The evolution of the microstructure of a Co-27Cr-5Mo-0.05C alloy was investigated during isothermal aging between 650 °C and 950 °C. The main structural change observed as a result of aging was an fcc (metastable) → hcp isothermal martensitic transformation. The relationships between transformation, temperature, and time for this phase transition were determined using two different techniques: (1) room-temperature X-ray diffraction on samples aged after quenching from 1150 °C to 25 °C and (2) high-temperature in situ X-ray diffraction on samples cooled at 50 °C/min from 1150 °C to the aging temperature. The results show that the intermediate water quench significantly retards the kinetics of the phase transition by up to one order of magnitude in time. In addition, it was found that the grain size of the metastable fcc phase prior to aging does not affect the kinetics of the transformation. Age hardening resulting from this transformation varies linearly with the amount of hcp phase formed during the isothermal treatment and does not depend on the aging temperature. It is suggested that local plastic deformation, due to thermal and transformation stresses induced by quenching, reduces the number of hcp martensite embryos formed in the metastable fcc phase. This effect decreases the number of nucleation sites available for the fcc → hcp transformation during isothermal aging and leads to the slower transformation rates observed in water-quenched material.

I. INTRODUCTION

RECENT concerns regarding the negative effects of polyethylene wear debris on the in vivo long-term performance of hip and knee implant prostheses manufactured using Co-27Cr-5Mo-0.3C casting alloys has led to increased clinical and materials research to improve the conditions of friction and wear at the metal-polyethylene interface. It appears that there is general agreement that the use of low-C wrought Co-27Cr-5Mo alloys to manufacture the femoral heads of modular hip prosthesis designs significantly reduces the formation of particulate polyethylene debris. A significant contribution to this improvement arises from the elimination of the large volume fraction of hard second-phase carbide particles always present in casting alloys with higher C contents. The improved chemical and microstructural homogeneity produced by thermomechanical processing are also beneficial to the alloy’s corrosion resistance, uniform ductility, and fatigue strength. Sioshansi has shown that additional improvements in the tribological behavior of Co-Cr-Mo alloys can be obtained by nitrogen-ion implantation on the surface of finished products. Similar improvements may be expected in low-C wrought Co-based alloys if the surface crystal structure is hcp instead of the metastable fcc phase commonly present in these materials.

It is now well established that the fcc → hcp allotropic transformation in Co and Co-based alloys takes place by a diffusionless, martensitic mechanism. In pure Co, the transformation takes place at 427 °C, while, in a wrought Co-27Cr-5Mo-0.05C alloy, the equilibrium transformation temperature increases to values near 970 °C. The transformation on cooling from the fcc phase stability field is, however, very sluggish, due to the limited chemical driving forces available at the transformation temperatures. Thus, in general, under normal cooling conditions, the fcc phase is retained at room temperature in metastable form. Previous work has shown that the metastable fcc phase in a wrought Co-27Cr-5Mo-0.05C alloy can be transformed to hcp by plastic deformation. This behavior was found to depend strongly on the grain size of the metastable fcc phase prior to deformation.

In the present article, the interest is focused on the fcc → hcp transformation that takes place during isothermal aging of a Co-27Cr-5Mo-0.05C alloy at temperatures below 950 °C. At these temperatures, the fcc phase remains in metastable form after cooling from the fcc stability field. has shown that isothermal aging of a solution-treated and quenched Co-26.7Cr-5.5Mo-0.15C alloy promotes the fcc (metastable) → hcp transformation by a complex two-stage process, which occurs concurrently with discontinuous precipitation of second-phase carbide particles. The fcc → hcp transformation involves the formation of two microstructurally different forms of hcp product phases. During the early stages of aging, the hcp1 phase is formed by a martensitic mechanism similar to that observed in pure Co. In this case, the hcp1 phase appears as a series of straight bands of heavily faulted parallel platelets with a {111}fcc habit plane. In contrast, the hcp2 phase, formed later during aging, exhibits a morphology consisting of hcp lamellae with a low fault density. In addition, extensive carbide precipitation (with fibrous or blocky morphologies) occurs in the interior of the hcp2 phase. Later transmission electron

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microscopy (TEM) work by Rajan\cite{13} showed that the faultfree hcp, phase is also formed by the same martensitic mechanism as the hcp, phase, and its morphology can be described as hcp regions bounded by curved, irregularly shaped boundaries with an ill-defined \{111\}fcc habit plane.

Cong Dahn et al.\cite{14} studied the kinetics of this martensitic transformation during the isothermal aging of Co-27Cr-5.5Mo-0.25C powders homogenized at 1150 °C. Their conclusion was that the nucleation kinetics of the isothermal transformation was governed by the thermally activated motion of partial dislocations and the interaction of the Shockley partials with short-range obstacles such as solute clusters.

