THE ANNALS OF "DUNAREA DE JOS" UNIVERSITY OF GALATI
FASCICLE IX. METALLURGY AND MATERIALS SCIENCE
Nº. 2 - 2024, ISSN 2668-4748; e-ISSN 2668-4756
Article DOI: https://doi.org/10.35219/mms.2024.2.05

THE INFLUENCE OF CHEMICAL COMPOSITION ON COBALT-BASED ALLOYS

Mirabela Georgiana MINCIUNA[1,2], Petrică VIZUREANU[1,2]
[1] "Gheorghe Asachi" Technical University of Iasi, Faculty of Materials Science and Engineering, Blvd. Mangeron, No. 51, 700050, Iasi, Romania
[2] Centre of Excellence Geopolymer and Green Technology (CEGeoGTech), Universiti Malaysia Perlis (UniMAP), 01000 Perlis, Malaysia
e-mail: mirabela.minciuna@yahoo.ro

ABSTRACT

Cobalt-based alloys contain up to 50% cobalt, which means that they provide the material with increased abrasion resistance at high temperatures. Cobalt is similar to nickel because it is a hard material that is very resistant to wear and corrosion, especially at high temperatures. It is generally used as an element in alloys, due to its resistance to corrosion, but also due to its magnetic properties. In all cases, the introduction of an implant into an organism is likely to induce chemical, mechanical, electrical, thermal, magnetic and atomic interactions.

KEYWORDS: dilatometric analysis, cobalt, spectrometry, silicon

1. Optical emission spectrometry

The chemical composition was determined by optical emission spectrometry for two cobalt-based alloys (CoCrMo and CoCrSi). Preparation of the samples for optical emission spectrometry was performed by sanding with coarse-grained abrasive paper. The electronic discharge is done with the removal of a large amount of energy, which causes the formation of plasma and the emission of light. The light spectrum is divided by means of an optical diffraction network, and the results are processed with the help of specialized software. Since the discharge is at the surface of the sample and does not penetrate the sample, contamination of the sample surface is also measured.

The determined mass concentrations of the elements in the cobalt-based alloys are specified in Table 1.

***Table 1.** The chemical composition of the alloys expressed in mass percentages*

Alloying element	CoCrMo	CoCrSi
	(mass %)	
Co	62.10	56.70
Cr	26.79	26.23
Mo	6.00	5.29
Ni	2.90	2.84
Si	0.78	7.40
Mn	0.42	0.39
Fe	0.33	0.58
Other	0.68	0.57

Nº. 2 - 2024, ISSN 2668-4748; e-ISSN 2668-4756
Article DOI: https://doi.org/10.35219/mms.2024.2.05

Research on the chemical composition has highlighted the fact that the main elements identified in cobalt-based alloys are the following: Co, Cr, Si. For the analysed alloys, the determined chemical composition certifies that the percentage of silicon has increased, according to the values presented in Table 2.

Table 2. *Values determined by optical emission spectrometry*

Alloys	CoCrMo	CoCrSi
Silicon, [%]	0.78	7.40

By increasing the percent of silicon, the alloying elements showed lower values, a significant change being in the main element, cobalt. If it was initially found in a percent of 62.10% in the CoCrMo alloy, it came to be found in a 56.4% in the CoCrSi alloy. After the sampling, preparation and chemical attack of the samples, from cobalt-based alloys, we made chemical composition determinations using the EDX detector, type Quantax QW2, attached to the Vega Tescan LSH II electron microscope. The determined compositions are in points on the surface of the sample, after they have been previously prepared by grinding (on all types of abrasive paper) and polishing. The Table 3 presents the elemental composition in mass percentages evaluated from the EDX spectra of the samples, which allow highlighting the presence of cobalt on the surface, but also of the alloying element, silicon, plus a series of alloy component elements. The average elemental composition for cobalt, chromium, molybdenum and silicon was evaluated from EDX analysis of CoCrMo and CoCrSi alloys. This highlights the existence of silicon in varying percentages in cobalt-based alloys. The qualitative and quantitative chemical analysis (EDX) carried out on the alloys, confirms the increase in the percentage of silicon from 1.92 % as the CoCrMo alloy initially had, to a value of 6.40 for the CoCrSi alloy.

