JOURNAL OF MATERIALS SCIENCE 28 (1993) 1312–1316

Alloy design and microstructure of a biomedical Co–Cr alloy

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Two wrought Co–Cr alloys for dental and surgical implant and equipment applications were designed and their microstructures and hot workability determined and compared to a current dental alloy SC–H. The chemical composition of the alloys was selected with regard to the general requirements for biomedical alloys and the general principles of alloying theory. A phase-control law originally developed for nickel-base superalloys, PHACOMP, was utilized in order to avoid the formation of topologically close-packed (tcp) phases and to ensure the ductility and workability of the alloy. The alloys were cast using a vacuum induction melting technique which was found to allow a fairly good chemical composition control of the alloys. Hot forging of the as-cast alloys confirmed their good workability. Optical metallography showed the as-cast alloys to have a dendritic structure with some spherical carbide particles in the interdendrite regions. In contrast, the dental alloy SC–H in the as-cast condition had continuous carbide along the grain boundaries which impaired the ductility and prevented hot forging of this alloy due to cracking of the specimens. X-ray diffraction analysis showed that both alloys I and II have the fcc-Co matrix and $Cr_{23}C_6$ type carbide particles. No tcp phases were observed.

1. Introduction

A wide variety of biomedical materials are being, or have been used. These materials include porcelain, ceramics, cements, silicate glasses and silicophosphates, silica gel, polymers, amalgams, gold and its alloys, silver and its alloys, cobalt–chromium alloys, nickel–chromium alloys, titanium and its alloys, and stainless steel (type 316), etc. [1,2]. The basic requirements for these materials relate to the corrosion resistance, and to the mechanical and biochemical properties. The base-metal alloys have recently received considerable attention both in the biomedical and the metallurgical fields, because such metals and alloys provide excellent strength, toughness and wear resistance [3–6]. Cobalt–chromium alloys were first applied in dentistry in 1929. Besides their economic advantage over gold, these alloys are also attractive because they are less than half the density and are considerably stronger than gold [7]. It has also been shown that Co–Cr alloys have the required (bio)chemical inertness for use in surgical implants [8]. However, the low ductility of these base-metal alloys has been a problem and considerable research activity has taken place with the aim of improving the ductility by alloy additions.

In this work two wrought cobalt–chromium alloys for biomedical applications have been developed using the general principles of alloying theory. The chemical compositions have been selected so as to meet the requirements of both corrosion resistance and mechanical properties. The alloy ingots were first cast using a vacuum-induction melting technique and then hot forged. The microstructure was characterized by optical metallography and X-ray diffraction techniques.

2. Alloy design

In selecting the chemical composition of the experimental alloys, the general metallurgical principles of alloying theory [9–11] were applied. This alloy design focuses on the two main properties required of biomedical materials, namely good corrosion resistance and mechanical properties (strength, ductility and hot workability) [1]. The superalloy, base-metal group VIIIA elements, particularly cobalt and nickel, have very similar physical properties such as atomic size, melting point and density. Thus, the metallurgical principles used in the development of nickel-base alloys and austenitic stainless steels could be used to guide us in the design of the Co–Cr alloys.

Strengthening in the Co–Cr alloys is obtained primarily through a combination of solid-solution strengthening and carbide precipitation hardening

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[12, 13]. First of all, a carbon content of 0.1% was specified on the basis of previous experience on wrought cobalt-base superalloys [14]. Carbon has two functions in the alloy, namely that of carbide formation and solid-solution hardening (for example, the solution-hardening effect of carbon is about 300 times that of nickel in austenitic stainless steels [13]). Also like nickel, carbon is an austenite-forming element and contributes 30 times to the nickel equivalent for the austenitic steel [13]. The other alloying elements, e.g. chromium, nickel, molybdenum and tungsten, also have both solid-solution hardening and carbide-formation effects. However, these elements also significantly affect properties other than strength.

The addition of chromium is made to improve the corrosion and high-temperature oxidation resistance of the alloys [15,16]. Also, chromium is a carbide-forming element, and gives an $M_{23}C_6$-type carbide with a high chromium to carbon ratio (the ratio of [Cr/C] governs the type of carbide formed in the Co–Cr alloy [14,17]. On the basis of these requirements, the chromium contents of alloys I and II were specified as 20% and 22%Cr (the higher chromium content in alloy II is designed to increase corrosion resistance further).