The principal aim of the investigation reported in this article was to establish the basic transformation-temperature-time (TTT) relationship for the fcc (metastable) \rightarrow hcp transformation in the Co-27Cr-5Mo-0.05C alloy, to be used in optimizing the processing parameters for improved, low-friction hip and knee orthopedic implants. Two thermal cycles were investigated; one involving an intermediate water quench from 1150 °C to 25 °C prior to aging and the other consisting of a simple cooling from 1150 °C to the aging temperature. It will be shown that the microstructure and hardening of the material resulting from aging are determined by the fcc (metastable) \rightarrow hcp phase transformation and that water quenching prior to aging has profound effects on the kinetics of this phase transition.

II. EXPERIMENTAL MATERIALS AND PROCEDURES

The material used was a commercial, press forged Co-27Cr-5Mo-0.05C alloy round bar. The chemical composition was determined using “spark” emission spectroscopy, and the results are listed in Table I. Small samples with rectangular cross sections (15 × 7 mm) were cut parallel to the cross section of the original bar and then subjected to the two different thermal cycles illustrated schematically in Figure 1.

The thermal cycle identified as method A was carried out inside a high-temperature tubular furnace provided with an Ar gas inert atmosphere. Sets of ten, 5-mm-thick samples were heated to 1150 °C at 50 °C/minute and soaked for 1 or 8 hours at 1150 °C and then rapidly quenched in water at room temperature. Following this high-temperature heat treatment and quenching, the samples were placed again inside the tubular furnace on a ceramic rack. The rack was designed to facilitate the individual extraction and quenching of the samples after predetermined periods (1 to 24 hours) of isothermal aging at temperatures from 750 °C to 900 °C. The changes in structure caused by this type of thermal treatment were followed as a function of aging time by measuring X-ray diffraction patterns on the aged samples at room temperature.

The thermal cycle identified as method B in Figure 1 was carried out, using 0.5-mm-thick samples, inside an Anton–Paar high-temperature chamber adapted to a PHILIPS* X-ray θ-2θ powder diffractometer. The sample and the Pt heating element were protected against oxidation using an Ar gas inert atmosphere inside the high-temperature chamber. The Pt heating filament also acted as specimen holder during the X-ray diffraction measurements, and the temperature was measured and controlled within ±2 °C using a Pt/Pt-10 pct Rh thermocouple spot welded to the back of the filament. The thermal cycle consisted of (1) heating to 1150 °C at a rate of 50 °C/minute, (2) soaking for 1 hour at 1150 °C, (3) cooling at 50 °C/minute to aging temperatures in the range from 650 °C to 950 °C, and (4) isothermal aging. The changes in the structure of the sample were followed in situ by obtaining X-ray diffraction patterns at the end of the high-temperature heat treatment and then, as a function of time, during isothermal aging (up to 24 hours). After that, the samples were rapidly cooled to room temperature.

It is noteworthy that the experimental information of the effects of aging time at a specific temperature on the structure of the material aged according to method A comes from X-ray diffraction patterns obtained from different samples aged during specific times. In contrast, following the evolution of the structure of the material by in situ high-temperature X-ray diffraction, as in method B, required the use of only one sample for each aging temperature.

The main structural change detected by the X-ray diffraction techniques employed in this work was the allotropic fcc (metastable) \rightarrow hcp transformation. Therefore, the relative amounts of transformed hcp \((f_{hcp})\) and untransformed fcc \((1 − f_{hcp})\) phases were estimated by measuring the integrated intensities of the (200)fcc and (101)hcp X-ray diffraction peaks \((I_{200}^{fcc} \text{ and } I_{101}^{hcp}, \text{ respectively})\). The weight fraction of the hcp phase was calculated using the following expression, developed by Sage and Gillaud:\cite{15}

\[
f_{hcp}(wt \text{ pct}) = \frac{I_{101}^{hcp}}{I_{101}^{hcp} + 1.5 I_{200}^{fcc}} \tag{1}
\]

Table I. Chemical Analysis of Co-27Cr-5Mo-0.05C Alloy (Element Content in Weight Percent)

<table>
<thead>
<tr>
<th>Element</th>
<th>Mn</th>
<th>Si</th>
<th>Cr</th>
<th>Mo</th>
<th>Ni</th>
<th>Fe</th>
<th>Co</th>
</tr>
</thead>
<tbody>
<tr>
<td>%</td>
<td>0.055</td>
<td>0.759</td>
<td>0.595</td>
<td>25.74</td>
<td>5.47</td>
<td>0.49</td>
<td>0.304 balance</td>
</tr>
</tbody>
</table>

Fig. 1—Schematic representation of the thermal cycles employed in the present work to study the aging behavior of Co-27Cr-5Mo-0.05C alloy.

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