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MICROSTRUCTURE AND PROPERTIES OF SINTERED COBALT-CHROMIUM CARBIDE MATERIALS

MIKROSTRUKTURA I WŁAŚCIWOŚCI SPIEKANYCH MATERIAŁÓW KOBALT-WĘGLIK CHROMU

The main objective of the present work was to establish the effect of sintering temperature on as-sintered density, hardness and microstructure of Co-Cr₃C₂ materials. Compacts containing 10 wt.% Cr were sintered between 1000 and 1200°C in a reducing atmosphere. The highest density was attained at 1050°C, whereas further increase in the sintering temperature resulted in a marked decline in both density and hardness of the material, which was associated with a pore formation and swelling due to dissolution of chromium carbide particles in the cobalt matrix.

Keywords: sintering, cobalt, chromium carbide, microstructure, as-sintered density, as-sintered hardness

W artykule przedstawiono wyniki badań, których celem było ustalenie wpływu temperatury spiekania na zmiany wymiarów, gęstość, mikrostrukturę i twardość spieków kobalt-węglík chromu. Spiekanie prowadzono w zakresie temperatur 1000-1200°C, w atmosferze redukującej. Najwyższą gęstość uzyskano po spiekaníu w temperaturze 1050°C. Dalsze podwyższenie temperatury spiekania powoduje obniżenie gęstości i twardości uzyskanych materiałów. Podczas spiekania badanych materiałów ma miejsce rozpuszczanie się węglíka chromu w kobalcie i powstawanie dodatkowych porów.

1. Introduction

Cobalt forms the basis of cast prosthetic Co-Cr-Mo alloys, which are now accounting for around 50% of all materials used to produce hip and knee replacement joints. The corrosion resistance and toughness of these alloys are dependent on phase stability of the matrix and dispersion of carbides.

To date numerous studies have been devoted to development of microstructure of Vitallium type cast alloys. They are mostly focused on the morphology and distribution of the carbide phase which increases mechanical strength of cobalt-base alloys but, on the other hand, enables initiation of cracks at the carbide-matrix interface. The presence of a grain boundary carbide network results in a marked decrease in the alloy's ductility, impact strength and fracture toughness. Precipitation of chromium carbides depletes the matrix of chromium and thus worsens corrosion resistance of the alloy. Additionally, stresses generated around carbide precipitates promote the A₁ → A₃ phase transformation which, in turn, induces nucleation of secondary carbides due to unbalanced solubility of carbide forming elements on either site of the transformation front.

In alloys subjected to a homogenisation heat treatment the dissolution of carbides induces formation of harmful porosity, as reported in Refs [1, 2]. As the carbide forming atoms diffuse faster into the matrix than the matrix atoms into the carbide, vacancies are accumulated on the original carbide sites to form Kirkendall pores which promote nucleation of cracks.

Extensive research has been carried out in an effort to manufacture prosthetic alloys by the powder metallurgy (PM) technology [3-6]. The advantage of application of the PM techniques is three-fold. First, they enable modification of the alloy composition to a wide extent. Second, the precipitation of carbide particles is suppressed by rapid solidification of the molten alloy during powder atomisation. And third, it is easy to attain a fine-grained microstructure. The PM processing route must, however, assure near-full densification of the material and its protection against oxidation.

Leaving aside the prosthetic alloys, another important application of cobalt is as a base matrix material for diamond impregnated tools manufactured by various PM routes [7]. The application behaviour of diamond tools is affected in a complex manner by both diamond related parameters, such as its type, quality, size and concen-

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tration, and by the characteristics of the metallic matrix which has to hold the diamonds tight and wear at a rate compatible with the diamond breakdown. For long cobalt has been highly praised, as a matrix, for its unique combination of high yield strength and toughness resulting in excellent capacity for diamond retention and good resistance to wear, which can be broadly modified by alloying.

In this context, the objective of the present work was to study the effect of sintering temperature on the microstructure of cobalt-chromium carbide PM materials.

2. Experimental procedure and results

The investigated material was produced from a powder mix containing 90 wt.% *Extrafine* Co and 10 wt.% Cr_3C_2 chromium carbide. The starting powders are shown in Figs 1 and 2.

