

## MICROSTRUCTURE AND HARDNESS OF Co-Cr-Ti ALLOYS FOR DENTAL CASTINGS

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Effect of adding titanium on the microstructure and hardness of as-cast Co-Cr base dental alloys have been investigated with the purpose to determine the region of their optimal characteristics. Twelve samples of Co-Cr-Ti alloys with increasing titanium content (4 to 12 at.%), which were prepared by arc-melting technique in argon atmosphere, revealed similar two-phases dendritic microstructure. It consists of dendrites and interdendritic region, which differ in crystal structures (fcc, hcp) and slightly in compositions. The hardness of alloys increases significantly with titanium and chromium content. The as-cast alloys with smaller titanium content (samples 3 to 5) have promising features for dental applications, because their hardness values are in good agreement with that of similar commercial dental alloys.

**Key words:** *Co-Cr-Ti alloys, microstructure, hardness, dental alloys*

**Mikrostruktura i tvrdoća Co-Cr-Ti legura za dentalne odljevke.** Ispitivanje utjecaja dodatka titana na mikrostrukturu i tvrdoću lijevanih dentalnih legura na osnovi kobalta i kroma provedeno je s ciljem, da se ustanovi područje njihovih optimalnih karakteristika. Dvanaest uzoraka Co-Cr-Ti legura s rastućim udjelom titana (4 -12 at.%), koji su preparirani u elektro-lučnoj peći pod zaštitnom atmosferom argona, pokazuje sličnu dvo-faznu dendritnu mikrostrukturu. Ona se sastoji od dendrita i međudendritnog područja, koji se razlikuju u kristalnim strukturama (fcc, hcp) i neznatno u sastavima. Tvrdoća legura značajno raste s udjelima titana i kroma. Lijevene legure s manjim sadržajem titana (uzorci 3-5) mogle bi se primijeniti u stomatologiji, jer je njihova tvrdoća slična vrijednostima za komercijalne dentalne legure.

**Ključne riječi:** *Co-Cr-Ti legure, mikrostruktura, tvrdoća, dentalne legure*

### INTRODUCTION

Since stainless steel was first used as an implant material in surgery in the early 1930's, a number of metallic materials, such as cobalt base alloys, titanium or titanium alloys, have been developed for biomedical applications [1]. They belong to the wide group of biomaterials, which are the tools leading the way in the battle to make the life longer, healthier and more complete for many individuals. Each biomaterial has advantages as well as disadvantages, and no one is the best material, but suited for different circumstances. Therefore, research and development of new metallic materials with higher quality in terms of both biomedical and mechanical properties, are of interest.

Cobalt-chromium alloys are used over 60 years as implant materials in dentistry and medicine owing to their high corrosion resistance and biocompatibility. Commercial den-

tal as-cast alloys (with optimal composition approx. 70 at.% Co - 30 at. % Cr) contain small quantities of alloying elements as carbon, molybdenum, wolfram, nickel, etc. The outstanding properties of Co-Cr alloys result from the crystallographic nature of cobalt, the solid-solution-strengthening effect of chromium and alloying elements, the formation of extremely hard carbides and corrosion resistance imparted by chromium. The problem, however, is rather low ductility of these base-metal alloys. Therefore considerable research activities take place with the aim of improving ductility by the alloying elements addition [2, 3].

In recent years, titanium and its alloys have received much attention. They are currently the most commonly used dental and orthopedic implant materials because of their excellent biocompatibility, high corrosion resistance, low density, good balance of mechanical properties and relatively low price. However, these alloys have low shear strength, wear resistance, castability and formability [4 - 6].

Considering that Co-Cr alloys and titanium belong to a few metallic materials which fulfill the strong requirements

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for corrosion resistance and biocompatibility, the good performances for Co-Cr-Ti alloys can be also expected. The available data confirm that the addition of titanium to Co-Cr alloy can improve some mechanical and physical properties [7 - 9] but on the other side, they show insufficiency in the investigation of this topic. Therefore, the purpose of this study was to prepare and investigate some selected Co-Cr-Ti alloys as potential for biomedical application.

## MATERIALS AND METHODS

Alloys of cobalt-chromium and titanium were prepared by melting the elements (with purity better than 99,9 %) in a laboratory arc-furnace in argon atmosphere.

The samples were remelted three times in order to achieve homogeneity. Their casting was performed using specially constructed cooper anode which served also as a casting mould (Figure 1.).

