerjee [a,**]

[a] Department of Materials Engineering, Indian Institute of Science, Bangalore 560012, India
[b] Materials Science and Engineering, Indian Institute of Technology Gandhinagar, Gujarat 382355, India
[c] Bruker Nano Surfaces, Minneapolis, MN 55344, USA
[d] Department of Metallurgical & Materials Engineering, Indian Institute of Technology Madras, Chennai 600 036, India

ARTICLE INFO

Article history:
Received 11 May 2018
Received in revised form 15 July 2018
Accepted 26 July 2018
Available online xxxx

Keywords:
Intermetallic eutectics
Phase equilibria
Microstructure
Mechanical properties
Oxidation

ABSTRACT

We introduce a novel material based on microstructural engineering of intermetallics at an ultrafine scale. A unique microstructure was developed in a ternary alloy composition (Ni-12 at.% Al-11 at.% Zr) containing two coupled intermetallic phases (Ni_3Al and Ni_5Zr) consisting of colonies with interconnected lamellae that degenerate into irregular morphologies during growth. This architecture exhibits excellent high temperature microstructural stability, exceptional high strength with adequate tensile ductility at room temperature, and outstanding cyclic oxidation resistance.

Several decades of effort towards the development of new generation of intermetallic alloys through the 80's and 90's have largely gone unrewarded, with the exception of TiAl based alloys that have been introduced in recent generation of aircraft engines [1–3]. The promise of intermetallics as a high temperature material is limited by their poor ductility and toughness that fundamentally originates from the existence of directionality in bonding as well as from several intrinsic properties such as low grain boundary cohesive strength (in the case of Ni_3Al) or an insufficient number of slip systems (as in NiAl) or extrinsic effects such as embrittlement by hydrogen (Fe_3Al) [1, 2]. However, low ductility or toughness can often be alleviated by limiting the length scale for slip [4, 5]. We have therefore explored the possibility of combining intermetallics to form submicron spaced layered structures through eutectic solidification that can potentially limit slip lengths within each intermetallic constituent. Combinations of three elements or more would enable a significantly larger set of permutations of eutectic intermetallics, provided that the constituent binary phase diagrams contain either eutectic or peritectic reactions involving intermetallic phases, as well as intermediate intermetallic phases.

The ternary Ni-Al-Zr system meets our criterion in several ways. The Ni-Al binary phase diagram exhibits a peritectic reaction [6] where intermetallic NiAl (space group of $Pm\overline{3}m$, B2 structure with a lattice parameter of 0.288 nm) reacts to form intermetallic Ni_3Al ($Pm\overline{3}m$, $L1_2$ with a lattice parameter of 0.356 nm). The Ni-Zr system also shows a peritectic reaction [7] between liquid and the intermetallic Ni_7Zr_2 (C12/m1 with a lattice parameter $a = 0.469$ nm, $b = 0.823$ nm, $c = 1.219$ nm) that yields the intermetallic Ni_5Zr (space group of $F\overline{4}3m$ with a lattice parameter of 0.670 nm). Zr has been reported to improve strength and ductility of Ni_3Al and NiAl [8]. Both Al and Zr form stable oxides and might promote oxidation resistance. In a developmental programme, we have recently explored different possible Ni rich compositions in Ni-Al-Zr system [9, 10] Among the alloys evaluated in this study, the Ni-12 at.% Al-11 at.% Zr composition, shows unique microstructural features and potential for alloy development. This alloy is presented and discussed in this paper.

Our assessment of phase equilibria in the Ni-Al-Zr system using Thermo-Calc software suggested that a variety of eutectic reactions forming multiple combinations of intermetallic phases are possible in this system (details are described in supplementary information) One

---

[*] Corresponding author at: Department of Materials Engineering, Indian Institute of Science, Bangalore 560012, India.
[**] Corresponding authors.
E-mail addresses: cst311@gmail.com (C.S. Tiwary), kamanio@materials.iisc.ernet.in (K. Chattopadhyay), dbanerjee@materials.iisc.ernet.in (D. Banerjee).
[1] Present address: Karlsruhe Institute of Technology, Germany.

