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JAN RYSZARD DĄBROWSKI*, JERZY FRYDRYCH**, HANNA FRYDRYCH**, WIKTORIA RATUSZEK**

EFFECT OF SINTERING ATMOSPHERE ON STRUCTURE AND PROPERTIES OF VITALIUM TYPE SINTERED MATERIALS

WPŁYW ATMOSFERY SPIEKANIA NA STRUKTURĘ I WŁASNOŚCI SPIEKANYCH MATERIAŁÓW TYPU VITALIUM

The aim of the present research was to determine the effect of atmosphere of preliminary annealing and subsequent sintering on a structure and properties of sintered alloys produced of Co–Cr–Mo powders, which are applied for production of endo-prostheses. Sintering was performed in vacuum, under the hydrogen or argon atmospheres. Measurements of density, hardness and bending strength of sintered alloys were performed as well as *X*-ray phase analysis and structure observations by means of optical and scanning microscopy. Line analysis using CAMECA *X*-ray microanalyser was conducted additionally to determine chromium and molybdenum distributiom within the structure of sintered materials.

W ramach pracy przeprowadzono badania, których celem było ustalenie wpływu atmosfer wstępnego wyżarzania oraz spiekania na strukturę i własności spieków wykonanych z proszków Co–Cr–Mo stosowanych na endoprotezy. Spiekanie przeprowadzono w atmosferze wodoru, argonu lub w próżni. Wykonano pomiary gęstości, twardości i wytrzymałości na zginanie spieków, badania mikroskopowe ich struktury, rentgenowską analizę fazową oraz analizę wzdłuż linii na mikroanalizatorze rentgenowskim CAMECA, w celu określenia rozmieszczenia chromu i molibdenu w strukturze badanych materiałów.

1. Introduction

Cobalt base alloys are materials commonly used for prostheses of hip-joints. Serviceableness of these alloys results from bio-tolerance within the habitat of tissue and amniotic fluids, considerable capacity for repassivation in physiological sol-

* POLITECHNIKA BIAŁOSTOCKA

** WYDZIAŁ METALURGII I INŻYNIERII MATERIAŁOWEJ, AKADEMIA GÓRNICZO-HUTNICZA, 30-059 KRAKÓW, AL. MICKIEWICZA 30

utions as well as crevice and pitting corrosion resistance. Mechanical properties and corrosion resistance of these materials result from the chemical composition and the structure, which depends on the parameters of technological process [1].

It is estimated that about 50% of hip-joint implants is produced from cast Co–Cr–Mo alloys [2]. However fatigue strength and dustility of casts is very small, mainly due to the presence of ε-phase, formation of coarse-grained structure and the arrangement of carbides. To obtain better properties, these alloys are subjected to heat treatment or thermo-mechanical treatment.

The first investigations concerning application of powder metallurgy for productiom of some parts of endo-prostheses were undertaken in the sixties [3]. Application of this technology enables to produce materials having more with homogenous fine-grained structure, gives practically unlimited possibilities to introduce additional components and in consequence allows to obtain any chemical composition of the material [4, 5]. Suitable choice of atomizing parameters of liquid alloy enables additionally to stop carbide precipitation upon crystallization process. There is also possibility for physico-chemical modification of the surface of sintered alloy. Application of powder metallurgy method to produce prostheses may increase probability of particle spalling in comparisom to compact materials. However appropriate porosity enables fast ingrowing of bones and leads to nearly natural junction. Appropriate parameters of the processes of sintering and heat treatment allow to obtain materials with assumed porosity as well as sufficient strength and corrosion resistance. Unfortunately there is relatively small number of hitherto performed investigations concerning this subject.