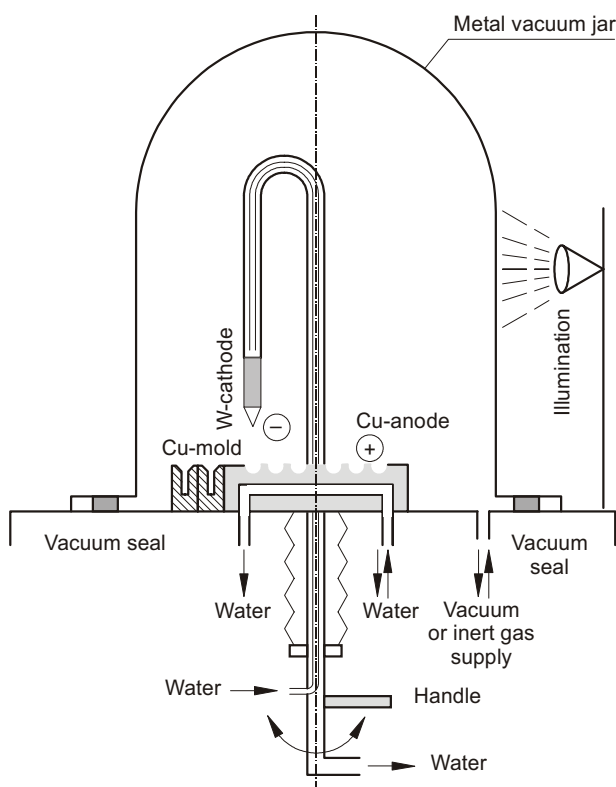


Figure 1. Experimental arc-melting furnace  
Slika 1. Eksperimentalna peč za lučno taljenje

The samples of cylindrical shape (dimensions about 7×12 mm) were obtained after melting. They were embedded in an epoxy resin and metallographically prepared with wet grinding on 120 - 1200 grit SiC paper and final polishing with Al<sub>2</sub>O<sub>3</sub> water suspension. Etching was accomplished with solution of 50 ml HCl, 5 ml HNO<sub>3</sub> and 50 ml H<sub>2</sub>O warmed on 50 °C, or with Kroll's reagent (1-3 ml 40% HF, 2 - 6 ml HNO<sub>3</sub> conc., 100 ml H<sub>2</sub>O).

The microstructure of the alloys was investigated using quantitative optical metallography and scanning electron microscopy. The etched samples were observed by optical microscope (Leitz, Ortholux) at the magnification of 280 ×. Optical micrographs taken with digital camera (Olympus DP11), were analysed with the corresponding programmes (Olympus DP-Soft, UTHSCA Image Tool). Selected sample of Co-Cr-Ti alloy was analysed by scanning electron microanalyser (Jeol, JXA 50 A).

X - ray diffraction pattern are taken on polished disc surface from 10 to 100° of 2θ value using CuK<sub>α</sub> - radiation (Philips, PW 3710).

Hardness was measured by Vickers method (30 N, 10 s) on the equipment of Otto-Wolpert-Werke. Microhardness measurements were performed on the microhardness tester Leica, VHMT (0,49 N, 10 s). Heat treatment was performed on the sample discs approximately 5 mm thick, which were cut from the as-cast cylindrical samples.

## RESULTS AND DISCUSSION

Twelve samples of Co-Cr-Ti alloys have been prepared to examine the effect of titanium on the microstructure and hardness of cobalt-chromium alloys. Their chemical compositions with increasing titanium content from 4 at.% to 12 at.%, were selected to be close to that of similar commercial as-cast dental alloys (Table 1.). Positions of experi-

Table 1. Compositions of as-cast Co-Cr-Ti alloys and the results of quantitative optical metallography  
Tablica 1. Sastav lijevanih Co-Cr-Ti legura i rezultati kvantitativne optičke metalografije