https://doi.org/10.1016/j.scriptamat.2018.07.036
1359-6462/© 2018 Acta Materialia Inc. Published by Elsevier Ltd. All rights reserved.

such eutectic reaction leads to a eutectic comprising the Ni_3Al and Ni_5Zr phases (Fig. 1a). Based on the predicted composition, we have prepared alloys using high purity elements (Ni (99.9%), Al (99.9%) and Zr (99.4%)), by non-consumable vacuum arc melting several times followed by suction casting into a water cooled copper mold to obtain rods of 3 mm diameter. Fig. 1b and c shows the microstructure that results from this eutectic reaction. Each eutectic nodule initiates in a lamellar morphology (β) and subsequently degenerates into a more irregular (α) form as the solidification proceeds. This leads to the emergence of various length scales in the microstructure. The lamellar portion has a spacing that ranges from 200 to 500 nm while necklace of coarser irregular eutectic constituent has an average interphase spacing from 100 to 900 nm. The microstructure of this ternary eutectic is very different from classical binary eutectics. The tomography of the structure was performed through focussed ion beam (FIB) slicing with a FEI Helios Nanolab 600i with a section spacing of 50 nm, and 3D microstructures were reconstructed using Amira (Thermo Scientific™). The 3D reconstruction of the microstructure (Fig. 1d) shows that the lamellar morphology consists of alternating plates of Ni_3Al and Ni_5Zr that degenerate into a completely interconnected network of the two phases (Fig. 1e–f). The bright field TEM image of both regions is shown in Fig. 1g–h. The two phases exist in a clearly defined orientation relationship shown in Fig. 1i, j. The HRTEM images of the interface show good lattice matching (Fig. 1k). The alloy melts at 1215 °C as determined by differential thermal analysis (supplementary information, Fig. S3). The stability of the as cast structure was investigated through long term exposure at high temperatures (900 °C) and we could find no detectable instability (see supplementary information Fig. S3). XRD analysis using a X'Pert PRO diffractometer (PANalytical) with Cu K-Alpha1 radiation at a step size of 0.002 and a scan speed of 0.008/s of the alloys confirms the presence of only Ni_3Al and Ni_5Zr (see supplementary information Fig. S3).

Mechanical behaviour of the alloy was assessed using indentation, uniaxial compression and tension tests. Fig. 2a shows the compressive strength of the as-grown alloy as a function of temperature (measured on 5 samples to demonstrate consistency), along with that of conventional cast, forged, or powder metallurgy-based Ni-base superalloys (IN718, N18, CSMX10, UD 720). High strength levels of around 2 GPa are accompanied by reasonable room temperature tensile plasticity ranging from 3 to 4% as demonstrated in Fig. 2b. Tensile data have also been evaluated in 3 samples to establish repeatability. The current alloy has density of 7.4 ± 0.2 g/cc, which is lower than that of conventional high temperature alloys (W, Ta, Mo, Nb and Ni based alloys) and has a higher strength as compared to these alloys. The introduction of the respective primary phases of Ni_3Al or Ni_5Zr results in decrease of strength.

The origins of high strength have been analysed using low load indentation, as described in detail in the supplementary information. The Ni_5Zr and Ni_3Al phases have shown similar hardnesses (600–650 Hv) and modulii (275–300 GPa) (see supplementary information Fig. S5) as measured by an SEM PicoIndenter, PI 85, on relatively coarse primary solidification grains of these phases in off eutectic compositions. An application of the rule of mixtures would result in hardness values that are substantially lower than those measured in the

