Materials Science & Engineering A 692 (2017) 17–23

Contents lists available at ScienceDirect

Materials Science & Engineering A

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

Ultrafine-structured Ni-based bulk alloys with high strength and enhanced ductility

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ARTICLE INFO

Keywords:
Ultrafine-structure
Dendrite
Composites
Mechanical properties

ABSTRACT

High-strength ultrafine eutectic-dendrite composites were produced from arc-melted ingots of a novel Ni-Hf alloy system. The composites are composed of micron-scale dendritic phases (Ni_5Hf intermetallic phase or Ni solid solution) and an ultrafine lamellar eutectic matrix (Ni_5Hf + fcc-Ni). The optimization of the Ni-Hf alloy composition is performed from the viewpoint of both high strength and ductility. The strongest $Ni_{90}Hf_{10}$ has an ultrafine lamellar eutectic structure and exhibits a high strength of 3.56 GPa and a plastic deformation of 34% under compression. In particular, the material's plasticity can be monotonically improved by reinforcing the ductile dendritic phases in the eutectic matrix. The high strength and ductility values can be achieved without using the injection mould casting or rapid solidification procedure. The microstructure–property relationship of these ultrafine-structured composites is also discussed here.

1. Introduction

Nanograined metals (NGMs) and bulk metallic glasses (BMGs) offer record-high strength but have very limited plasticity, which sometimes limits their practical application [1–4]. Nowadays, nano/ultrafine-structured composites have become a key topic in the development of advanced structural materials and have overtaken both BMGs and NGMs in importance owning to their optimized strength and plasticity [5–13]. Following the strategy typically used to synthesize BMG composites, a nanostructured composite containing a mixture of β-Ti micron-scale dendrites and a nano-scale eutectic matrix was successfully synthesized for the alloy $Ti_{60}Cu_{14}Ni_{12}Sn_2Nb_{10}$, which showed a remarkably high compressive strength of ~2.4 GPa and a plastic strain of ~14.5% [5]. Moreover, a similar strategy was adopted to develop nano/ultrafine-structured composites for simple binary Ti-Fe [6], Fe-Zr [7], Ni-Zr [8], Cu-Zr [9] and pseudobinary Ti-Fe-(Sn, Co, Ta) [10–12], (Fe, Al)-Nb [13] alloy systems with excellent mechanical properties. Systematic investigations have suggested that the plastic deformation of ultrafine eutectic-dendrite composites is strongly related to the occurrence of slip/shear bands in the micron-scale dendrites and the propagation of primary and secondary shear bands in the ultrafine eutectic matrix. This shear banding in the ultrafine eutectic matrix stems from the formation of a stepped morphology, which is indicative of the dissipation of shear stress; thus in turn, enhances the macroscopic plasticity [5–14]. Recently, homogeneous nano- and ultrafine-eutectic composites containing length scale heterogeneity without any micrometer-sized second phase dispersions with a combination of high strength and good plasticity were developed for Ti-Fe-(Sn, Nb) alloys. The improved ductility of the Sn and Nb co-modified Ti-Fe alloy was attributed to the effects of refinement of the phase constituents and their particular morphologies [15]. Hence, it is very important to control microstructural factors including the volume fraction, morphology, length scale, and structural coherency of each different phase to optimize the strength and plasticity of ultrafine-structured composites.

Ni-based alloys usually exhibit high thermal stability, good mechanical properties and excellent corrosion resistance [16,17]. Since Ni and Hf have quite a deep eutectic reaction near the Ni-rich composition in the phase diagram, it is possible to form ultrafine eutectic-dendrite composites consisting of primary dendrites in an ultrafine-scale eutectic structure, which forms upon solidification. In this work, we report on the formation of ultrafine-structured composites with high strength and large plasticity for a novel Ni-Hf alloy system, which has not been reported yet. The Ni content was systematically modified to control phase volume fractions and length scales during phase formation in Ni-Hf alloys. We investigated the deformation behavior and the microstructure–property relationship of the composites in detail. We expect our results to be

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http://dx.doi.org/10.1016/j.msea.2017.03.019
Received 3 August 2016; Received in revised form 19 January 2017; Accepted 5 March 2017
Available online 06 March 2017

helpful in developing high-performance materials via manipulation of their microstructures.