Sample No.	Composition / %	Dendrites region dark / %	Interdendritic region light / %	Average area of grains / μm <sup>2</sup>	Average perimeter of grains / μm
1	Co <sub>76</sub> Cr <sub>20</sub> Ti <sub>4</sub>	33,28	66,72	53,65	40,48
2	Co <sub>71</sub> Cr <sub>25</sub> Ti <sub>4</sub>	36,79	63,21	130,14	83,35
3	Co <sub>66</sub> Cr <sub>30</sub> Ti <sub>4</sub>	30,83	69,17	172,54	67,49
4	Co <sub>61</sub> Cr <sub>35</sub> Ti <sub>4</sub>	34,18	65,82	310,06	100,17
5	Co <sub>72</sub> Cr <sub>20</sub> Ti <sub>8</sub>	38,89	61,11	192,06	79,15
6	Co <sub>67</sub> Cr <sub>25</sub> Ti <sub>8</sub>	29,18	70,82	175,10	78,85
7	Co <sub>62</sub> Cr <sub>30</sub> Ti <sub>8</sub>	59,04	40,96	607,26	189,21
8	Co <sub>57</sub> Cr <sub>35</sub> Ti <sub>8</sub>	54,01	45,99	422,73	143,19
9	Co <sub>68</sub> Cr <sub>20</sub> Ti <sub>12</sub>	58,13	41,87	151,42	60,29
10	Co <sub>63</sub> Cr <sub>25</sub> Ti <sub>12</sub>	42,68	57,32	67,01	54,31
11	Co <sub>58</sub> Cr <sub>30</sub> Ti <sub>12</sub>	64,31	35,69	55,72	54,76
12	Co <sub>53</sub> Cr <sub>35</sub> Ti <sub>12</sub>	74,25	25,75	79,99	72,35

mental alloys are illustrated on the isothermal section of ternary system Co-Cr-Ti at room temperature (Figure 2.).

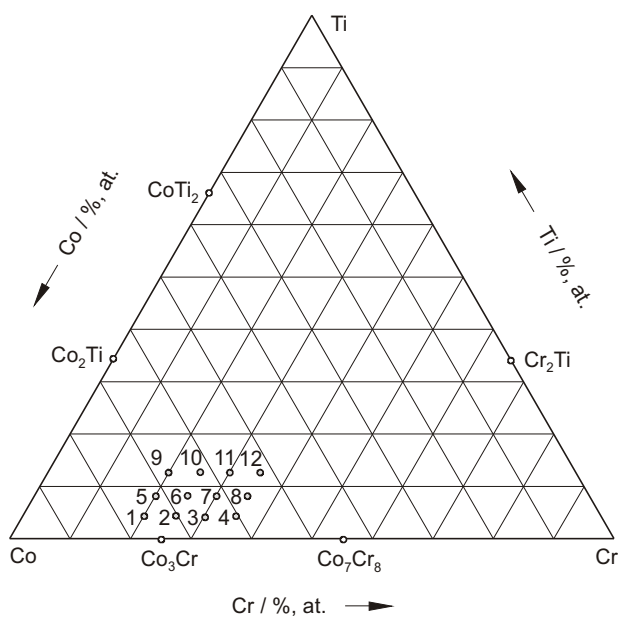


Figure 2. Compositions of experimental alloys presented on the isothermal section of ternary Co-Cr-Ti system at room temperature  
 Slika 2. Prikaz sastava eksperimentalnih legura na izotermičkom presjeku ternarnog Co-Cr-Ti sustava kod sobne temperature

The microstructural examination of the as-cast Co-Cr-Ti alloys by optical microscopy shows that all samples have nearly the same typical dendritic two phases microstructure. This type of microstructure can be seen on the microphotograph of representative sample 4 (Figure 3.)

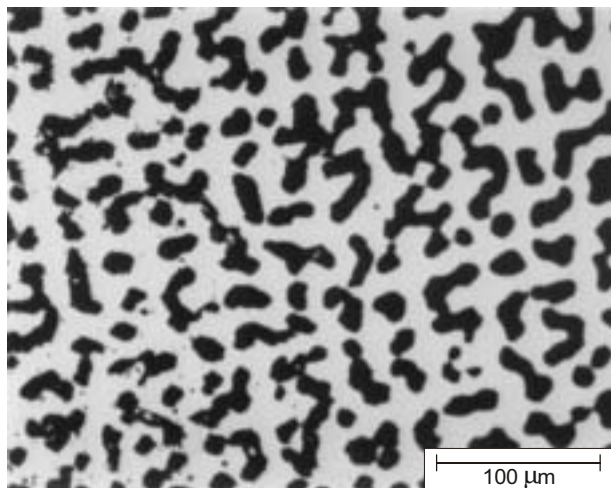


Figure 3. Optical micrograph of as-cast  $Co_{61}Cr_{35}Ti_4$  alloy  
 Slika 3. Metalografska snimka lijevane  $Co_{61}Cr_{35}Ti_4$  legure

with the composition  $Co_{61}Cr_{35}Ti_4$ , which is close to that of commercial dental alloys. It consists of dendrites (dark phase) and interdendritic region (light phase), with two types of Co-Cr-Ti solid solutions [9]. Figure 4. shows the

microstructure of sample 12 with the highest content of titanium. The results of quantitative metallography (Table 1.) indicate that the content of phases depend on alloy compositions, so that the percentage of dendrites increases with titanium content.

