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Effects of carbon concentration on microstructure and mechanical properties of as-cast nickel-free Co–28Cr–9W-based dental alloys

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ABSTRACT

We determined the effects of carbon concentration on the microstructures and tensile properties of the Ni-free Co–29Cr–9W–1Si–C (mass%) cast alloys used in dental applications. Alloy specimens prepared with carbon concentrations in the range 0.01–0.27 mass% were conventionally cast. Scanning electron microscopy (SEM) and electron probe microanalysis (EPMA) revealed that precipitates had formed in all the alloy specimens. The σ phase, a chromium-rich intermetallic compound, had formed in the region between the dendrite arms of the low-carbon-content (e.g., 0.01C) alloys. Adding carbon to the alloys increased the amount of interdendritic precipitates that formed and changed the precipitation behavior; the precipitated phase changed from the σ phase to the $M_{23}C_6$ carbide with increasing carbon concentration. Adding a small amount of carbon (i.e., 0.04 mass%) to the alloys dramatically enhanced the 0.2% proof stress, which subsequently gradually increased with increasing content of carbon in the alloys. Elongation-to-failure, on the other hand, increased with increasing carbon content and showed a maximum at carbon concentrations of ~0.1 mass%. The $M_{23}C_6$ carbide formed at the interdendritic region may govern the tensile properties of the as-cast Co–Cr–W alloys similar to how it governed those of the hot-rolled alloys prepared in our previous study.

1. Introduction

Computer-aided design and computer-aided manufacturing (CAD/CAM) technologies in dentistry have attracted considerable interest as advanced methods of producing dental restorations such as crowns, bridges, and inlays. These methods enable the rapid, low-cost, and precise fabrication of custom-made dental restorations for patients. Selective laser melting [1] and CAD/CAM-based milling [2–4] have recently been introduced in this field. In the latter process, three-dimensional CAD data are used to mill the products from block disks or pellets of ceramics, composite resins, or metallic materials. Although all ceramic systems produced from zirconia-based materials are currently primarily used in CAD/CAM-based dentistry, metal-ceramic systems still play an important role because they show a good combination of esthetics and mechanical rigidity originating from the ceramic veneer and metallic framework, respectively [4,5]. The Co–Cr or Ni–Cr alloys consisting of nonprecious elements are promising for application to CAD/CAM-based dentistry because their components are less expensive than those of the Au-based alloys that have conventionally been used for such applications. The Co–Cr-based alloys show corrosion resistances higher than the Ni–Cr ones [6]. Furthermore, Ni may cause allergies and even cancer in living organisms [7], despite greatly enhancing the ductility of Co–Cr-based alloys [8]. Therefore, biocompatible Ni-free Co–28Cr–9W–1.5Si (mass%) cast alloys have been used for practical applications.

We previously thermomechanically processed Co–Cr–W-based dental alloys to enhance their mechanical properties and produce uniform, refined grain structures [9–11]. The grains in the alloys dynamically recrystallized during the hot-deformation, and the sizes of the grains significantly decreased (The minimum grain size was 0.9 μm.) [10,11]. The developed fine-grained alloys exhibited superior tensile strength and ductility even though they did not contain Ni [9].

In addition, we previously added carbon to the Ni-free Co–28Cr–9W–1Si alloys whose microstructures had been modified through thermomechanical processing (i.e., hot rolling) in order to evaluate the effects of carbon content on the tensile properties of the alloys [12]. Carbon doping improved the tensile strength of the alloys through the formation of $M_{23}C_6$ carbides and carbon-induced grain refining. Adding carbon to the alloys also enhanced their ductility under optimized conditions. Although we characterized the solidification microstructures of the carbon-doped Co–28Cr–9W alloys [13], it remains unclear how adding carbon to the alloys affects their microstructures and, ultimately, how it affects the mechanical responses of our as-cast Ni-free Co–Cr–W-based alloys.

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We aim to fundamentally determine the effects of carbon on the relation between the microstructure and the mechanical properties of Ni-free Co–Cr–W-based cast alloys. In this work, we focused on tensile deformation behavior as a preliminary work, although the dental restorations are subjected to the complex stress states including tension, compression, torsion and so on. We prepared the as-cast Co–28Cr–9W–1Si–C (mass%) alloys with carbon concentrations ranging from 0.01 to 0.27 mass% and systematically investigated the effects of carbon concentration on the phase distributions, precipitates, and tensile deformation behaviors of the alloys.

2. Materials and methods

2.1. Sample preparation

We used high-frequency induction melting to prepare the Co–28Cr–9W–1Si–C (mass%) alloys in an argon atmosphere. The chemical compositions of the alloys are given in Table 1. The nickel contents of all of the alloys were <0.01 mass%. Hereafter, these alloys are referred to as the 0.01C, 0.04C, 0.10C, 0.17C, and 0.27C alloys. Note that the carbon concentration of 0.01 mass% represents the impurity concentration. Five 15-mm-diameter, ~200-mm-long ingots were cast in a steel mold.

2.2. Tensile tests

Electrical discharge machining was used to prepare the tensile specimens (gauge section: $1.6 \times 1.0\ mm^2$; gauge length: 10.5 mm). Uniaxial tensile tests were performed on the specimens at room temperature. The specimens were strained to failure at a $1.6 \times 10^{-4}\ s^{-1}$ nominal strain rate. We performed tensile tests at least three times on each specimen and calculated the averages and standard deviations of the 0.2% proof stress, the ultimate tensile strength, and the elongation-to-failure.