B. S. B e c k e r et al. [6] conducted investigations of prostheses made of sintered Co–Cr–Mo alloy, which concerned optimisation of sintering process of this material. Disintegrated powders after grinding and powders atomized in water were applied. The effect of sintering atmosphere on density and relevant porosity of sintered alloy was analysed. It was found that sintering atmosphere has not considerable influence on density of sintered alloy made on the base of atomized powders, contrary to the material produced from the mixture of atomized and grinded powders. In the latter case the highest density have samples sintered under argon atmosphere and the smallest one material prepared in vacuum. Moreover vacuum sintering leads to decarburization and changes in chromium contents at the surface of sintered alloy and in consequence decrease in hardness of material. On the other hand sintering in dissociated ammonia results in absorption of nitrogen, formation of chromium nitrides (Cr_2N) and as a consequence hardening of sintered alloy proceeds. Application of argon atmosphere does not lead to decarburization of the samples. It should be noted however that increased carbon contents results in decreases of the temperature of euthectoid transformation and the appearance of liquid phase upon sintering at elevated temperatures. Liquid penetrating into pores makes difficult the control of sintering process and production of the material with assumed porosity [7]. Thus further investigations should be focused on the optimisation of sintering conditions to obtain materials with foredesigned structure.

2. Experimental

Two Vitalium powders with particle size 20—200 μm were examined. Powders were obtained by applying the method of water atomization in air atmosphere (Vitalium II) or in argon atmosphere (Vitalium III). Chemical compositions of both powders are given in table 1 (without oxygen and carbon contents). Vitalium powders were annealed under hydrogen atmosphere or in vacuum at the temperature 1000°C for 2 hours. Table 2 includes results of the analysis of carbon and oxygen contents performed by means of LECOCS-125 and TC-336 analysers.

Samples having the size $5 \times 5 \times 40$ mm were prepared by single action pressing under the pressure 800 MPa. Sintering was performed under hydrogen or argon atmospheres and in vacuum at the temperature 1250°C for 2 hours. The investigations of sintered material included measurements of density, hardness and bending strength. Structure examination was additionally performed by means of the optical and scanning electron microscopy, *X*-ray phase analysis as well as the line analysis using CAMECA *X*-ray microanalyser to determine chromium and molybdenum arrangement within the structure of sintered material.

TABLE 1

Chemical analysis of Vitalium powders

Material	Mo %	Si %	P %	Ni %	Fe %	S %	Mn %	Cr %	W %	Co %
Vitalium II	4.40	0.50	0.01	—	0.55	0.01	0.88	28.22	0.02	64.87
Vitalium III	5.40	0.50	0.01	0.20	1.37	< 0.01	0.49	29.29	< 0.10	62.32

TABLE 2

Carbon and oxygen content analysis in Vitalium powders

Material	C, %	O_2, %
Vitalium II	0.119	0.616
Hydrogen	0.120	0.591
1000°C, 2 h	0.120	0.605
Vitalium III	0.316	0.572
Hydrogen	0.324	0.585
1000°C, 2 h	0.312	0.566
Vitalium II	0.0162	0.278
Vacuum	0.0146	0.263
1000°C, 2 h	0.0152	0.285
Vitalium III	0.121	0.154
Vacuum	0.123	0.155
1000°C, 2 h	0.123	0.155

3. Results and discussion

The present investigations of Vitalium powders show that the preliminary annealing in hydrogen atmosphere does not decrease the contents of oxygen. On the other hand considerable decarburization of both powders accompanied by significant decrease in the amount of oxygen proceeds upon vacuum annealing due to the mutual reation of carbon and oxygen. Determination of carbon contents and important procedure in the case of Vitalium powders since possible carbide precipitation may decrease the properties of sintered alloys.

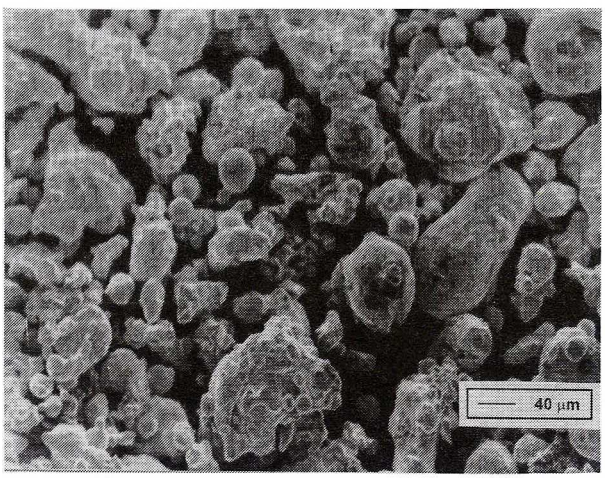

Fig. 1. Powder Vitalium II initial state (before annealing)