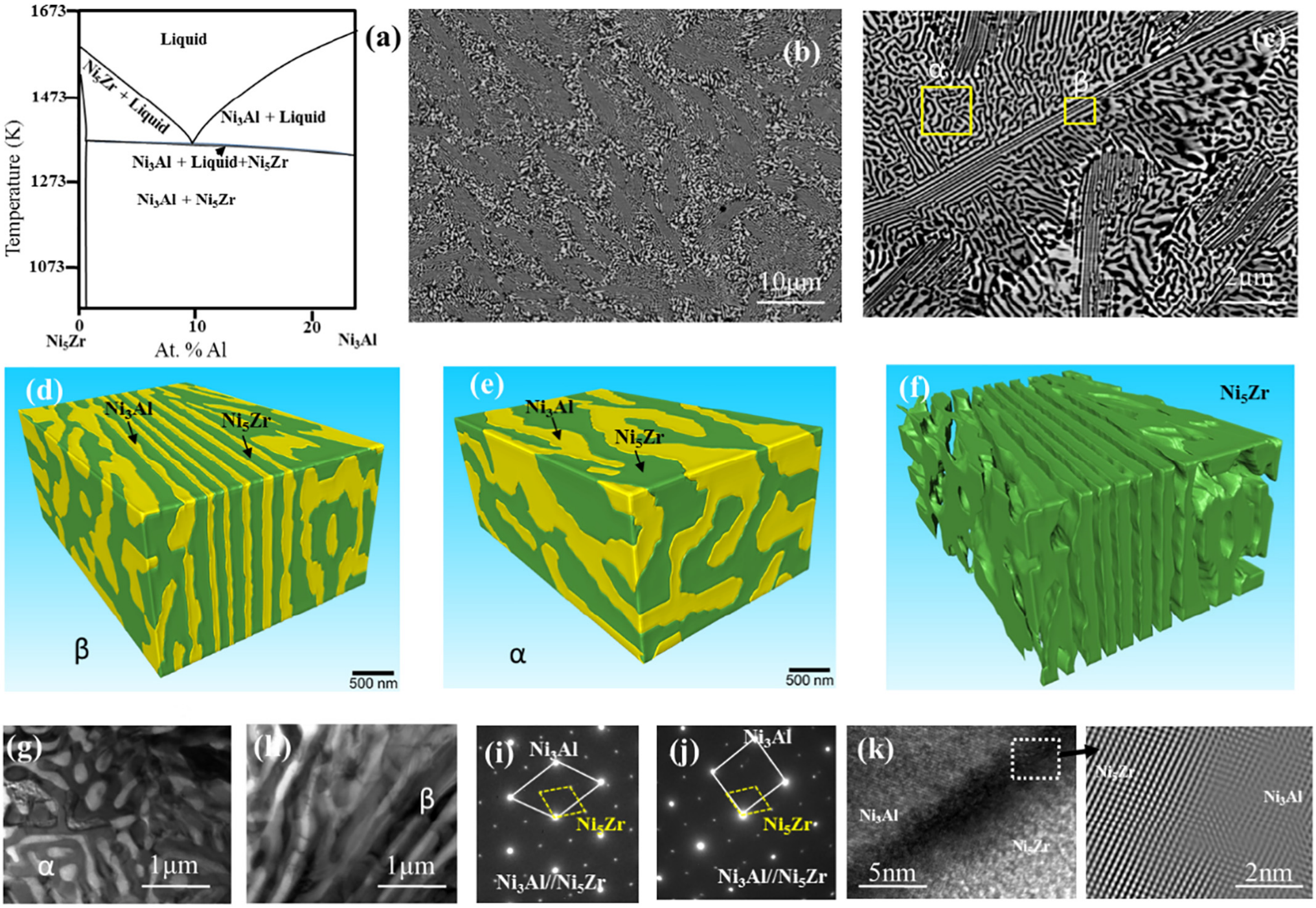

Fig. 1. Phase diagram and microstructural evaluation of intermetallic eutectic alloy: (a) vertical section of composition line joining Ni_3Al and Ni_5Zr in the Ni-Al-Zr ternary system generated using Thermo-Calc (b)–(c) back scattered electron (BSE) images at different magnification of the alloy. (d–e) 3D microstructures of regular and irregular morphologies as indicated by β and α in the alloy (Ni-12 at.% Al-11 at.% Zr), (f) 3D structure of Ni_5Zr (g) bright field image of irregular (α) eutectic region (g) regular (β) eutectic region. (i–j) diffraction patterns along the [110 Ni_3Al//110 Ni_5Zr] zone axis and [100 Ni_3Al//110 Ni_5Zr] zone axis respectively. (k) HRTEM image and processed image of the interface of Ni_3Al-Ni_5Zr lamellae.