JOURNAL OF THE MECHANICAL BEHAVIOR OF BIOMEDICAL MATERIALS 29 (2014) 417–426

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Research Paper

Effects of nitrogen addition on microstructure and mechanical behavior of biomedical Co–Cr–Mo alloys

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

[a]*Institute for Materials Research, Tohoku University, Sendai 980-8577, Japan*
[b]*NISSAN ARC, LTD., Yokosuka 237-0061, Japan*

ARTICLE INFO

Article history:
Received 19 July 2013
Received in revised form
28 September 2013
Accepted 7 October 2013
Available online 23 October 2013

Keywords:
Biomedical Co–Cr–Mo alloys
Nitrogen addition
Microstructures
$\gamma \rightarrow \varepsilon$ martensitic transformation
Mechanical properties

ABSTRACT

In the present study, the microstructures and tensile deformation behaviors of biomedical Co–29Cr–6Mo (wt%) alloys containing different concentrations of nitrogen (0–0.24 wt%) were systematically investigated. As the nitrogen concentration increased, the volume fraction of athermal ε martensite decreased, because nanoprecipitates hindered the formation of stacking faults (SFs) by acting as obstacles to Shockley partial dislocation formation, and athermal ε martensite usually forms through the regular overlapping of SFs. The formation of the athermal ε martensite was completely suppressed when the nitrogen concentration exceeded 0.10 wt%, resulting in a simultaneous improvement in the strength and ductility of the alloys. It was found that the glide of the Shockley partial dislocations and the strain-induced γ (fcc)$\rightarrow\varepsilon$ (hcp) martensitic transformation (SIMT) operated as the primary deformation mechanisms. However, adding nitrogen reduced the work hardening by suppressing the formation of the SFs and preventing the SIMT from taking place. This resulted in an intrinsic decrease in the tensile ductility of the alloys. It is also shown that all the alloys exhibited premature fractures owing to the SIMT. The formation of annealing twins in the γ grains is found to be enhanced by nitrogen addition and to promote the SIMT, resulting in a reduction in the elongation-to-failure due to nitrogen addition. These results should aid in the design of alloys that contain nitrogen.

1. Introduction

Co–Cr–Mo alloys exhibit excellent biocompatibility, corrosion resistance, and wear resistance, and are therefore widely used for orthopedic implants such as artificial hip and knee joints (Niinomi, 2002; Buford and Goswami, 2004; Chiba et al., 2007). It is known that metal-on-metal bearings made of Co–Cr–Mo alloys allow large-diameter femoral head components to be used, which provide a greater range of motion than that possible with conventional artificial hip joints (Cuckler et al., 2004). Thus, further improvements in the characteristics of these alloys, especially in their wear resistance and mechanical durability, are essential to expand further the biomedical applications of these alloys, and it is of great importance to understand the mechanisms of their functions. In Co–Cr–Mo alloys that comply with the ASTM F75 standard, up to 0.35 wt% carbon can be incorporated to allow for carbide precipitation, which is a major strengthening mechanism (Rajan, 1982; Caudillo et al., 2002; Mineta et al., 2010). However, recent studies have revealed that hard

*Corresponding author. Tel.: +81 22 215 2118; fax: +81 22 215 2116.
E-mail address: k_yamanaka@imr.tohoku.ac.jp (K. Yamanaka).

1751-6161/$ - see front matter
http://dx.doi.org/10.1016/j.jmbbm.2013.10.006

carbide precipitates are sometimes detrimental to the wear resistance, corrosion resistance, and biocompatibility of the alloys (Chiba et al., 2007; Battini et al., 2011; Liao et al., 2012). Therefore, significant efforts are being made to formu late novel alloys and devise hot deformation processes for these alloys (Salinas-Rodriguez and Rodriguez-Galicia, 1996; Escobedo et al., 1996; Kilner et al., 1987; Hsu and Lian, 2003; Chiba et al., 2007; Matsumoto et al., 2010; Mani, Salinas-Rodriguez, López, 2011; Yamanaka et al., 2009, 2011, 2012a, 2012b; Mori et al., 2010, 2012; Lee et al., 2008a).

The matrix phase also significantly influences the mechanical and tribological properties of Co–Cr–Mo alloys. Generally, these alloys consist of a metastable γ (fcc) matrix and/or plate-like ε (hcp) martensite. The ε martensite is formed during quenching, plastic deformation, and isothermal heat treatments and is known to enhance the strength and wear resistance of the alloy (Chiba et al., 2007; Mani et al., 2011). However, the formation of ε martensite also leads to poor deformability (Mori et al., 2010; Mani et al., 2011; Yamanaka et al., 2011, 2012a). Nickel addition is usually employed to prevent such fractures due to the presence of the ε martensite in cobalt-based alloys. In fact, biomedical Co–Cr alloys containing large amounts of Ni (10–37 wt%) (conforming to ASTM F90 and F562) exhibit excellent ductility and have been used in a number of practical applications (Nagai et al., 2012; Marrey et al., 2006). However, nickel is known to cause allergies and cancer in living organisms (Denkhaus and Salnikow, 2002).