2. Experimental

Ingots with a nominal composition of $Ni_{100-x}Hf_x$ (x=8, 10, 12 at%) of 17–20 mm in diameter and 7–10 mm in height were prepared by arc melting the pure elemental constituents under a Ti-gettered high-purity argon atmosphere. Each alloy was re-melted at least four times to ensure compositional homogeneity. From the as-arc-melted ingots, rectangular samples (2.1 mm×2.1 mm ×4.2 mm) were machined by electrical-discharge machining (EDM) and were then well polished to obtain mirror like surface for compressive tests using a CMT5305 electronic universal testing machine at a strain rate of 2×10^{-4} s^{-1} at room temperature. A Bruker AXS D8 X-ray diffractometer (XRD) with Cu Kα radiation was used for structural investigations of the central part of the as-arc-melted ingots. A Hitachi S-3400N scanning electron microscopy (SEM) equipped with an energy-dispersive spectrometer (EDS) was used to investigate the microstructure of as-polished samples as well as the surface morphology of deformed specimens. Transmission electron microscopy (TEM) bright field (BF) imaging and selected area electron diffraction (SAED) were performed on the deformed samples using a JEOL JEM-1200EX electron microscope. TEM samples were prepared using standard procedures involving ion milling (Gatan, model 600). HV was measured in a DHV-1000 microhardness tester, equipped with a Vickers diamond pyramid indenter. Multiple tests were conducted for all samples to maintain repeatability, using a 100-g load, with a duration of 10 s.

3. Results and discussion

Fig. 1 shows the XRD patterns of the as-arc-melted $Ni_{100-x}Hf_x$ (x=8, 10, 12) alloys. The diffraction peaks can be identified as a mixture of face-centered cubic (fcc) Ni solid solution ($Fm\bar{3}m$) and fcc Ni_5Hf ($F\bar{4}3m$). The lattice parameters of the Ni solid solution for the studied $Ni_{92}Hf_8$, $Ni_{90}Hf_{10}$, and $Ni_{88}Hf_{12}$ alloys are 0.3531, 0.3528, and 0.3526 nm, respectively, which are larger than that of pure fcc-Ni (0.3524 nm) because of the supersaturation with Hf. In contrast, the lattice parameters of the Ni_5Hf phases in the $Ni_{92}Hf_8$ (0.6661 nm), $Ni_{90}Hf_{10}$ (0.6667 nm), and $Ni_{88}Hf_{12}$ (0.6676 nm) alloys are smaller than that of pure Ni_5Hf (0.6680 nm) due to the deviation from the stoichiometry.

Fig. 2(a)–(c) illustrate the overall and magnified (insets) microstructures obtained from backscattered electron SEM images of the three Ni-Hf alloys. The microstructure of the $Ni_{92}Hf_8$ alloy [Fig. 2(a)] exhibits typical hypoeutectic characteristics and consists of primary dendrites (dark) embedded in the eutectic matrix with an ultrafine

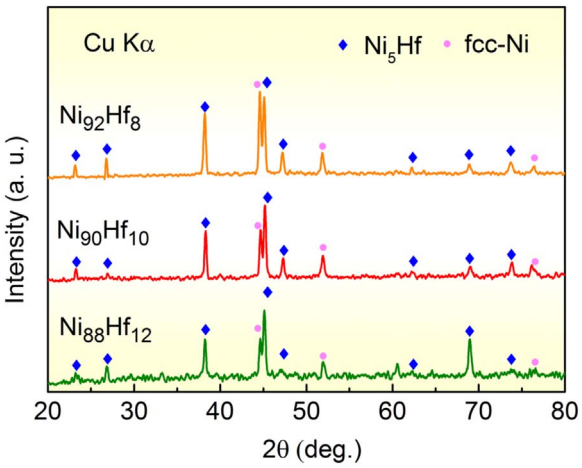

Fig. 1. XRD patterns of the as-arc-melted $Ni_{100-x}Hf_x$ (x=8, 10, 12) alloys.