Table 3. *Chemical composition of the alloys, determined by EDX*

CoCrMo			CoCrSi		
Element	Chemical composition (mass %)	Error (%)	Element	Chemical composition (mass %)	Error (%)
Cobalt	60.85	1.72	Cobalt	28.05	0.80
Chromium	27.06	0.86	Chromium	60.47	1.62
Molybdenum	6.59	0.39	Silicon	6.40	0.33
Silicon	1.92	0.20	Molybdenum	5.45	0.26

Due to the short analysis time and the accuracy of the method, optical emission spectrometry is considered the most effective analysis method in controlling the elaboration of cobalt-based alloys, being able to further establish the mechanical processing required by the field of use of the materials (medicine). With the increase in the percentage of silicon, certified by the two analyses (optical emission spectrometry and qualitative and quantitative analysis (EDX)), the properties of cobalt-based alloys can be improved, having the obligation to remove the general disadvantages encountered in the case of classic alloys such as: low resistance to corrosion, modulus of elasticity higher than that of bone, but also low biocompatibility with human tissues.

2. Dilatometric analysis

The dilatometric analysis is based on the appearance of deviations on the expansion-temperature curves, more precisely from the normal spectrum of these curves, from the transformation temperatures, deviations caused by the dimensional changes of the parts [2]. Differential dilatometric curves are used to determine the transformation points, being the most frequently used method, while absolute dilatometric curves are used to determine the real expansion coefficient and transformation points. The purpose of the experiments is to record the length variation (Δl) that a sample tolerates, when it is subjected to heating at a certain temperature [4]. Under the specified conditions, we decided that the dilatometric analyses should not be performed only for the field of use of cobalt-based alloys, the experimental tests covering all the temperatures reached during the technological phases necessary for the manufacture of a skeletal partial prosthesis. There is a close relationship between the coefficient of thermal expansion and the melting point of the alloys in the CoCrMo system. The alloys subjected to experimental research have high melting temperatures, falling within the range of 1330-1400 °C [6]. In this analysis, the melting temperature is high and the coefficient of expansion is low, the reason being due to strong interatomic bonds. In the situation where the tooth and the restorative material

THE ANNALS OF “DUNAREA DE JOS” UNIVERSITY OF GALATI
FASCICLE IX. METALLURGY AND MATERIALS SCIENCE
N°. 2 - 2024, ISSN 2668-4748; e-ISSN 2668-4756
Article DOI: https://doi.org/10.35219/mms.2024.2.05

made of the CoCrMo alloy system have different expansion coefficients, then the materials will expand and contract differently, which will result in unwanted leaks and sliding of the restorative material against the tooth. The melting range of the alloys in the CoCrMo system must be at least 150-200 °C higher than the firing temperature of the ceramic masses. Ceramic masses that burn on alloys belong to the category of those with a low sintering range (850-1100 °C), to ensure easy processing, the melting range of the alloys is indicated to be below 1400 °C, a category in which the alloys ours fit perfectly. The dilatometric analysis was performed with the help of a Linseis L75H/1400 type differential dilatometer. Cobalt alloys subjected to dilatometric analysis have plane-parallel ends, and the section is square, with a side of 5 mm and a sample length of 30 mm, dimensions that fall within the standards of the dilatometer. The alloys from the CoCrMo system were placed on the sample holder where they were linearly heated. The modified length was transmitted via a quartz rod to a displacement transducer. The temperature of the sample was recorded by means of a thermocouple [6]. The heating of the standard samples was carried out in a tubular furnace, with electric resistance, up to the maximum temperature of 1200 °C, the heating speed of the sample was 10 °C/min, the cooling speed of the furnace being influenced by the cooling system with water that has a water flow rate of 5 m^3/h.