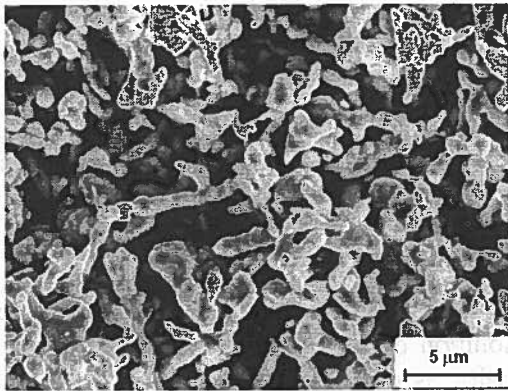


Fig. 1. SEM micrograph of cobalt powder

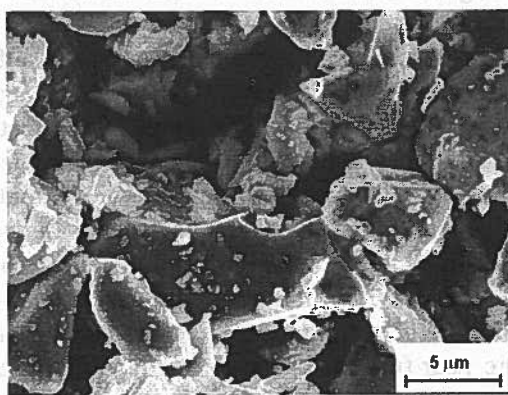


Fig. 2. SEM micrograph of chromium carbide powder

The powders were initially mixed and comminuted for 40 minutes in a mortar grinder. The mixture was subsequently cold pressed at 600 MPa on a single action press. The green compacts were sintered for 60 minutes in a reducing $\text{N}_2/10\%\text{H}_2$ atmosphere at 1000, 1050, 1100, 1150 and 1200°C.

The specimens were tested for density and hardness by means of the water displacement technique and Brinell test, respectively. The effect of sintering temperature on as-sintered density, dimensional change and hardness is presented in Figs 3-6.

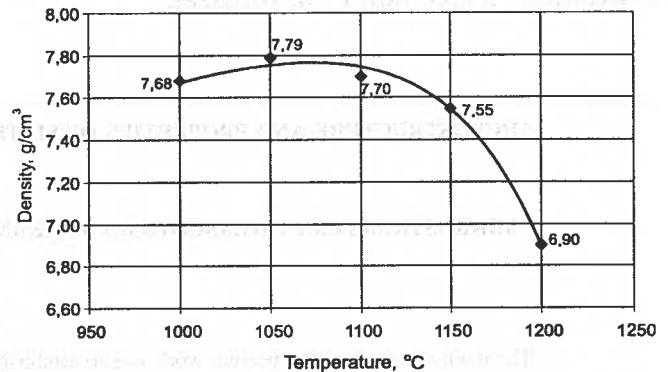


Fig. 3. Effect of sintering temperature on density of $\text{Co-Cr}_3\text{C}_2$ specimens

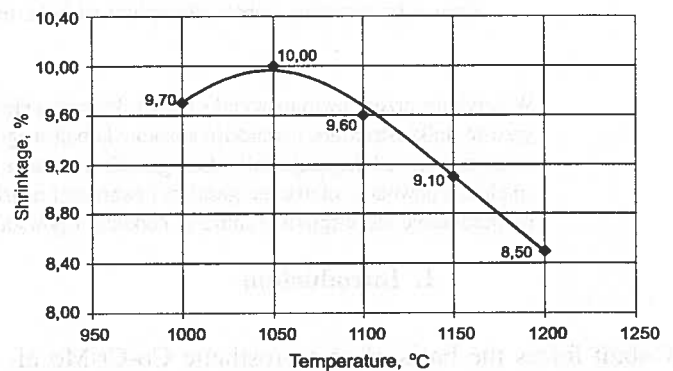


Fig. 4. Effect of sintering temperature on radial shrinkage of $\text{Co-Cr}_3\text{C}_2$ compacts