Tungsten was added in order to have a strong carbide-forming tendency and solid-solution hardening (due to its large atomic size with respect to the cobalt atom) [18]. Molybdenum in our alloys is designed to replace part of the tungsten. When added to stainless steel (e.g. type 316 with 3%–4% Mo) molybdenum gives the alloy a much better resistance to pitting, sulphuric acid, and hot organic acids [15]. This is a desirable feature for a biomedical material.

All three elements discussed above, namely chromium, molybdenum and tungsten, stabilize the h c p–Co structure. All three also lower the stacking fault energy (SFE) thus producing a high tendency to form stacking faults. The formation of stacking faults may be one of the prime causes of ductility and workability problems in cobalt alloys [14, 17]. To obtain good ductility in cobalt-base alloys, an f c c-Co matrix is necessary. Nickel is generally added for this purpose. Elements which increase SFE are also those which stabilize the f c c phase. It is generally considered good practice to add 5%–15% nickel to most cobalt alloys. It was first reasoned that this "stabilized" the f c c-Co structure. However, it is now clear that this also increases SFE and controls the tendency of cobalt alloys to form excessive stacking faults; this helps counteract the effect of chromium, tungsten, molybdenum and other refractory elements essential for strength, but which lower the SFE [14].

On the basis of the above considerations, the chemical composition for the two experimental alloys were selected to be (in wt %): C (0.1), Cr (20 or 22), Mo (4), W (10), Ni (15) and Co (balance). These "optimum" compositions were verified further using a phase computation technique, namely PHACOMP [14,17,19]. It is essential to avoid the formation of topologically close-packed (t c p) structures which include the Sigma phase (AB or A_xB_y type), the Laves phases (AB_2 type), and other phases closely related to the Sigma phase (α-Mn type, P, R, μ and Δ) [20]. These phases are of concern because they can cause a significant loss of both strength and ductility at service temperatures and a severe loss of room-temperature ductility. The PHACOMP technique utilizes the mean electron-hole number, $\bar{N}_v$

$$\bar{N}_v = \sum_{i=1}^{n} m_i (N_v)_i \qquad (1)$$

where $\bar{N}_v$ is the average electron hole number for the alloy, m_i is the atomic fraction of particular element, N_v is the individual electron-hole number of a particular element and n is the number of elements in the alloy matrix. For alloy SC–H, alloys I and II, the following formula was used to calculate $\bar{N}_v$

$$\bar{N}_v = 5.60\text{Mo} + 4.66(\text{Cr} + \text{W}) + 1.71\text{Co} + 0.61\text{Ni} \qquad (2)$$

In the initial alloy design stage, nominal compositions were used for the calculation of $\bar{N}_v$. The results for $\bar{N}_v$ are given in Table I. It shows that all alloys have an $\bar{N}_v$ value less than 2.70 which is considered to be the critical $\bar{N}_v$ value above which t c p phases are expected to form [14,17,19,21].

3. Experimental details

3.1. Materials

The purity of metals used for the alloy preparation were as follows (in wt %): chromium 98.64%, molybdenum 99.93%, tungsten 99.90%, and nickel 99.80%.

The approximate chemical compositions of our alloys are: C (0.10%), Cr (20 or 22%), Mo (3.80%),

TABLE I Chemistries and average electron-hole numbers for the two developmental alloys (alloys I and II) and dental alloy SC–H .

Alloy	Composition (wt %)						$\bar{N}_v$
	C	Cr	Mo	W	Ni	Co	
Nominal compositions							
I	0.10	20.00	4.00	10.00	15.00	50.90	2.41
II	0.10	22.00	4.00	10.00	15.00	48.90	2.48
Actual compositions of as-cast alloys							
I	0.09	19.27	3.82	9.18	15.12	50.50	2.42
II	0.11	22.07	3.75	9.30	15.20	48.80	2.50
SC–H	0.41	27.32	Trace	None	2.77	61.50	2.58

W (9.20%), Ni (15.10%), Co (balance). A comparison material, as-cast SC–H alloy, has the chemical composition of C (0.41%), Cr (27.32%), Mo (trace), Ni (2.77%), Co (balance). This dental alloy, SC–H, is currently used in dentistry for removable partial dentures and in some cases for joint implants. The major problems associated with its application are poor ductility and hot workability. The cause of the low ductility and poor hot workability, as will be shown in the present study, is the presence of continuous grain-boundary carbides.

3.2. Experimental techniques

3.2.1. Vacuum induction melting (VIM)

The VIM technique was used to prepare the Co–Cr alloys in order to minimize the oxidation of the alloying elements such as molybdenum and tungsten. The casts were made using a 10 kg vacuum induction furnace. The VIM operating parameters were: vacuum 4×10^{-3} mm Hg, argon protective atmosphere 200 mm Hg, power 5 kW and melting time about 30 min. The crucible was made from Al_2O_3 material. The casting mould was cast iron. The casts were made in the furnace and the alloy ingots were cooled in the furnace. The alloy ingots were cylinders with a diameter of 35 mm and a length of 900 mm.

3.2.2. Forging

The cast ingots were forged into alloy bars with a diameter about 14.8 mm. The forging temperature was controlled between 900 and 1150 °C and 14–20 hot-forging and reheating cycles were utilized. The forging machine was an air-hammer type. Hot forging of the as-cast SC–H dental alloy was not possible due to cracking of the specimen during the hot-forging process.

3.2.3. Optical metallography and X-ray diffraction analysis

Optical microstructure observations were made on the as-cast alloys, SC–H, alloys I and II. Samples for metallography were mechanically polished (fine grinding with 600 Grit SiC paper and finally polished with Al_2O_3 paste) and etched in aqua regia for about 30 s at 80 °C. The phase compositions of alloys I and II were analysed using X-ray diffraction. The experimental parameters were as follows: target, molybdenum; accelerating voltage, 50 kV; filament current, 13 mA; filter, zirconium; exit window slit, 2°; receiving slit, 0.3 mm; spectrometer scanning speed, $2° \text{ min}^{-1}$; paper speed, 16 mm min^{-1}; paper scale magnification 3×10^4; time constant, 3.3 s.

4. Results

4.1. Chemical composition

The chemical analysis results for the as-cast SC–H dental alloy and the two Co–Cr alloys are given in Table I (all compositions in wt %), together with the nominal compositions (designed). Nominal and "actual" compositions are very similar, thus confirming the suitability of vacuum induction melting for the preparation of the cast Co–Cr alloys.

4.2. Microstructure of the alloys

The microstructure of the as-cast SC–H alloy (Fig. 1a) shows a typical eutectic carbide along the grain boundaries and interdendritic regions. We believe that this microstructure, i.e. continuous grain-boundary carbide, is the cause of the poor hot workability and ductility of the dental alloy SC–H. The as-cast specimens of alloy I (Fig. 1b) and alloy II (Fig. 1c) have a typical dendritic f c c-Co structure. The carbides are in the form of spherical particles in the interdendritic regions, and no continuous grain-boundary carbides were formed in these two alloys. Fig. 1d is a higher magnification micrograph (compared to Fig. 1c) of as-cast alloy II, showing the carbide particles formed within the dendrite structure.

4.3. X-ray analysis

The X-ray diffraction results of alloys I and II in the as-cast condition are given in Table II. Both alloys I and II were found to contain both f c c-Co and some $Cr_{23}C_6$ type carbides.

5. Discussion

Alloying theory as used in alloy development or design [9–11, 22] relates the properties of alloys to their chemistries and microstructures. A required property is obtained by selection of "suitable" chemical compositions and fabrication processes (e.g. melting, casting, forming and heat treatment) to obtain the desired microstructure(s). For biomedical materials, such as dental and joint implant materials, corrosion resistance and mechanical properties (e.g. strength, ductility and work-ability, etc.) are of prime importance for optimum clinical performances [23, 24]. As we saw from the optical metallography, the dental alloy SC–H had continuous grain-boundary carbides (see Fig. 1a). This type of microstructure is far from ideal given the complex dynamic loading and working environment (surplus of oxygen and a variety of different foods, liquids, medicines, etc., being brought into contact with the alloy) typical for dental alloys [1]. The grain-boundary carbides can cause stress concentrations along the grain-boundary regions [25]. Under actual dental application performance conditions (which are similar to these found for joint implant alloys), these stress concentrations can induce stress corrosion cracking along the grain boundaries due to the chemical heterogeneity between the grain-boundary carbide and the f c c-Co grains [26]. When the carbide particles are evenly distributed throughout the matrix, such as in our alloys I and II, this situation can be avoided.

As described in the alloy design section, in order to obtain the necessary ductility and hot workability of the Co–Cr alloys, the chemical composition must be adjusted so as to avoid the formation of t c p phases.

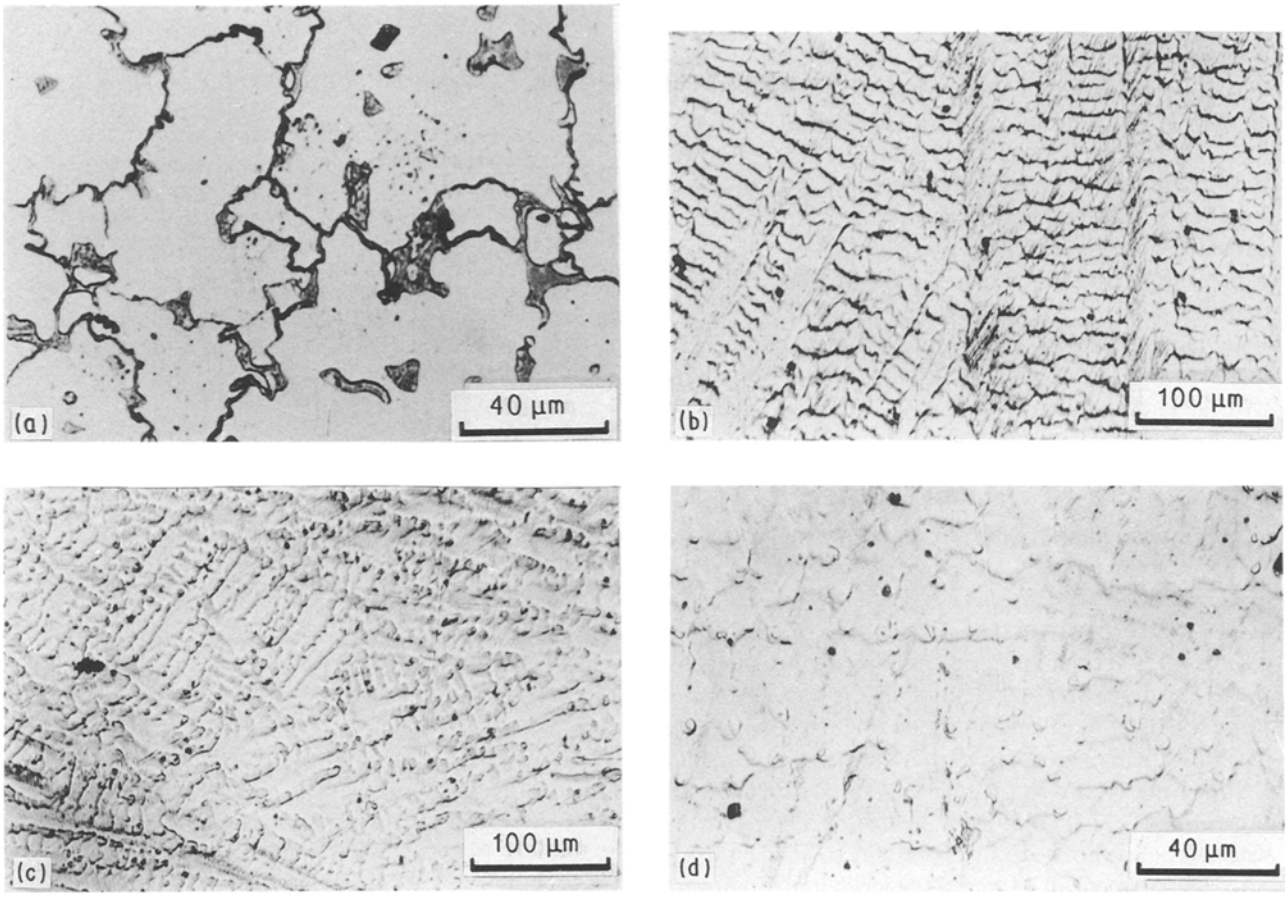

Figure 1 Optical micrographs of the three Co–Cr alloys. (a) As-cast SC–H alloy with eutectic carbides along grain boundaries and interdendrite regions. (b) As-cast alloy I with dendritic f c c-Co structure. (c) As-cast alloy II with a similar dendritic f c c-Co structure to alloy I. (d) As-cast alloy II: higher magnification micrograph showing spherical carbide particles which are formed within the dendrite structure.

TABLE II X-ray diffraction results for alloys I and II in the as-cast condition

Alloy I				Alloy II			
2θ (deg)	*d* (nm)	*h k l*	Phase	2θ (deg)	*d* (nm)	*h k l*	Phase
17.50	0.233 12	4 2 0	$Cr_{23}C_6$	17.50	0.233 12	4 2 0	$Cr_{23}C_6$
20.03	0.203 92	1 1 1	fcc-Co	20.16	0.202 74	1 1 1	fcc-Co
23.00	0.177 88	2 0 0	fcc-Co	23.00	0.177 88	2 0 0	fcc-Co
28.55	0.143 83	6 4 0	$Cr_{23}C_6$	28.63	0.143 58	6 4 0	$Cr_{23}C_6$
32.70	0.125 98	2 2 0	fcc-Co	32.74	0.125 98	2 2 0	fcc-Co
33.65	0.122 52	5 5 5	$Cr_{23}C_6$	33.77	0.122 17	5 5 5	$Cr_{23}C_6$
38.50	0.107 56	3 1 1	fcc-Co	38.56	0.107 43	3 1 1	fcc-Co
40.50	0.102 46	2 2 2	fcc-Co	40.33	0.102 95	2 2 2	fcc-Co

In our case, this was done using a phase computation technique, namely the PHACOMP [14, 17, 19, 21] technique, which was originally developed for the nickel-base superalloys and was later applied to cobalt-base alloys. Both alloys I and II have a microstructure consisting of an f c c-Co matrix plus randomly distributed spherical carbides and no t c p phases were present (see X-ray diffraction analysis, Table II, and optical metallography, Fig. 1). Alloys I and II both exhibited good hot workability in the hot-forging process. This good hot workability results from the f c c-Co matrix (rather than an h c p-Co matrix) and the randomly distributed spherical carbides (rather than a continuous grain-boundary carbide). To obtain the desired chemical composition, a vacuum induction melting technique was employed for the alloy preparation. The actual chemical composition was very close to the nominal (design) composition for both alloys I and II (see Table I) and the desired microstructure (phase compositions) and hence properties were thus obtained.

6. Conclusions

1. Existing alloying theory as previously applied to nickel-base alloys and stainless steels has been used as a guide in the design of two Co–Cr alloys for potential biomedical applications.

2. Two wrought cobalt–chromium biomedical alloys with chemical compositions (wt %): C (0.1), Cr

(20 or 22), Mo (4), W (10), Ni (15) and Co (balance) were prepared using a vacuum induction melting technique. The VIM technique allowed for fairly good chemical composition control of the alloys.

3. The as-cast alloys have a dendritic f c c-Co structure with some spherical carbide ($M_{23}C_6$) particles in interdendritic regions. No continuous grain-boundary carbides were formed. Also no t c p phases, which can cause significant loss of strength and ductility, were detected.

4. The ingots with diameters of 35 mm and lengths of 900 mm were successfully hot forged into alloy bars with a diameter about 14.8 mm. This demonstrated the good hot-workability of the as-cast alloys.

5. The two Co–Cr alloys were compared to a current dental alloy (SC–H) and found to be superior in terms of desired microstructure and hot workability.

Acknowledgements

The cast SC–H dental alloy sample was provided by the Hangzhou Medical School, Hangzhou, People's Republic of China. The continued financial support to Mr Shi is being provided by the Natural Sciences and Engineering Research Council of Canada through an Operating Grant (A4391) to Professor D.O. Northwood. The authors are also grateful to Professor H. Yao, Department of Materials Science and Engineering, Zhejiang University, for his interest in, and critical discussion of this work.

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Received 2 December 1991
and accepted 25 June 1992