Fig. 1. *Linseis L75H/1400 dilatometer*

The use of small samples usually ensures a better precision of temperature regulation and the repeatability of the results, while large samples favour a better precision regarding the determination of elongation [8]. Figure 1 shows the thermal expansion of the specimen made of an alloy from the CoCrMo system, specific to partially skeletonized prostheses. The maximum thermal expansion reached by the sample at a temperature of 1200 °C is 377 µm.

The Table 4 shows the elongation variation depending on the heating temperature for the CoCrMo alloy.

The behavior of the CoCrSi alloy is shown in Figure 3. It shows a linear and uniform expansion. The CoCrSi alloy shows an elongation of 290 µm at a temperature of 1200 °C.

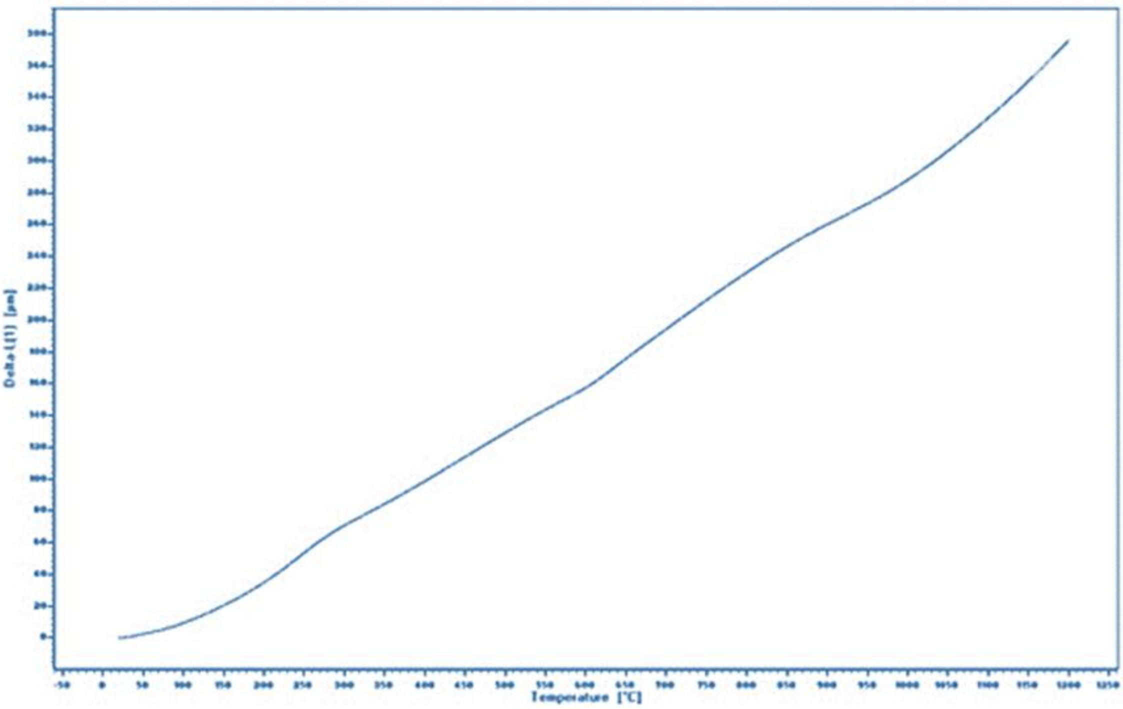

Fig. 2. *Variation of elongation with temperature, for the CoCrMo alloy*

THE ANNALS OF "DUNAREA DE JOS" UNIVERSITY OF GALATI
FASCICLE IX. METALLURGY AND MATERIALS SCIENCE
N°. 2 - 2024, ISSN 2668-4748; e-ISSN 2668-4756
Article DOI: https://doi.org/10.35219/mms.2024.2.05

