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Nitrogen-induced dynamic strain aging in a biomedical-grade Co–Cr–Mo alloy

Kenta Yamanaka[a,b], Manami Mori[c], Akihiko Chiba[b,*]

[a] Department of Materials Processing, Graduate School of Engineering, Tohoku University, 6-6-02 Aoba-yama, Aoba-ku, Sendai 980-8579, Japan
[b] Institute for Materials Research, Tohoku University, 2-1-1 Katahira, Aoba-ku, Sendai 980-8577, Japan
[c] NISSAN ARC, LTD., 1 Natsushima-cho, Yokosuka 237-0061, Japan

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ABSTRACT

The present study examined plastic deformation behavior of a biomedical-grade Co–29Cr–6Mo (wt.%) alloy at intermediate temperatures, focusing on dynamic strain aging (DSA) induced by nitrogen doping (0.2 wt.%). The compression tests were performed at strain rates in the range of 10^{-4} to 10^{-1} s^{-1} at temperatures between room temperature and 1073 K. Gliding of Shockley partial dislocations bounding stacking faults played a dominant role in the plastic deformation over a wide temperature range. The nitrogen-associated DSA resulted in enhanced in-grain lattice distortions even when there was little macroscopic serrated flow. Shear band formation was identified after the lamellar structures developed, in spite of quite small macroscopic strain (5% in height reduction). Cr–N short-range ordering can be responsible for the observed DSA.

1. Introduction

Co–Cr–Mo alloys have been used for orthopedic implants such as artificial hip and knee joints due to their excellent corrosion and wear resistances [1–3]. There is a strong demand to improve the mechanical reliability of biomedical metallic materials to realize orthopedic implants with long lifetimes. Consequently, much effort has been made to enhance alloy design and optimize hot deformation processing for improving the mechanical properties of the Co–Cr–Mo alloys [4–8].

Biomedical-grade Co–Cr–Mo alloys generally exhibit a duplex microstructure consisting of a metastable γ (fcc) matrix and athermal ε (hcp) martensite with a plate-like morphology [5,9]. Since this microstructure has a low deformability [5]; large amounts of nickel are usually added to obtain stable deformation by suppressing the martensitic transformation. However, nickel may cause allergies and cancer in living organisms. Nitrogen addition is an alternative methodology for enhancing mechanical properties. We found that nitrogen can stabilize the γ phase in a similar manner to Ni, improving the tensile elongation [4,6] and cold workability [7]. Recent studies also indicate that a substantial strength–ductility balance is obtained in hot-deformed N-doped alloys [6,8]. Thus, in order to optimize the mechanical properties of Co–Cr–Mo–N alloys, the effect of nitrogen on the plastic deformation behavior and its underlying mechanisms need to be elucidated.

In Co–Cr–Mo alloys, nitrogen atoms occupy the octahedral sites in the fcc structure, similar to austenitic steels. Therefore they can diffuse interstitially and interact with lattice defects such as vacancies and dislocations. Dynamic strain aging (DSA) is one indication of such a phenomenon. DSA (i.e., dynamic interactions between mobile dislocations and diffusing solute atoms) causes serrated flow, which is generally referred to as the Portevin–Le Chatelier (PLC) effect [10]. However, to the best of our knowledge, no studies have investigated the behavior of nitrogen atoms from this viewpoint because nitrogen has been considered to be an impurity in this alloy system. Especially, hot-deformed alloys usually exhibit very high dislocation densities of the order of 10^{15} m^{-2} [8]; thus, besides solid solution hardening, the dislocation-solute nitrogen interaction may also contribute to strengthening these alloys.

The present study investigates the plastic deformation behavior and resultant structural evolution of an N-doped Co–Cr–Mo alloy at ambient and elevated temperatures by focusing on the DSA.

2. Experimental procedures

A nitrogen-doped alloy Co–29Cr–6Mo–0.2N (wt.%), which is a representative composition in ASTM F75 standard, was prepared by high-frequency vacuum induction melting. A Co–29Cr–6Mo alloy without N addition was also prepared for comparison. Table 1 lists the chemical compositions of these two alloys. The cast ingot was subjected to homogenizing heat treatment at 1498 K for 43.2 ks (12 h) and hot forging at 1473 K, followed by water quenching. Cylindrical specimens (diameter: 5 mm; height: 7.5 mm) for compression tests were cut from the hot-forged materials. The compression tests were performed at strain rates ($\dot{\varepsilon}$) in the range of

* Corresponding author. Tel.: +81 22 215 2115; fax: +81 22 215 2116.
E-mail address: a.chiba@imr.tohoku.ac.jp (A. Chiba).

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Table 1
Chemical compositions (in wt.%) of the two alloys used in this study.

Specimen	Co	Cr	Mo	Ni	Mn	Si	C	N
N-doped	Bal.	28.5	5.9	<0.01	0.22	0.16	0.001	0.20
N-free	Bal.	28.7	6.3	<0.01	<0.01	<0.1	0.002	0.001

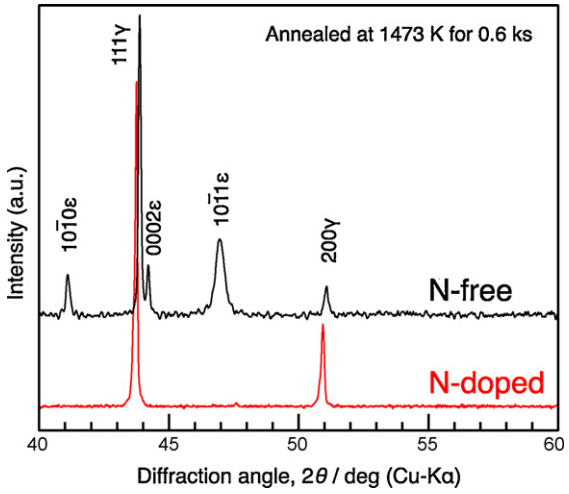

Fig. 1. X-ray diffraction patterns of the N-free and N-doped alloys after annealing at 1473 K for 0.6 ks.