2.3. Microstructural characterization

We used X-ray diffraction (XRD), scanning electron microscopy (SEM), electron backscatter diffraction (EBSD), electron probe microanalysis (EPMA), and transmission electron microscopy (TEM) to investigate the microstructures of the alloy specimens.

The XRD measurements were conducted using a PANalytical X'Pert MPD diffractometer with Cu-Kα radiation. The precipitates were revealed using field-emission scanning electron microscopy SEM (FE-SEM) with a microscope that had an angle-selective backscattered-electron (AsB) detector, and field-emission electron probe microanalysis (FE-EPMA; JEOL JXA-8430 F). The microscope and electron probe microanalyzer were operated at an acceleration voltage of 15 kV. EBSD scans were performed using an FE-SEM (FEI XL30S-FEG) operated at 20 kV. We used an orientation image microscope (OIM; TexSEM Laboratories, Inc.) system to accumulate and analyze the EBSD data where we used a 1.5-μm step in the hexagonal scan grid. The samples used for XRD, SEM, EPMA, and EBSD were mechanically ground and were subsequently polished using emery papers and a 0.3-μm alumina suspension and were then mirror polished using a 0.04-μm colloidal silica solution. The samples were observed in the center of the cross-sections perpendicular to the longitudinal axis of cast bars.

Table 1
Chemical compositions (mass%) of Co–28Cr–9W–1Si–C alloys used in this study.

Alloy	Co	Cr	W	Si	C	N	Ni	Mn	O
0.01C	Bal.	27.8	8.85	0.98	0.005	0.0010	<0.01	<0.01	0.025
0.04C	Bal.	28.5	8.99	0.94	0.043	0.0004	<0.01	<0.01	0.020
0.10C	Bal.	27.9	8.99	1.19	0.098	0.0005	<0.01	<0.01	0.015
0.17C	Bal.	28.9	9.12	0.92	0.169	0.0003	<0.01	<0.01	0.022
0.27C	Bal.	28.7	8.96	1.03	0.265	<0.0001	<0.01	<0.01	0.020

The samples used for TEM were produced by cutting 3-mm-diameter disks from the alloy specimens, which were subsequently ground using a dimple grinder (Gatan Model 656) to form thin films. We then used ion-beam milling (Gatan Model 691, precision ion-polishing system (PIPS™)) to prepare thin foils from the disks. The TEM observations were conducted using a Topcon EM002B instrument operated at 200 kV.

We also used FE-SEM (Carl Zeiss, Ultra 55) to observe the fracture surfaces of the tensile-tested specimens.

3. Results

3.1. Tensile properties

The nominal stress–nominal strain curves for the as-cast Co–28Cr–9W–1Si–C alloys, which were obtained by performing tensile tests on the alloy samples at room temperature, are shown in Fig. 1. All the stress–strain curves showed uniform elongation followed by sudden fractures without macroscopic necking. This type of tensile deformation is typically observed in the present Co–28Cr–9W-based alloys and in Co–Cr–Mo orthopedic alloys [9,11–17]. The yielding in the stress–strain curves became clearer with increasing carbon concentration.

Fig. 2 shows the tensile properties, obtained by analyzing the stress–strain curves, plotted as functions of carbon concentration. Adding a small amount (i.e., 0.04 mass%) of carbon to the alloys dramatically increased the 0.2% proof stress then it gradually increased with increasing carbon concentration and reached 580 MPa for the 0.27C alloy. The 0.17C and 0.27C alloys both showed strengths standardized to the type 5 criteria in ISO 22764 for dental restorations (>500 MPa). The ultimate tensile strength also increased with increasing carbon concentration and then decreased to ~850 MPa when the carbon concentration exceeded ~0.1 mass%. The elongation-to-failure also strongly depended on the carbon concentrations (Fig. 2b). There was a significant difference between tensile ductilities of the 0.01C and 0.04C alloys. However, the elongation peaked at ~31% for the alloys containing ~0.1 mass% C and then gradually decreased for higher carbon concentrations. The trends for the tensile strength and ductility of the C-doped alloys prepared in the present study are similar to those for the hot-rolled Co–28Cr–9W alloys prepared in our previous studies [9,12] and similar to those for the Co–29Cr–6Mo orthopedic alloys [18].

3.2. Microstructures

First, we examined the equilibrium phase constituents of the Co–28Cr–9W–1Si–C system based on thermodynamic calculations. Fig. 3 shows a vertical section of the calculated phase diagram for

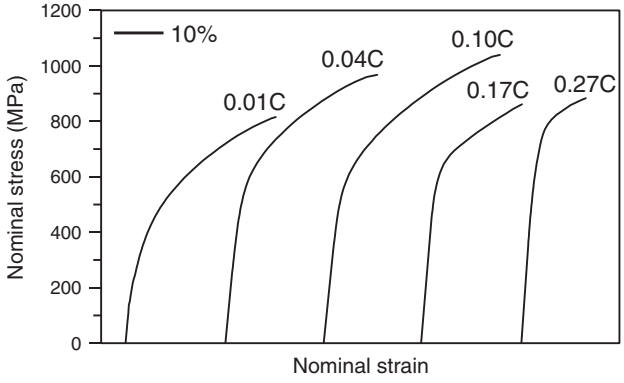

Fig. 1. Tensile stress–strain curves for as-cast Co–28Cr–9W–1Si–C alloys prepared with various carbon concentrations.