Table 4. *Elongation values as a function of temperature for the CoCrMo alloy*

Temperature [°C]	20	190	290	400	550	650	750	850	1000	1100	1200
Elongation [µm]	0	31	68	97	140	180	215	235	280	330	380

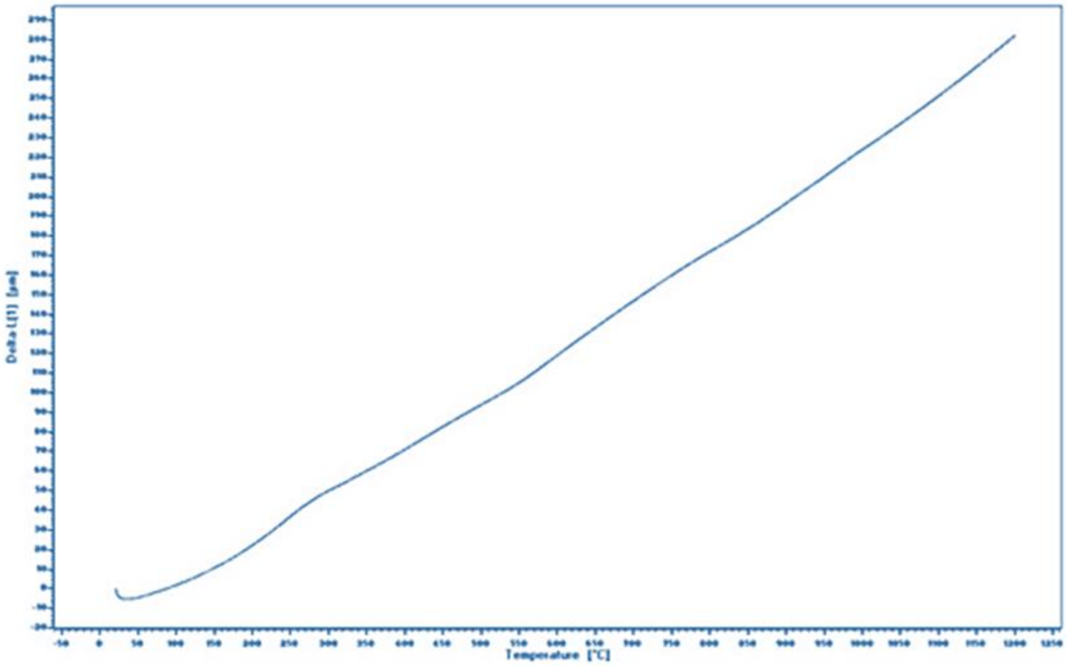

Fig. 3. *Variation of elongation with temperature, for the CoCrSi alloy*

Table 5. *Elongation values as a function of temperature for the CoCrSi alloy*

Temperature [°C]	20	150	280	380	450	570	670	780	950	1050	1200
Elongation [µm]	0	12	46	66	83	111	141	168	207	242	290

The most pronounced thermal expansion, with a value of 380 µm, is presented by the sample made from the CoCrMo alloy system, instead the CoCrSi alloys obtained elongation values below 290 µm, which confirms that increasing the percentage of silicon improved the coefficient of thermal expansion. In the case of alloys from the CoCrMo system, it is important to know the value of the coefficient of thermal expansion α for the following reasons:

- the value of the coefficient should be reduced in order to keep the tolerances of the implant constant;
- the value of the coefficient of the metal implant to be correlated with that of the biological materials with which it comes into contact.

3. Conclusions

Chemical composition research has shown that the main elements identified in cobalt-based alloys are Co, Cr, Mo and the element Si. By increasing the percentage of silicon, the alloying elements showed lower values, a significant change being in the main element, cobalt. If it was initially found in a percentage of 62.1 % in the CoCrMo alloy, it came to be found in a percentage of 56.4% in the CoCrSi alloy. With the help of dilatometric analysis, we obtained the 'thermal elasticity' of cobalt-based alloys. The fact that no inflection points appear on the dilatograms confirms that there are no phase transformations in the solid state, thus we are certain of a stable behavior in the average ambient temperature range – 1200 °C, of the two analysed alloys. The analysed CoCrMo and CoCrSi alloys obtained elongation values below 290 µm, which confirms that increasing the percentage of silicon improved the coefficient of thermal expansion.