10^{-4} to 10^{-1} s^{-1} at various temperatures between room temperature and 1073 K. Specimens were heated to each test temperature at a heating rate of 5 K s^{-1}, hold for 60 s, and then deformed up to 40% (a true strain of 0.51) in a vacuum. After compression, specimens were cooled to room temperature using a He–N_2 gas mixture at a cooling rate of 50 K s^{-1}. We performed stress relaxation tests to evaluate the dislocation mobility at each temperature. The as-forged N-doped specimens were heated to each test temperature at a rate of 5 K s^{-1}, hold for 60 s, compressed by 5% at a strain rate of 10^{-4} s^{-1} and then held for 0.5 ks. For the compression and stress relaxation tests, the relatively short but sufficient soaking time at deformation temperatures were selected to avoid structural changes during holding. These tests were done more than two times for each deformation conditions to ensure the reproductivities. Their microstructures were investigated by X-ray diffraction (XRD), scanning electron microscopy (SEM), electron backscatter diffraction (EBSD) and transmission electron microscopy (TEM). The XRD measurements were conducted with a Philips X'Pert MPD diffractometer. Electron channeling contrast imaging (ECCI) was employed to investigate crystallographic and interface contrasts of microstructures, such as dislocation structures and deformation twins [11], using a SEM. ECCI observations were carried out in a Carl Zeiss ULTRA 55 with a field emission gun and an angle selective backscattered electron detector. For ECCI, an acceleration voltage and a working distance were set to 15 kV and 6 mm, respectively. The EBSD measurements were carried out using a field-emission scanning electron microscope (FEI XL30S-FEG) operated at 15 kV equipped with a TSL OIM system. The specimens for XRD, ECCI and EBSD were polished to a mirror finish using emery paper, alumina, and a colloidal silica suspension. They were then polished electrolytically with a mixture of sulfuric acid and methanol (sulfuric acid:methanol = 1:9) to remove the surface-worked layer produced by grinding. TEM examinations of dislocation structures were conducted on a TOPCON EM002B operated at 200 kV. To remove the complexity caused by a high dislocation density (>10^{15} m^{-2} [8]) in as-forged specimens, microstructure observations were performed on those had been annealed at 1473 K for 0.6 ks prior to compression tests.

3. Results

3.1. Compressive flow behavior

First, we checked phase constituent of both N-free and N-doped alloys before compression tests. Fig. 1 shows the XRD results for the annealed N-free and N-doped alloys. The XRD analysis reveals that the N-doped alloy consisted of a single-phase γ matrix, while the N-free alloy had a γ/ε duplex microstructure. No diffraction peaks from the precipitation of the σ phase (intermetallic compound: CoCr), Cr_2N, or other components were observed for any of the specimens.

Fig. 2(a) and (b) shows compressive stress–strain curves of the as-forged N-doped alloys obtained at $\dot{\varepsilon} = 10^{-4}$ s^{-1} and $\dot{\varepsilon} = 10^{-3}$ s^{-1}, respectively. At $\dot{\varepsilon} = 10^{-4}$ s^{-1} (Fig. 2(a)), serrations that are initiated immediately after yielding appear in the stress–strain curves tested at temperatures ranging from 773 to 973 K, whereas the stress–strain curves obtained at other temperatures are relatively smooth. There is a significant stress drop below the general curves at 773 and 873 K. The serrations were generally not observed in the specimens deformed at $\dot{\varepsilon} = 10^{-3}$ s^{-1} (Fig. 2(b)), although small-amplitude oscillations were still identified in the above-mentioned temperature range (i.e., 773 and 873 K) even at this strain rate. Apparent flow softening was observed at 973 and 1073 K at 10^{-4} s^{-1}

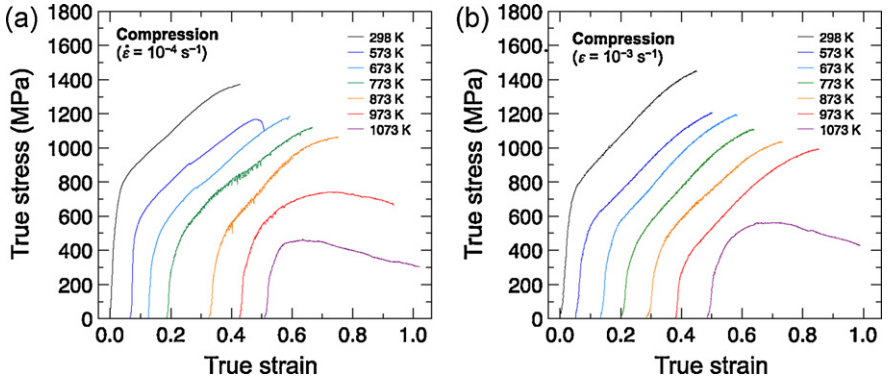

Fig. 2. Stress–strain curves obtained by compression tests of as-forged N-doped specimens: (a) $\dot{\varepsilon} = 10^{-4}$ s^{-1} and (b) $\dot{\varepsilon} = 10^{-3}$ s^{-1}.