lamellar structure (gray). The volume fraction of the micron-scale dendrites is approximately 10–20%. The EDS analysis results of the phases in the specimens are summarized in Table 1. The primary dendrites in the $Ni_{92}Hf_8$ alloy contain a high Ni content (98.4 at%) compared with the ultrafine eutectic matrix (91.3 at%). By combining the results from the XRD (Fig. 1) and SEM (Fig. 2) with the EDS results (Table 1), the primary dendrites can be identified as a micrometer-size fcc Ni solid solution phase domains, whereas the ultrafine matrix is composed of sandwich-like layers of a Ni solid solution and a Ni_5Hf intermetallic compound. The dendrite length of the primary dendrites in the $Ni_{92}Hf_8$ alloy is 10–30 μm. Higher magnification SEM image reveals that the average lamellar spacing of the ultrafine eutectic matrix and the dendrite arm spacing of the primary dendrites are about 100–200 nm and 1–3 μm, respectively. Fig. 2(b) presents the microstructure of the eutectic alloy ($Ni_{90}Hf_{10}$), which displays blurry image contrast at low magnification. EDS results show that the Ni content in the ultrafine eutectic lamellar of the $Ni_{88}Hf_{12}$ alloy is 88.9 at%. The magnified view in the inset of Fig. 2(b) depicts an ultrafine (Ni + Ni_5Hf) eutectic matrix with a lamellar spacing of about 100–200 nm. Fig. 2(c) demonstrates the microstructure of the hypereutectic alloy ($Ni_{88}Hf_{12}$), which consists of lath-shaped primary phase domains and an ultrafine eutectic lamellar structure. The volume fraction of the lath-shaped dendrites is approximately 20–30%. Via EDS analysis we manifest that the Ni content in the primary dendrites of the $Ni_{88}Hf_{12}$ alloy is quite low (85.3 at%) compared with the nanoscale eutectic matrix (86.9 at %). It is feasible to conclude that the brighter lath-shaped primary phase is a Ni_5Hf intermetallic phase and the dark contrast area is a (Ni + Ni_5Hf) eutectic matrix.

The room temperature uniaxial compressive stress-strain curves for the Ni-Hf ultrafine composites are depicted in Fig. 3(a). The obtained mechanical properties of Ni-Hf alloys are summarized in Table 2 and are compared with those of other high-strength alloys. The $Ni_{92}Hf_8$ dendrite-ultrafine eutectic composite with bimodal length-scale distribution exhibits a high compressive strength and a large plasticity together with pronounced work hardening. The yield stress σ_y (0.2% offset), maximum compressive stress σ_{max}, and plastic strain ε_p for the hypoeutectic $Ni_{92}Hf_8$ alloy are 1.40 GPa, 3.11 GPa, and 39.4%, respectively. The eutectic $Ni_{90}Hf_{10}$ alloy shows a much higher σ_y of 1.91 GPa compared with its hypoeutectic alloy, and a σ_{max} of 3.56 GPa as well as a ε_p of 34.4%. Its enhanced strength and slightly decreased plasticity are consistent with its specific microstructure: namely, an ultrafine eutectic lamellar without a soft, ductile Ni solid solution phase. For the hypereutectic $Ni_{88}Hf_{12}$ alloy, the σ_y, σ_{max}, and ε_p are 1.48 GPa, 2.36 GPa, and 17.4%, respectively. It is clear that an increase in the Hf content of $Ni_{88}Hf_{12}$ alloy leads to a significant decrease in its strength and plasticity compared with the eutectic $Ni_{90}Hf_{10}$ alloy, which can be related to the embrittlement effect of the lath-shaped Ni_5Hf primary intermetallic phase. Comparing the mechanical properties of the present Ni-Hf ultrafine composites with some previously reported advanced high-strength alloys [Fig. 3(b)], including Ni-based BMGs [17–20] and some nano- or ultrafine-eutectic structured alloys [5–15], yields the following conclusions: Compared with Ni-based BMGs, the Ni-Hf alloys (i.e. the $Ni_{90}Hf_{10}$ and $Ni_{92}Hf_8$) display a slightly lower yield strength but an appreciably larger plasticity and a distinctly higher maximum compressive strength. They also demonstrate a similar yield strength but a superior plasticity together with a higher maximum compressive strength when compared with some previously reported high-strength bimodal alloys (e.g. Ni-Zr [8], Cu-Zr [9], Fe-Zr [7], Fe-Al-Nb [13], Ti-Fe-Sn [10,21], Ti-Fe-Sn-Nb [13] and Ti-Cu-Ni-Sn-Nb [5] systems) and commercial Inconel alloys [22–24]. Altogether, the as-developed Ni-Hf alloys exhibit not only a high maximum compressive strength >3000 MPa but also a high yield strength approaching 2000 MPa along with a plasticity of over 30%, which renders these alloys superior to the high-strength Ni-based BMGs and bimodal composites.

Fig. 4 presents the secondary electron and backscattered SEM