References

[1]. Henriques B., Silva F., Soares D., J. Mech. Behav. Biomed. Mater., 4, (8), p. 1718-1726, 2011.

[2]. Nowacki J., Pieczonka T., *Dilatometric analysis of sintering of iron–boron–cobalt P/M metal matrix composites*, Journal of

Materials Processing Technology, vol. 157-158, p. 749-754, Achievements in Mechanical and Materials Engineering Conference, 20 December 2004.

[3]. Li W., Lee L. J., *Low temperature cure of unsaturated polyester resins with thermoplastic additives: I. Dilatometry and morphology study*, Polymer, vol. 41, Issue 2, p. 685-696, January 2000.

[4]. Bobby R. Lanier, *et al.*, *Making chromium-cobalt removable partial dentures: A modified technique*, The Journal of Prosthetic Dentistry, vol. 25, Issue 2, p. 197-205, 1971.

[5]. Bernhard Wunderlich, *Chapter 6 - thermomechanical analysis and dilatometry, Thermal Analysis*, p. 311-369, 1990.

[6]. Moon J. H., Won D. M., *Analysis of sintering kinetics at different heating rates by dilatometry*, Metal Powder Report, vol. 55, Issue 2, p. 39, February 2000.

[7]. Sam Katz, *Dilatometry, Methods in Enzymology*, vol. 26, p. 395-406, 1972.

[8]. ***, www.academia.edu/4713685/ALIAJE_DENTARE.

[9]. Baba N., *et al.*, *Mechanical strength of laser-welded cobalt-chromium alloy*, J Biomed Mater Res B, 69B, p. 121-124, 2004.

[10]. Bagby M., *et al.*, *Metal Ceramic compatibility*, J Prosthet Dent. 63, p. 21-25, 1990.

[11]. Behazin M., *et al.*, *Combined Effects of pH and γ-Irradiation on the Corrosion of Co-Cr Alloy Stellite-6*, Electrochimica Acta, vol. 134, p. 399-410, 2014.

[12]. Baciu E. R., Forna N. C., *Influenţa tehnicilor de finisare asupra rugozităţii suprafeţelor componentelor metalice ale restaurărilor protetice*, Revista Medico-Chirurgicală a Societăţii de Medici şi Naturalişti din Iaşi, vol. 114, no. 4, ISSN: 0048-7848, p. 1198-2003, 2010.

[13]. Bollen C. M., Lambrechts P., Quirynen M., *Comparison of surface roughness of oral hard materials to the threshold surface roughness for bacterial plaque retention: a review of the literature*, Dent Mater, 13, p. 258-69, 1997.

[14]. Black J., Hastings G. W., *Handbook of Biomaterial Properties*, Chapman & Hall, 1998.

[15]. Bezzon O. L., *et al.*, *Effect of casting technique on surface roughness and consequent mass loss after polishing of (Ni-Cr) and (Co-Cr) base metal alloys: a comparative study with titanium*, J Prosthet Dent, 92, p. 274-279, 2004.

[16]. Bojin D., *et al.*, *Microscopie electronică de baleiaj şi aplicaţii*, Ed. Agir, Bucureşti, 2005.

[17]. Barbosa F. O., Araújo M. C., *Fractographic Analysis of K3 Nickel-Titanium Rotary Instruments Submitted to Different Modes of Mechanical Loading*, Journal of Endodontics, vol. 34, Issue 8, p. 994-998, 2008.

[18]. Black J., Hastings G. W., *Handbook of Biomaterial Properties*, Chapman & Hall, 1998.

[19]. Baynes J., Domniczak M. K., *Medical Biochemistry*, St. Louis: Mosby, ISBN 0723430128, 1999.