Acta Materialia 109 (2016) 314–322

Contents lists available at ScienceDirect

Acta Materialia

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

Full length article

Spherical nanoindentation creep behavior of nanocrystalline and coarse-grained CoCrFeMnNi high-entropy alloys

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A R T I C L E   I N F O

Article history:
Received 13 January 2016
Received in revised form
12 February 2016
Accepted 19 February 2016
Available online xxx

Keywords:
Creep
High-entropy alloy
High-pressure torsion
Nanocrystalline metal

A B S T R A C T

Time-dependent plastic deformation behavior of nanocrystalline (nc) and coarse-grained (cg) CoCrFeMnNi high-entropy alloys (HEAs) was systematically explored through a series of spherical nanoindentation creep experiments. High-pressure torsion (HPT) processing was performed for achieving nc microstructure in the HEA, leading to a reduction in grain size from ~46 μm for the as-cast state to ~ 33 nm at the edge of the HPT disk after 2 turns. Indentation creep tests revealed that creep deformation indeed occurs in both cg and nc HEAs even at room temperature and it is more pronounced with an increase in strain. The creep stress exponent, *n*, was estimated as ~3 for cg HEA and ~1 for nc HEA and the predominant creep mechanisms were investigated in terms of the values of *n* and the activation volumes. Through theoretical calculations and comparison of the creep strain rates for nc HEA and a conventional face-centered-cubic nc metal (Ni), the influence of sluggish diffusion on the creep resistance of nc HEA was analyzed. In addition, sharp indentation creep tests were performed for comparison purposes and the results confirmed that the use of a spherical indenter is clearly more appropriate for investigating the creep behavior of this HEA.

1. Introduction

High-entropy alloys (HEAs) containing five or more elements in almost equal atomic proportions, exhibit high strengths, large strain hardening capability, high toughness, excellent resistance to high-temperature softening and creep, and good tribological properties. Hence, these are emerging as an exciting class of new structural materials and are drawing considerable attention in terms of research [1–8]. Despite a large number of principal elements, HEAs can often form simple solid solutions due to high configurational entropy [1–4]. It is well known that the mechanical performance of a material can be substantially enhanced by imparting a finer microstructure to it. In fact, nanocrystalline (nc) metals and alloys (having average grain size, d < 100 nm) exhibit improved mechanical properties in comparison with their coarse-grained (cg) counterparts [9–13]. Then, it may be possible to achieve significantly improved materials by incorporating both the advantages of HEA and nc structure and, in fact, the authors' previous study [14] reported that nc CoCrFeMnNi HEA exhibits significant strengthening and reasonably high plasticity both of which were achieved by extensive grain refinement.

Hitherto, nc HEAs have been synthesized by magnetron sputtering (MS) [15], mechanical alloying (MA) [16–19], and high-pressure torsion (HPT) [14,20,21]. Among them, HPT may be the most effective single-step processing to directly achieve

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http://dx.doi.org/10.1016/j.actamat.2016.02.049

excellent grain refinement in fully-dense bulk solids [22] because the sample synthesized by MS is only in thin film form and MA processing inevitably requires additional steps of consolidation. In addition, ability to achieve grain refinement in HEAs may be much higher in HPT than in MA, which can be supported by the fact that the average d of HPT processed CoCrFeMnNi alloys (~38–59 nm [14,21]) is reported to be significantly smaller than that of the same component nc HEA processed through MA followed by spark plasma sintering (~50–200 nm [19]).

In the case of exceptionally fine-grained materials processed by severe plastic deformation (SPD) including HPT and equal-channel angular pressing (ECAP), the large fraction of grain boundaries (GBs) are often considered to be in a non-equilibrium state [21,23–30]. These severe-strain-induced non-equilibrium GBs contain an excess of extrinsic dislocations, higher energy, and larger free volume or vacancy concentration than in normal GBs in cg or annealed materials [27]. This, in turn, can result in significantly faster diffusion along non-equilibrium GBs than along normal GBs [25–27]. Due to this specific feature of a large portion of non-equilibrium GBs, materials processed by ECAP or HPT often exhibit diffusion-related deformation processes such as GB sliding and creep even at relatively low temperatures [10,31,32]. By comparison with ECAP, HPT processing has the advantage of introducing higher plastic strains and hence producing finer structures and a higher fraction of high-angle GBs [33–35], thereby facilitating the occurrence of diffusion-related phenomena.

HEAs are well known to exhibit improved diffusion resistance due to the different local cohesive energy at any lattice site as well as the lattice distortion arising from the difference in atomic size of the constituent elements [36,37]. Thus, the creep behavior of nc HEAs may conceivably be different from conventional nc metals and alloys as well. However, only a few studies have been performed thus far to examine the creep behavior of nc HEAs. Chang et al. [38] performed creep tests on nc $(AlCrTaTiZr)N_x$ coatings and investigated the influence of N addition on creep strain rate quantitatively. Ma et al. [15] studied the effects of peak load and loading rate on the creep deformation in a nc CoCrFeNiCu HEA thin film. However, almost no effort has been made to systematically indentify the creep mechanism of nc HEAs or to investigate the influence of sluggish diffusion on the creep properties of nc HEAs.