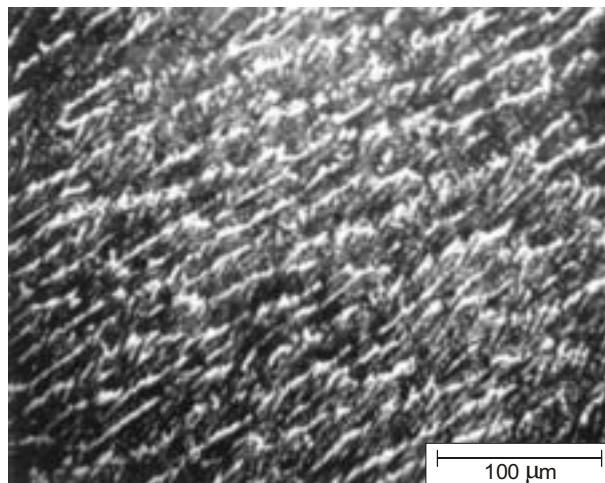


Figure 4. Optical micrograph of as-cast  $Co_{53}Cr_{35}Ti_{12}$  alloy  
 Slika 4. Metalografska snimka lijevane  $Co_{53}Cr_{35}Ti_{12}$  legure

Compositions of dendrites and interdendritic region in sample 4 were determined by the method of point analysis in EDX. The non-etched samples were used for obtaining the correct average concentration of elements. The selective chemical etching results in enrichment or impoverishment of elements on the sample surface and therefore, to the ambiguous results of the phase compositions (Table 2.) and subsequently to the wrong conclusions in [10]. Correct data from Table 3. show that chemical compositions of dendrites and interdendritic region are very close. That suggests, that not the composition, but the crystal structure is the reason for different properties of these phases [11].

X-ray diffraction data for sample 4 (Table 4.) confirm that dendrites and interdendritic region are Co-Cr-Ti solutions with hcp and fcc type of crystal structures.

Table 2. Chemical compositions of dendrites and interdendritic region for as-cast  $Co_{61}Cr_{35}Ti_4$  etched alloy  
 Tablica 2. Kemijski sastav dendrita i međudendritnog područja lijevane  $Co_{61}Cr_{35}Ti_4$  nagržižene legure

Alloy $Co_{61}Cr_{35}Ti_4$	Composition / %		
	Co	Cr	Ti
Interdendritic region (light phase)	62,35	35,52	2,42
Dendrites (dark phase)	51,05	45,38	3,55

Table 3. **Chemical compositions of dendrites and interdendritic region for as-cast Co<sub>61</sub>Cr<sub>35</sub>Ti<sub>4</sub> non-etched alloy and microhardness HV values (0,49 N, 10 s)**Tablica 3. **Kemijski sastav dendrita i međudendritnog područja za lijevanu Co<sub>61</sub>Cr<sub>35</sub>Ti<sub>4</sub> nenagriženu leguru i HV vrijednosti mikrotvrdoće (0,49 N, 10 s)**

Alloy Co <sub>61</sub> Cr <sub>35</sub> Ti <sub>4</sub>	Composition / %			Microhardness HV	HV
	Co	Cr	Ti		
Interdendritic region (light phase)	63,07	34,65	2,27	459	452
				446	
				450	
Dendrites (dark phase)	61,67	35,51	2,80	248	248
				236	
				261	

The results of hardness measurement (Table 5.) indicate significant hardness change with the alloy composition. Hardness of as-cast alloys increases primary with titanium content and than with chromium content. The highest hardness of 1012 HV has very brittle sample 12 with the greatest contents of titanium and chromium. This value

Table 4. **The results of diffraction analyses for alloy Co<sub>61</sub>Cr<sub>35</sub>Ti<sub>4</sub> in the as-cast condition**Tablica 4. **Rezultati difrakcijske analize za lijevanu Co<sub>61</sub>Cr<sub>35</sub>Ti<sub>4</sub> leguru**

No.	2θ / °	d <sub>(obs.)</sub>	d <sub>Co(hcp)</sub> -solid solution	d <sub>Co(fcc)</sub> -solid solution
1	42,1	2,15	2,17	-
2	43,0	2,10	-	2,05
3	45,7	1,99	2,02	-
4	46,7	1,94	1,91	-
5	50,8	1,79	-	1,77
6	90,7	1,08	-	1,07
7	91,0	1,08	1,07	-

is triple compared to the hardness of sample 1, with the minimum contents of mentioned elements. Microhardness measurements on sample 4 (Table 3.) indicate that interdendritic region has greater microhardness, as noble phase with fcc structure, which etched more slowly (light phase). Dendrites which etched easier (dark phase) have lower microhardness, as a less noble phase.

Effect of two different heat treatments on the microstructure and hardness of all as-cast alloys have been investigated. After heat treatment at 800 °C for 10 hours and quenching into water all samples show higher hardness values (average 10 %). Another heat treatment was performed at 800 °C for 10 hours followed by slow cooling in the furnace. Comparing with the first treatment, no change of microstructure and hardness was observed. That suggests an important role of cooling conditions during

alloy solidification, which determine the morphology of the grains. Therefore, the subsequently heat treatments of as-cast alloys, without preliminary deformation, can not induce nucleation and crystal growth i.e. recrystallization and thereby decrease of hardness. Among twelve samples of as-cast Co-Cr-Ti alloys only the samples 3 to 5 have hardness values in good agreement with that of commercial Co-Cr base dental alloys (for example Wironit) i.e. about 350 HV (MPa) [9].

Table 5. **The results of Vickers hardness (30 N, 10 s) for Co-Cr-Ti alloys**Tablica 5. **Rezultati Vickersove tvrdoće (30N, 10 s) za Co-Cr-Ti leguru**

Sample No.	Alloy / %	HV			$\bar{HV}$
1	Co <sub>76</sub> Cr <sub>20</sub> Ti <sub>4</sub>	298	307	302	302
2	Co <sub>71</sub> Cr <sub>25</sub> Ti <sub>4</sub>	299	308	307	305
3	Co <sub>66</sub> Cr <sub>30</sub> Ti <sub>4</sub>	318	314	314	315
4	Co <sub>61</sub> Cr <sub>35</sub> Ti <sub>4</sub>	364	370	356	363
5	Co <sub>72</sub> Cr <sub>20</sub> Ti <sub>8</sub>	373	366	379	373
6	Co <sub>67</sub> Cr <sub>25</sub> Ti <sub>8</sub>	396	397	382	392
7	Co <sub>62</sub> Cr <sub>30</sub> Ti <sub>8</sub>	518	486	504	503
8	Co <sub>57</sub> Cr <sub>35</sub> Ti <sub>8</sub>	660	665	661	662
9	Co <sub>68</sub> Cr <sub>20</sub> Ti <sub>12</sub>	513	506	514	511
10	Co <sub>63</sub> Cr <sub>25</sub> Ti <sub>12</sub>	555	561	555	557
11	Co <sub>58</sub> Cr <sub>30</sub> Ti <sub>12</sub>	689	681	699	690
12	Co <sub>53</sub> Cr <sub>35</sub> Ti <sub>12</sub>	1050	1019	966	1012

## CONCLUSIONS

The investigations of the microstructure and hardness of as-cast Co-Cr-Ti alloys resulted with the following conclusions:

1. Optical metallography showed that all twelve samples of the as-cast Co-Cr-Ti alloys have similar two-phases dendritic solidification microstructure, typical for commercial dental alloys.
2. The chemical compositions of dendrites and interdendritic region in sample Co<sub>61</sub>Cr<sub>35</sub>Ti<sub>4</sub> were found to be very close to each other using scanning electron microanalyser and method of point analysis.
3. X - ray diffraction indicates that dendrites and interdendritic region are Co-Cr-Ti solid solutions with different, hcp and fcc type of crystal structures.
4. The results of hardness measurement revealed strong influence of different alloy chemistry, so that hardness increases with titanium and chromium content. Among all experimental alloys, only the samples 3 to 5 with smaller titanium content have hardness values in agreement with that of similar commercial dental alloys.

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