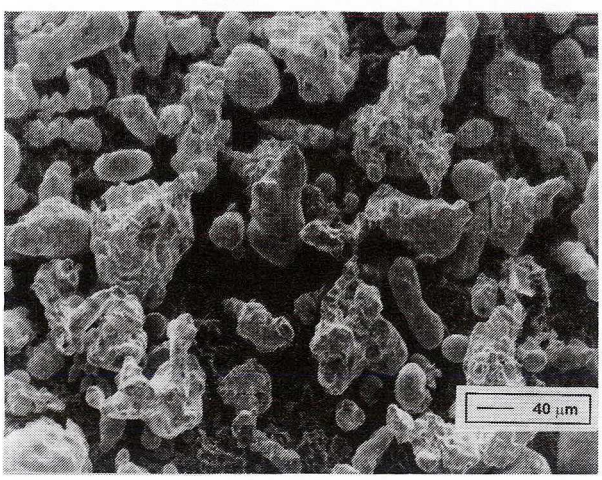

Fig. 2. Powder Vitalium III initial state (before annealing)

Powders under examination have not good compressibility and formability. The pressure of 800 MPa had to be applied to obtain stable compacts. In the case of Vitalium II powder the change of annealing environment from hydrogen atmosphere to vacuum has not significant influence on density of compacts in spite of considerable differences in carbon and oxygen contents. On the contrary the amounts of carbon and oxygen have some effect on the behaviour of Vitalium III powder upon pressing. Compacts made of this powder, having smaller carbon and oxygen contents after vacuum annealing, reveal higher density in comparison to compacts obtained from powder annealed in hydrogen atmosphere. Small increase in density of all samples in comparison to the density of compacts occurs upon sintering at the temperature 1250°C. These changes of density are within the range 0.5%—4% for the sintered Vitalium II powder and 2%—5% for Vitalium III powder. For the case of powders annealed in hydrogen atmosphere the highest

TABLE 3

Properties of sintered alloys produced of Vitalium II and Vitalium III powders annealed in hydrogen atmosphere

Material	Density of compacts g/cm^3	Sintering atmosphere	Sintered density g/cm^3	Bending strength N/mm^2	Hardness HB
Vitalium II	6.01	Hydrogen	6.11	366	86
		Argon	6.07	294	85
		Vacuum	6.15	366	87
Vitalium III	5.84	Hydrogen	6.00	446	86
		Argon	5.99	403	82
		Vacuum	6.10	427	80

TABLE 4

Properties of sintered alloys produced of Vitalium II and Vitalium III powders annealed in vacuum atmosphere

Material	Density of compacts g/cm^3	Sintering atmosphere	Sintered density g/cm^3	Bending strength N/mm^2	Hardness HB
Vitalium II	5.98	Hydrogen	6.17	545	91
		Argon	6.03	414	86
		Vacuum	6.07	353	80
Vitalium III	6.02	Hydrogen	6.13	504	84
		Argon	6.18	561	82
		Vacuum	6.19	457	83

density have the samples sintered in vacuum and the smallest one the samples sintered under argon atmosphere. The highest density from among all samples under examination was observed for samples sintered in vacuum or argon atmosphere, which were obtained from Vitalium III powder annealed in vacuum. In general the effect of sintering atmosphere on density of sintered materials under examination is not unique.

Much more clear results were obtained when analysing the effect of annealing and sintering atmospheres on bending strength of examined materials. In spite of comparable density, samples made of powders annealed under hydrogen atmosphere have generally worse strength properties than the samples prepared of powder after vacuum annealing. It should be noted that in the case of powders annealed under hydrogen atmosphere higher bending strength have the samples made of Vitalium III powder despite of lower density and carbon contents in comparison to the samples prepared of Vitalium II powder. This result testifies to better particle sintering of Vitalium III powder, as it is well known that strength properties of porous materials depend not only on their density but also on the surface and quality of interparticle contact.

From among all sintered samples under examination the highest bending strength (561 N/mm^2) have the samples made of Vitalium III powder annealed in vacuum and sintered under argon atmosphere. In the case of Vitalium II powder the highest bending strength have the samples prepared of powder annealed in vacuum and sintered under hydrogen atmosphere. Comparison of bending strength of all sintered samples indicates that vacuum annealing is more beneficial for the case of both powders i.e. Vitalium II and Vitalium III.

Hardness values of all sintered samples are within the range 80—87 HB except the specimen prepared of Vitalium II powder, annealed in vacuum and sintered under

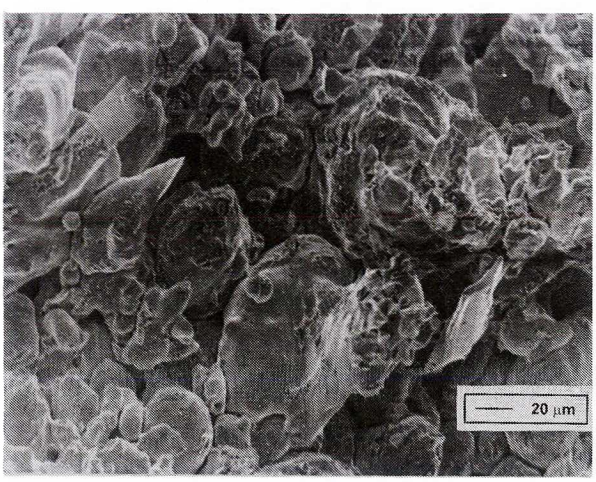

Fig. 3. Fracture of Vitalium II annealed and sintered in vacuum

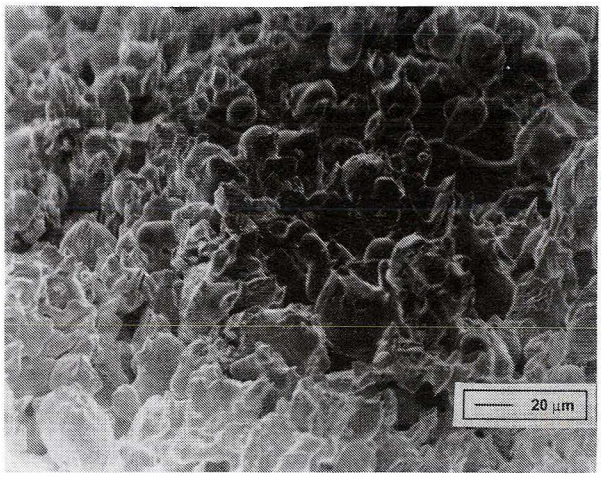

Fig. 4. Fracture of Vitalium III annealed and vacuum and sintered in hydrogen

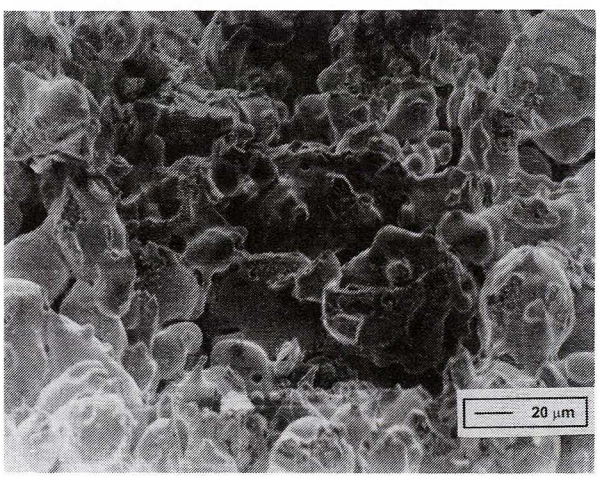

Fig. 5. Fracture of Vitalium III annealed in hydrogen and sintered in argon

hydrogen atmosphere. Neither annealing atmosphere nor sintering environment were found to exert any considerable effect on hardness of sintered samples. There are also no significant differences in hardness between samples sintered of Vitalium II and Vitalium III powders despite of different carbon contents in both materials. Figure 3—5 presents some examples of fracture surface of selected sintered samples. Fractures are crossing through the interparticle contacts. Smooth pore surfaces are also visible without the appearance of oxides. Irrespectively of the type of powder and the atmosphere of annealing or sintering, the structure of all sintered

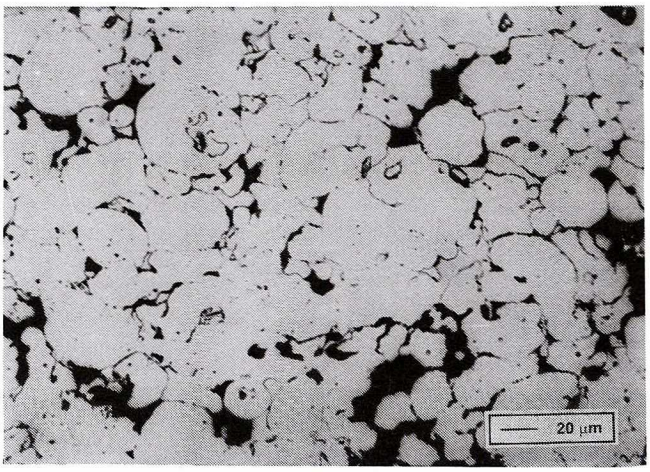

Fig. 6. Microstructure of Vitalium II annealed in vacuum and sintered in argon

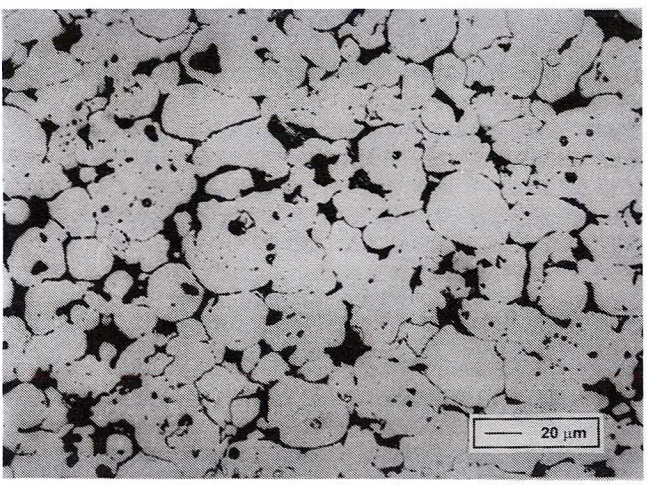

Fig. 7. Microstructure of Vitalium II annealed and sintered in vacuum

samples is one-phase and fine-grained, consisting of solid solution of chromium and molybdenum in α-cobalt (Fig. 6—9). This result was confirmed by *X*-ray phase analysis, which revealed only the appearance of the cobalt α-phase (Fig. 10). The results of line analysis performed by means of CAMECA microanalyser point at almost homogeneous arrangement of basic alloying elements, chromium and molybdenum, within the solid solution (Fig. 11—14). The ranges of chromium and molybdenum content, recorded from the line analysis, are given in table 5. It should be noted additionally that pores are arranged irregularly within the structures under examination, i.e. areas with low and high porosity are visible.

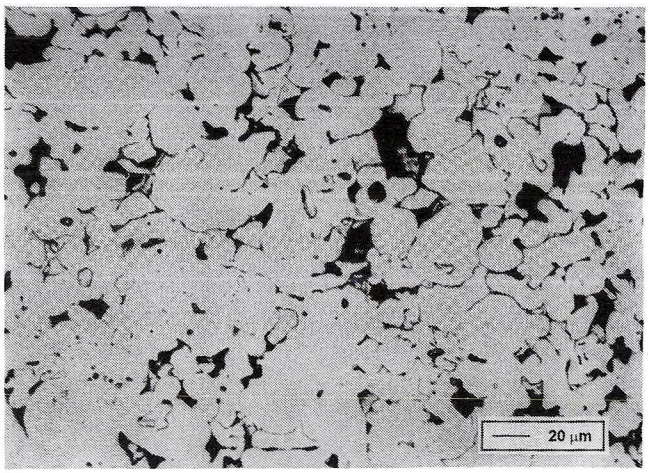

Fig. 8. Microstructure of Vitalium III annealed in vacuum and sintered in argon

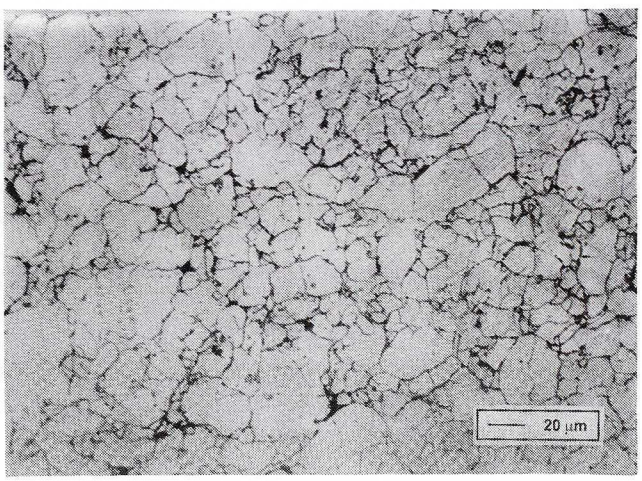

Fig. 9. Microstructure of Vitalium III annealed and sintered in vacuum

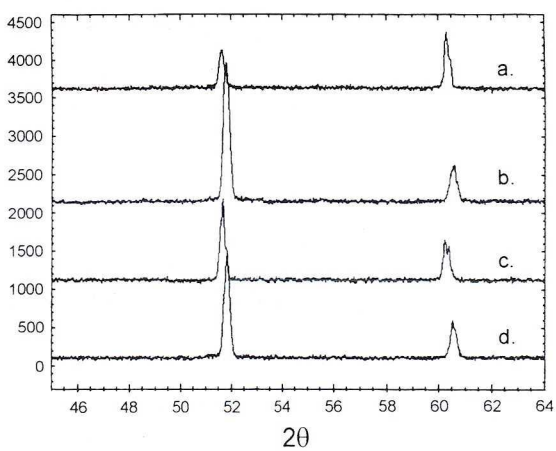

Fig. 10. Diffraction patterns of Vitalium powders after annealing and sintering respectively in: (a) — vacuum/hydrogen atmosphere (Vitalium II); (b) — vacuum/vacuum (Vitalium II); (c) — vacuum/hydrogen atmosphere (Vitalium III); (d) — vacuum/vacuum (Vitalium III)

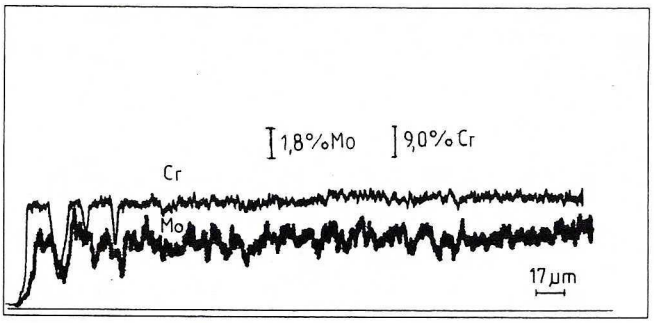

Fig. 11. Record of line analysis showing the arrangement of chromium and molybdenum within the structure of Vitalium II annealed in vacuum and sintered in argon

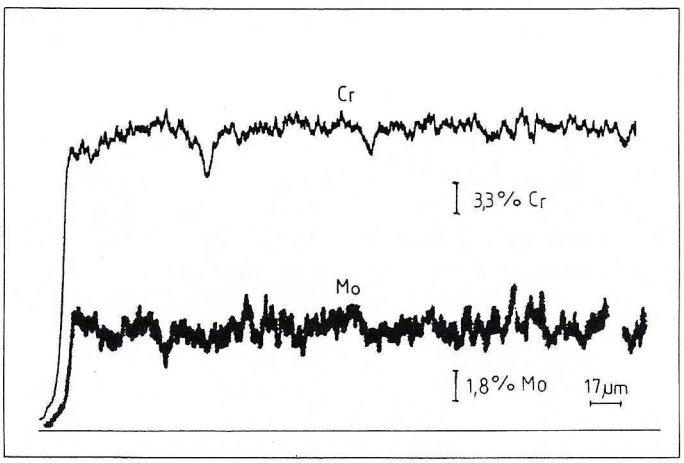

Fig. 12. Record of line analysis showing the arrangement of chromium and molybdenum within the structure of Vitalium II annealed and sintered in vacum

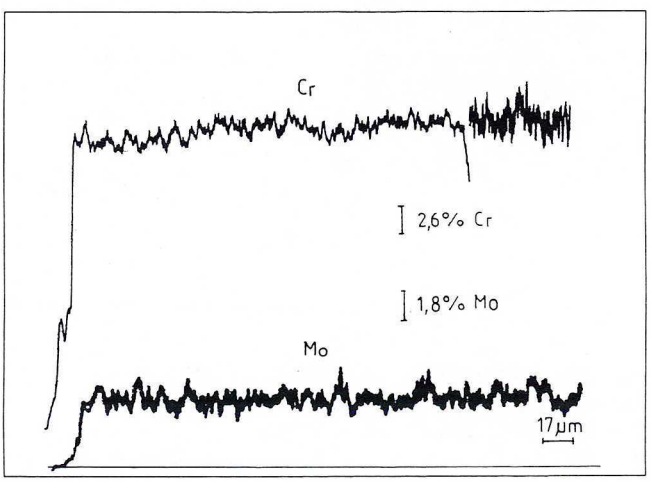

Fig. 13. Record of line analysis showing the arrangement of chromium and molybdenum within the structure of Vitalium III annealed in vacuum and sintered in argon

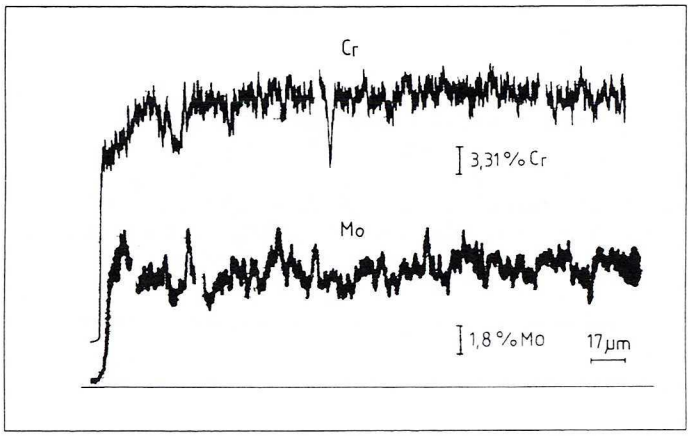

Fig. 14. Record of line analysis showing the arrangement of chromium and molybdenum within the structure of Vitalium III annealed and sintered in vacuum

TABLE 5

Contents of chromium and molybdenum measured by means of X-ray microanalysis in sintered alloys produced — of Vitalium II and Vitalium III powders annealed in vacuum

Material	Sintering atmosphere	Cr, %	Mo, %
Vitalium II	Hydrogen	30.0—32.5	3.5—5.0
	Argon	31.0—34.0	4.5—5.4
	Vacuum	31.5—33.5	4.5—6.0
Vitalium III	Hydrogen	29.5—33.0	5.0—5.5
	Argon	29.0—32.5	4.1—5.4
	Vacuum	30.0—33.0	6.0—8.0

4. Summary

Results of the present investigations indicate that the atmosphere of the preliminary annealing and the subsequent sintering have not unique influence on the properties of samples sintered of both Vitalium powders. However significantly better properties were obtained after annealing of powders in vacuum. The highest strength properties have the samples made of Vitalium III powder after vacuum annealing and subsequent sintering in argon atmosphere.

Comparing the properties of sintered alloys made of Vitalium II and Vitalium III powders better results were obtained for the case of Vitalium III samples.

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REVIEVED BY: PROF. DR HAB. JERZY SĘDZIMIR

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