Nitrogen is known to be an alloying element that can replace nickel. It also stabilizes the γ phase and improves the mechanical properties of Co–Cr–Mo alloys. Early studies have reported that the addition of nitrogen to Co–Cr–Mo alloys results in improvements in the tensile strength, plastic deformability, fatigue strength, and wear properties of the alloys (Escobedo et al., 1996; Hsu and Lian, 2003). Recently, Lee et al. (2008a) and Yoda et al. (2012) investigated the microstructures and tensile properties of as-cast Co–Cr–Mo–N alloys and found that alloys with high nitrogen contents exhibit good combinations of strength and ductility that make them suitable for dental applications. However, the studies performed so far either employed specimens containing relatively large amounts of nickel (~2.5 wt%) and carbide precipitates (carbon contents ~0.45 wt%) (Escobedo et al., 1996; Hsu and Lian, 2003) or varied the chromium concentrations of the samples in order to change their nitrogen concentrations (Lee et al., 2008a; Yoda et al., 2012), which prevents the understanding of the intrinsic effects of nitrogen in Co–Cr–Mo alloys. On the other hand, we have previously reported that Ni- and C-free Co–29Cr–6Mo–N (wt%) alloys exhibit high tensile ductility as well as cold workability while maintaining their high strength (Lee et al., 2008a; Mori et al., 2010, 2012; Yamanaka et al., 2012b). Nevertheless, a systematic investigation of the effects of nitrogen on the structures and mechanical properties of the Ni- and C-free Co–Cr–Mo biomedical alloys has not been done yet.

An important point to note regarding nitrogen-containing Co–Cr–Mo alloys is their decomposition on the nanoscale in the γ phase (Yamanaka et al., 2013). Nanometer-sized nitride precipitates formed in the γ matrix were found to interact with extended dislocations consisting of Shockley partial dislocations and stacking faults (SFs), ultimately inhibiting the $\gamma\rightarrow\varepsilon$ martensitic transformation (Yamanaka et al., 2013).

In this context, the aim of the present study was to investigate the dependence of the microstructures, phase distributions, stabilities of the γ matrices, dislocation structures, and tensile deformation behaviors of Co–29Cr–6Mo–N alloys on the nitrogen concentration.

2. Materials and methods

2.1. Specimen preparation

Co–29Cr–6Mo (wt%) alloys with different compositions were prepared in an argon atmosphere using a high-frequency induction furnace. A Cr_2N powder was used as the nitrogen source. The chemical compositions of the alloys are shown in Table 1. All the alloys conformed to the ASTM F75 standard and are denoted as 0N, 0.05N, 0.07N, 0.10N, 0.17N, and 0.24N in accordance with the concentration of nitrogen in each alloy. Cast ingots of these alloys of 15 mm in diameter and ~200 mm in length were subjected to a homogenizing heat treatment at 1473 K for 1.8 ks and subsequently processed by multipass hot caliber rolling, resulting in a change in their diameter from 15 mm to 9.6 mm. This was followed by the quenching of the hot-rolled alloy bars in water. The equivalent strain, ε_{eq}, generated during the rolling process, which was found to be 0.89, was calculated using the following equation:

$$\varepsilon_{eq} = \ln \frac{A_0}{A} \tag{1}$$

Here, A_0 and A are the cross-sectional areas of the initial and hot-rolled specimens, respectively. Next, the hot-rolled bars were heat treated in air at 1473 K for 0.6 ks and then quenched in water.

Table 1 – Chemical compositions of alloys used in the present study (wt%).

Alloy	Co	Cr	Mo	N	Ni	Mn	Si	O	C
0N	Bal.	28.7	6.3	0.00	<0.01	<0.01	<0.1	0.022	0.0016
0.05N	Bal.	27.3	6.1	0.05	<0.01	<0.01	<0.1	0.021	0.0012
0.07N	Bal.	29.0	6.0	0.07	<0.01	<0.01	<0.1	0.021	0.0012
0.10N	Bal.	29.2	5.9	0.10	<0.01	<0.01	<0.1	0.038	0.0018
0.17N	Bal.	27.8	6.0	0.17	<0.01	<0.01	<0.1	0.025	0.0011
0.24N	Bal.	29.9	6.1	0.24	<0.01	<0.01	<0.1	0.028	0.0028