Based on this background, we explored time-dependent plastic deformation of nc HEAs in the present research through a series of spherical nanoindentation creep experiments. In general, the microstructure of HPT-processed material varies locally across the disk, therefore mechanical properties of HPT-processed metals have been extensively investigated through nanoindentation tests which require only a very small volume of material [14,39,40]. In this regard, nanoindentation creep testing [41–44] (especially, with a spherical tip; as we discuss later) is a promising way to successfully investigate small-scale creep behavior of HPT processed disks. Here, a CoCrFeMnNi HEA, which is one of the most widely studied HEA, was processed by HPT, and it was confirmed that the nc structure is readily achieved in the early stage of HPT processing. Thereafter, spherical nanoindentation creep experiments were performed on the nc HEA as well as their cg counterpart (i.e., as-cast HEA) for comparison purposes. The results revealed that the creep mechanism of nc HEA is different from that of cg HEA. By comparing the theoretically calculated creep strain rates of nc HEA to that of conventional face-centered-cubic (fcc) nc Ni, it is feasible to discuss the influence of sluggish diffusion on creep resistance of nc HEA.

2. Experimental

The alloy examined in this work was prepared by arc-melting a mixture of pure metals (purity > 99 wt.%) having a nominal composition of $Co_{20}Cr_{20}Fe_{20}Mn_{20}Ni_{20}$ (in atomic %) in a Ti-gettered high-purity Ar atmosphere. The ingots were remelted at least four times to promote chemical homogeneity. The melted alloys were then drop-cast into a mold with dimensions of 10 mm × 10 mm × 60 mm.

The as-cast samples (disks having a radius of 5 mm and a thickness of 0.83 mm) were subjected to HPT at room temperature (RT) with a pressure of 6.0 GPa for a total of either 1/4 or 2 turns using a rotational speed of 1 rpm [14]. To investigate the influence of straining on the quasi-static mechanical properties during HPT, the Vickers indentation hardness, H_V, was measured using a HMV-2 microindenter (Shimadzu, Tokyo, Japan) at a peak load P_{max} of 980 mN along diameters of the HEA disks processed by HPT. For each measurement position, the average value of H_V was determined from four separate measurements recorded at uniformly separated points displaced from the selected position by a distance of 0.15 mm [45]. The microstructures of the specimens were examined using an optical microscope (CK40M, Olympus, Tokyo, Japan), an electron backscattered diffraction (EBSD) instrument (FEI XL30 FEG, Philips, Cambridge, UK), and a transmission electron microscope (Tecnai F20, FEI Co., Hillsboro, OR). For the optical microscopy observations, the samples were mechanically polished to a mirror-like finish and etched with aqua regia solution which is a mixture of nitric acid and hydrochloric acid in a volume ratio of 1:3. The sample for the EBSD measurements was prepared by mechanical polishing with 0.05 μm colloidal silica and subsequent electrolytic polishing at 58 V for 20 s in a mixture of 90% acetic and 10% perchloric acid at RT. Samples for transmission electron microscopy (TEM) at the vertical cross-sections of the HPT-processed disks were obtained through focused ion beam (FIB; Nova 200 NanoLab, FEI Co, Hillsboro, OR) milling. A thin layer was milled by FIB in the through-thickness direction at the edges of the processed HEA disks and lifted for TEM.

For the nanoindentation tests, electrolytic polishing at 58 V for 50 s in a mixture of 90% acetic and 10% perchloric acid was performed on mirror-finished samples to remove any possible surface damage induced during prior mechanical polishing. Nanoindentation creep experiments were performed at the edge regions, within 0.3 mm from the edge, of the HPT disks using a Nanoindenter-XP (formerly MTS; now Keysight, Santa Rosa, CA) with two different indenters, i.e. a Berkovich tip and a spherical tip with R = 38.6 μm (which was estimated by Hertzian contact analysis [46] of the indentations made on fused quartz). During testing, the specimen was loaded to different P_{max} at a constant loading rate (dP/dt) of 0.5 mN^{-1}, held at P_{max} for 1000 s, and fully unloaded. More than 10 tests were conducted for each testing condition.

For analyzing the applied strain variation within the HPT disk, finite-element analysis (FEA) simulation was performed using ABAQUS (HKS Inc., Pawtucket, RI) software. The geometries of the anvils were designed based on the quasi-constrained HPT conditions [47] and meshes were generated with 46,620 elements in the disk having initial t and r of 0.8 mm and 5.0 mm, respectively. A high friction coefficient of 0.7 was applied between the anvil and the disk to maintain a reasonable traction between them [47]. The material parameters used for the present simulation were based on the flow curve reported for this specific HEA [48].

3. Results

3.1. Achievement of nanostructures by HPT process

During the HPT, the equivalent von Mises strain ε_{eq} imposed on the disk is given by the relationship [49]: