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Composition dependence of the structure and properties of as-cast Ti-Cr-Co alloys for biomedical applications

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Abstract

The examination of a series of as-cast Ti-Cr-Co alloys was performed with the purpose of obtaining new β-type Ti-alloys. Experimental results revealed that the alloys, containing 10–20 atomic percent Cr and 5 atomic percent Co, were single β-phase alloys.

They displayed hardness values in the order of 359 to 423 HV, high compressive strength (1620–1990 MPa), high yield strength (1050–1190 MPa) and low elastic modulus (47–72 GPa), which all increased with an increase in the chromium content. The β-phase alloys showed very high plastic strain which reduced from 79 to 64 % with an increase in the chromium content. All experimental alloys revealed very good corrosion resistance, according to the E_{pit} values (1200–1300 mV), which was not significantly influenced by the chemical composition of the alloys. According to the best combination of high strength, low elastic modulus and high plasticity, the new $Ti_{85}Cr_{10}Co_5$ and $Ti_{80}Cr_{15}Co_5$ β-type Ti-alloys showed a potential for biomedical applications.

Key words: Ti-Cr-Co alloys, β-alloys, structure, mechanical properties, corrosion resistance

1. Introduction

Advanced biomaterials must possess high hardness, excellent fatigue and tensile strength, superior corrosion and wear resistance, good biocompatibility and non-toxicity. In recent years, titanium and its alloys have been broadly used for dental and orthopaedic implants due to their properties, including their excellent high strength-to-weight-ratio, low elastic modulus, good corrosion resistance and biocompatibility [1].

Pure titanium undergoes an allotropic transformation from the *hcp* α-phase into the *bcc* β-phase at 882 °C, while the alloying elements either decrease or increase the transformation temperature, which is called the β transus. As a result of this structural change, titanium alloys are classified into three major categories, i.e., α, $\alpha + \beta$ and β alloys [2]. Compared to the classic TiAl6V4 $\alpha + \beta$-type alloy, the β-type titanium alloy shows better biocompatibility due to the absence of Al and V, which are considered potentially toxic elements, lower elastic modulus as well as other improved mechanical properties and workability [3]. Therefore, the recent trend in research into titanium alloys for biomedical applications has been to develop new β-type titanium alloys by adding certain strong β-phase forming elements (Nb, Ta, Mo, Zr) or certain β-phase improving elements (Cr, Fe, Sn), which can visibly reduce the elastic modulus. When the elastic modulus is reduced, the strength of the titanium alloy decreases. Some alloying elements (Co, Cu, Ni) can be used to strengthen the alloys [4].

This study describes the effect of the chemical composition on the structural, mechanical and electrochemical characteristics of a series of ternary titanium-rich alloys with chromium and cobalt. Since there are no studies dealing with Ti-Cr-Co alloys and their potential use as biomaterials, the main aim of this work was to examine the possibility of obtaining new β-type titanium alloys and evaluate the mechanical behaviour and electrochemical characteristics of such alloys as a function of their microstructure. The working hypothesis was that the formation of the β-phase could promote the addition of chromium and

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Table 1. Chemical compositions of experimental alloys, the established phases, and the lattice parameters of β-phase

Alloy No.	Alloy composition (at.%)	Established phases	β-phase, a (nm)
1	$Ti_{80}Cr_{10}Co_{10}$	β, Ti_2Co	0.31861
2	$Ti_{75}Cr_{15}Co_{10}$	β, Ti_2Co	0.31600
3	$Ti_{85}Cr_{10}Co_5$	β	0.32269
4	$Ti_{80}Cr_{15}Co_5$	β	0.31974
5	$Ti_{75}Cr_{20}Co_5$	β	0.31798

cobalt as the β-phase improving elements.

2. Experimental details

A series of ternary Ti-rich alloys with chromium and cobalt was prepared by arc melting a mixture of pure elements on a water-cooled copper hearth in an argon atmosphere. In order to achieve chemical homogeneity, the samples were remelted six times and button-like ingots weighting approximately 5 g were obtained. The casting was done using the same equipment and a water-cooled, especially constructed copper anode that also served as the casting mould. Cylindrical samples, dimensions: $8 \times 25\,mm^2$, were sectioned using a Buehler Isomet low-speed diamond saw to obtain specimens for various examinations.

The microstructures of the alloys were examined using optical and the Tescan Vega TS 5136 MM scanning electron microscope (SEM) with the Brukner energy dispersive X-ray (EDX) analyser. The samples were prepared using the standard metallographic techniques, i.e. grinding up to 1200 grit with SiC followed by polishing with 0.05 μm alumina powder to mirror finishing and etching with a solution of 50 ml HCl, 5 ml HNO_3 and 50 ml H_2O.

The phase analysis of the alloys was carried out on polished disc surfaces through X-ray diffraction (XRD) using the Philips PW 3710 diffractometer with Cu K_α radiation. The phases were identified by matching each characteristic peak with the JCPDS files [5].

Hardness measurements were conducted using the Vickers method (20 N, 10 s) and Otto-Wolpert-Werke equipment. The deformation behaviour and the mechanical properties were examined on the basis of compressive tests using an Amsler testing machine at a strain rate of $1 \times 10^{-4}\,s^{-1}$ at room temperature on as-cast cylindrical samples, dimensions: $8 \times 10\,mm^2$. The values of elastic modulus E, compressive strength, yield strength and plastic strain were determined on the basis of the stress-compression curves.

The corrosion behaviour of the designed alloys was determined using the method of cyclic potentiodynamic anodic polarization at a scanning rate of $5\,mV\,s^{-1}$ between −1000 and +3000 mV in an aerated 0.9 % NaCl aqueous solution at the temperature of 37 °C. A saturated calomel electrode and a platinum electrode served, respectively, as the reference and the counter electrode. The measuring was performed using Ametek Parstat 2273 equipment. The cast disc samples (working surface of approx. $50\,mm^2$) were used as electrodes. Pitting corrosion was stimulated by polarizing the specimens to noble potentials to the breakdown of the passive oxide film on the metal surface. The parameter of interest was the pitting potential E_{pit}, i.e., the potential of the passive film breakdown.

3. Results and discussion

In order to form the single β-phase alloy, five as--cast Ti-Cr-Co alloys containing 10–20 at.% chromium and 5 and 10 at.% cobalt were examined. Their chemical compositions (Table 1) were selected according to the results of our previous research, i.e. the finding that the region of the biomedically-acceptable Ti-Cr--Co alloys was situated within the lower concentration of alloying elements, i.e., in the field of about 10 at.% cobalt and 20 at.% chromium [6].

Optical microscopy showed that alloys with 10 at.% cobalt (1–2) were two-phase alloys and that those with 5 at.% cobalt (3–5) were single-phase alloys. The results of the XRD-analysis (Table 1) showed that alloys 1–2 consisted of the β-phase and the Ti_2Co intermetallic compound.

The examination of binary titanium alloys [7] also showed the presence of Ti_2Co which precipitated on the grain boundaries of the β-phase matrix in the Ti-Co alloys with more than 10 mass % cobalt. Since cobalt effectively reduces the M_s point, no eutectoid transformation ($\beta \rightarrow \alpha + Ti_2Co$) took place. Rather, Ti_2Co was formed from the eutectic reaction (liquid $\rightarrow \beta_{metastab.} + Ti_2Co$) [8]. The XRD-analysis showed that alloys 3–5 were single β-phase alloys. Diffraction patterns characteristic of two-phase and single-phase alloys can be seen in Fig. 1. The values of the lattice parameter for β-phase alloys (Table 1) were calculated using the Celref programme [9]. These values were reduced in relation to the lattice parameter of pure titanium ($a_{Ti} = 0.3306$ nm) through the formation of the β-Ti solid solution because of the difference between the atomic radius of titanium (0.147 nm) and the atomic radius of the substitutional alloy-

Table 2. The results of EDS analysis for as-cast Ti-Cr-Co alloys (in at.%)

Alloy No.	Alloy composition (at.%)	Phases	Ti	Cr	Co
1	$Ti_{80}Cr_{10}Co_{10}$	β	84.10	8.62	7.27
		Ti_2Co	69.71	8.07	22.22
		α	85.98	7.95	6.12
2	$Ti_{75}Cr_{15}Co_{10}$	β	77.35	14.47	8.18
		Ti_2Co	68.12	11.54	20.34
		α	78.18	14.26	7.56
3	$Ti_{85}Cr_{10}Co_5$	β	87.03	8.61	4.36
4	$Ti_{80}Cr_{15}Co_5$	β	82.32	13.29	4.39
5	$Ti_{75}Cr_{20}Co_5$	β	78.23	16.97	4.80

Table 3. Mechanical properties of as-cast Ti-Cr-Co alloys

Alloy No.	Alloy composition (at.%)	Vickers hardness HV2	Elastic modulus E (GPa)	Yield strength (MPa)	Compressive strength (MPa)	Compression ε (%)
1	$Ti_{80}Cr_{10}Co_{10}$	489	59	1400	1950	25.5
2	$Ti_{75}Cr_{15}Co_{10}$	516	46	1390	1900	12.5
3	$Ti_{85}Cr_{10}Co_5$	359	47	1050	1620	79.0
4	$Ti_{80}Cr_{15}Co_5$	359	57	1140	1710	74.0
5	$Ti_{75}Cr_{20}Co_5$	423	72	1190	1990	64.0

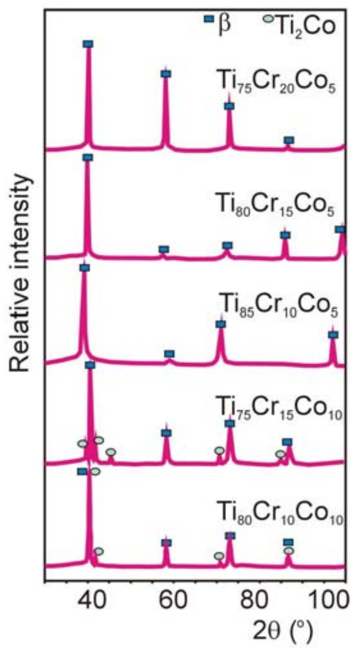


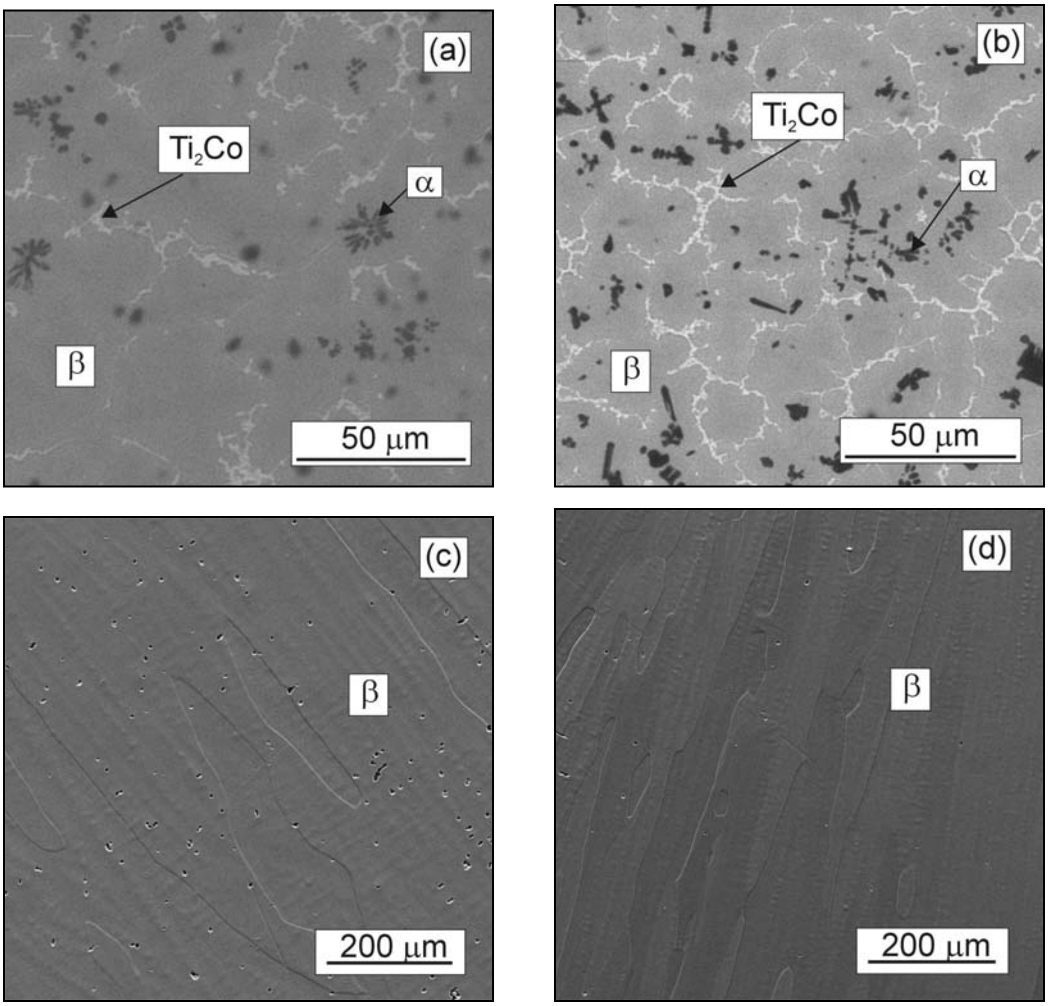
Fig. 1. XRD-patterns of as-cast Ti-Cr-Co alloys.

ing elements, i.e., chromium (0.130 nm) and cobalt (0.125 nm).

The SEM analysis performed applying the BSE technique (Fig. 2) indicated that alloys 1–2 consisted of the β-matrix, Ti_2Co and a small amount of the α-phase, a result which could not have been obtained on the basis of the XRD analysis. This analysis also confirmed that alloys 3–5 were single β-phase alloys. The average chemical composition of the phases was established on the basis of the EDS analysis. From the results presented in Table 2, it can be seen that the chemical composition of β- and α-Ti solid solutions, which contain cobalt and chromium, was similar to the alloy composition. The chemical composition of Ti_2Co or Ti_2(Co, Cr) precipitate was close to the equilibrium one.

The results of hardness measurements (Table 3) revealed a strong influence of the alloy chemistry and microstructure on the hardness values. The explanation of the hardness values would be rather complex considering various parameters, such as solid solution strengthening, precipitation hardening, grain size and crystal structure of phases, which could all affect the hardness of the alloy [10].

The hardness increment of multi-phase alloys 1–2 from 489 to 516 HV is a result of the solid solution strengthening through an increase in the chromium content and the presence of the Ti_2Co intermetallic compound [11]. The single-phase alloys 3–5 demonstrated less hardness (359–423 HV) which increased with an increase in the chromium content, which is in agreement with the reference values [12, 13]. The comparison of hardness for two groups of experimental alloys (Fig. 3) revealed that alloys with 10 at.% cobalt had generally higher hardness values than those



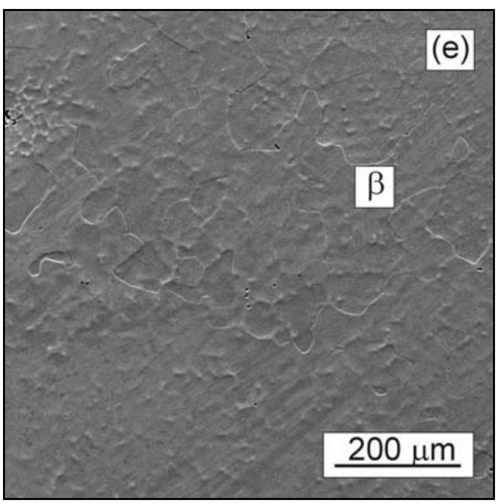


Fig. 2. SEM micrographs of as-cast Ti-Cr-Co alloys: (a) $Ti_{80}Cr_{10}Co_{10}$, (b) $Ti_{75}Cr_{15}Co_{10}$, (c) $Ti_{85}Cr_{10}Co_5$, (d) $Ti_{80}Cr_{15}Co_5$, (e) $Ti_{75}Cr_{20}Co_5$.

with 5 at.% cobalt, predominantly due to the presence of Ti_2Co and the α-phase which is harder than the β-phase [14].

The stress-compression curves for experimental alloys are presented in Fig. 4. As can be seen, alloys 3–5 showed an elastic deformation stage followed by a long plastic deformation stage and coexisting high strength and large plasticity.

The calculated values of elastic modulus, compressive strength, yield strength and plastic strain are shown in Table 3. All alloys exhibited relatively low elastic modulus depending on their chemical compositions and microstructures. The $Ti_{75}Cr_{15}Co_{10}$ alloy and the $Ti_{85}Cr_{10}Co_5$ single β-phase alloy had the low-

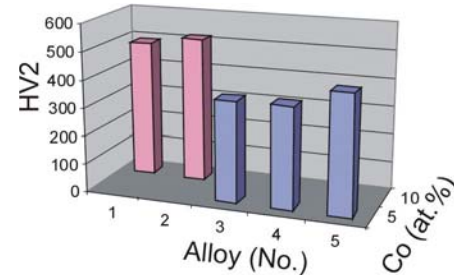


Fig. 3. Vickers hardness as a function of cobalt content for two groups of experimental alloys.

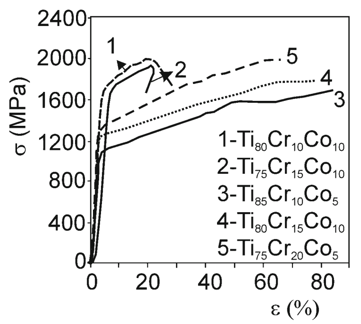


Fig. 4. Stress-compression curves of as-cast Ti-Cr-Co alloys.

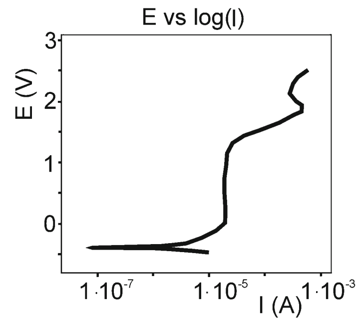


Fig. 5. Anodic polarization curve of $Ti_{85}Cr_{10}Co_5$ alloy in a 0.9 % NaCl at 37 °C.

Table 4. Electrode potential E_{pitt} (vs. SCE) for experimental alloys

Alloy No.	Alloy composition (at.%)	E_{pitt} (mV)
1	$Ti_{80}Cr_{10}Co_{10}$	1260
2	$Ti_{75}Cr_{15}Co_{10}$	1200
3	$Ti_{85}Cr_{10}Co_5$	1300
4	$Ti_{80}Cr_{15}Co_5$	1250
5	$Ti_{75}Cr_{20}Co_5$	1280

est elastic modulus values, i.e., 46 GPa and 47 GPa, respectively. These values proved significantly lower than the elastic modulus values of other Ti-Cr based biomedical alloys (80–165 GPa) [11, 15]. The yield strengths of the experimental alloys (1050–1400 MPa) were relatively high and in agreement with the values of some as-cast Ti-based biomedical alloys [4, 16, 17]. Their compressive strengths (1620–1990 MPa) were much higher than those of other similar titanium alloys [18, 19]. The compressive strength, yield strength and elastic modulus of single β-phase alloys increased with the chromium content. These alloys also exhibited very high plastic strain, which was reduced from 79 to 64 % with an increase in the chromium content. In terms of the desirable mechanical properties for biomedical use, the advantages of the $Ti_{85}Cr_{10}Co_5$ and $Ti_{80}Cr_{15}Co_5$ single β-phase alloys include the combination of high strength, low elastic modulus and high plasticity.

The corrosion behaviour of as-cast Ti-Cr-Co alloys was evaluated using the potentiodynamic polarization technique on the basis of E_{pitt} values. The anodic polarization curve for alloy 3 in a 0.9 % NaCl aqueous solution at 37 °C is presented in Fig. 5. Pitting corrosion was stimulated by polarizing the specimen to noble potentials up to the breakdown of the oxide film on the metal surface. The passive oxide film (mainly TiO_2, the most thermodynamically stable titanium oxide) forms naturally on titanium alloys and protects the underlying, highly reactive titanium metal against uncontrolled chemical or biochemical reactions and corrosion [20].

The measured breakdown potentials of the present alloys (Table 4) were rather similar, mainly higher than 1200 mV, and showed a very good stability of the passive film, which was not significantly influenced by their chemical compositions.

According to this, all experimental Ti-Cr-Co alloys showed prominent corrosion characteristics, which can be generally ascribed to the presence of titanium, as one of the most corrosion-resistant materials.

4. Conclusions

The study of five as-cast Ti-Cr-Co alloys containing 10–20 at.% Cr and 5 and 10 at.% Co revealed the following results:

The XRD and the SEM analyses indicated that alloys 1–2 with 10 at.% Co consisted of the β-phase, the Ti_2Co intermetallic compound and a small amount of the α-phase. Alloys 3–5 with 5 at.% Co were identified as single β-phase alloys.

According to the results of the EDS analysis, the average chemical composition of the β- and α-Ti substitutional solid solutions was similar to the alloy composition and those of the Ti_2Co or $Ti_2(Co, Cr)$ precipitate were close to the equilibrium one.

Higher hardness values of multi-phase alloys 1–2 (489 and 516 HV) were a result of the solid solution strengthening with an increase in the chromium content and the presence of the Ti_2Co intermetallic compound. The hardness of single β-phase alloys 3–5 increased from 359 to 423 HV with an increase in the chromium content.

The stress-compression curves for single β-phase alloys showed the coexistence of high strength and large plasticity. Their high values of compressive strength and yield strength and low elastic modulus increased with an increase in the chromium content. The β-phase alloys exhibited very high plastic strain which was reduced from 79 to 64 percent with an increase in the chromium content. Among them, the $Ti_{85}Cr_{10}Co_5$ alloy had the lowest elastic modulus of 47 GPa.

All experimental alloys revealed similar and high E_{pitt} values. They were mainly higher than 1200 mV and showed a very good stability of the passive oxide film, which was not significantly influenced by the chemical composition of the alloys. The excellent corrosion characteristics of alloys can be generally ascribed to the presence of titanium, one of the most corrosion-resistant materials.

With regards to the prominent properties, such as high strength, low elastic modulus, high plasticity and very good corrosion resistance, two single β-phase ternary titanium alloys, i.e. $Ti_{85}Cr_{10}Co_5$ and $Ti_{80}Cr_{15}Co_5$, could be considered candidates for biomedical applications.

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