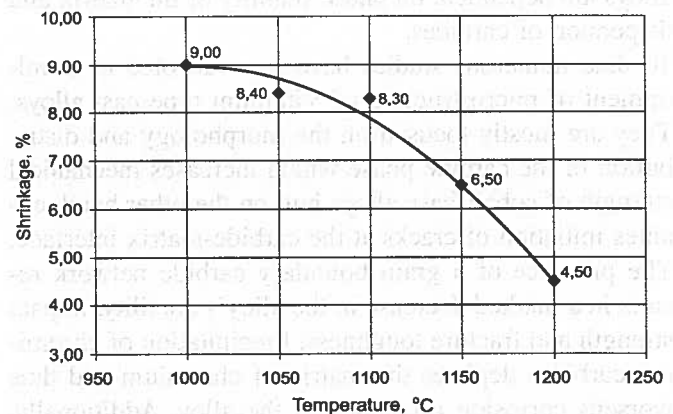


Fig. 5. Effect of sintering temperature on axial shrinkage of $\text{Co-Cr}_3\text{C}_2$ compacts

The powders, as-sintered microstructures and phase compositions were examined by scanning electron microscopy (SEM), light microscopy (LM), and X-ray diffraction (XRD) techniques.

The powder mix has low compressibility due to fine particle size and irregular particle shape of the starting powders that results in low green densities ranging between 5.48 and 5.65 g/cm³ (around 35% porosity). On the other hand, the powder displays very good sinterability as it is evident from the as-sintered densities, shown in Fig. 3, and specimens' dimensional change on sintering, presented in Figs 4 and 5. The highest density, of around 7.8 g/cm³, is observed after sintering at 1050°C, whereas further increase in the sintering temperature results in swelling. The specimens sintered at 1200°C have density of only 6.9 g/cm³. The dissolution of chromium carbide in the cobalt matrix, which takes place at 1200°C, may account for the swelling of compacts sintered beyond 1050°C.

In a similar way, the as-sintered hardness increases from 214 to 220 HB as the sintering temperature is raised from 1000 to 1100°C. Beyond 1100°C the hardness vs temperature curve has a downward trend, as it is demonstrated in Fig. 6, which coincides with the decline in density.

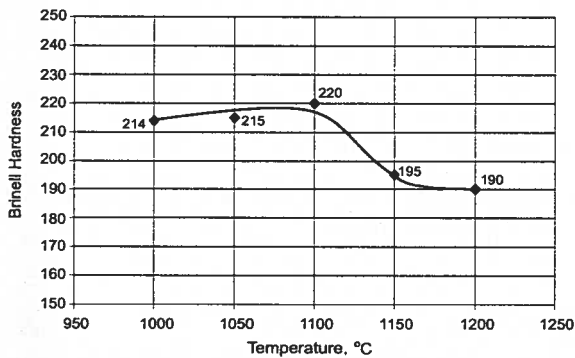


Fig. 6. Effect of sintering temperature on hardness of Co-Cr₃C₂ specimens

Metallographic observations have revealed fine-grained microstructures of specimens sintered between 1000-1050°C, with Cr₃C₂ carbide grains embedded in a cobalt matrix (see Fig. 7).

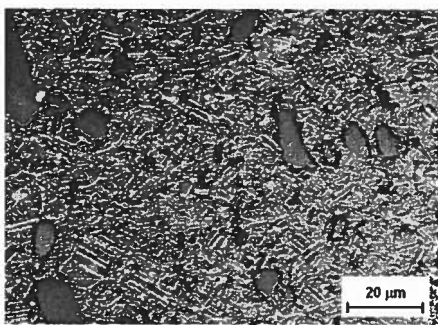


Fig. 7. Microstructure of Co-Cr₃C₂ material after sintering at 1000°C. LM-DIC

The grain size grows and pores appear at the carbide-matrix interface (see Fig. 8) as the sintering temperature is increased to 1100°C. The carbide grains are

completely dissolved in cobalt after sintering at 1200°C. In that case the microstructure consists of a solid solution of chromium, and carbon, in cobalt and pores located at the former carbide sites, as shown in Fig. 9.

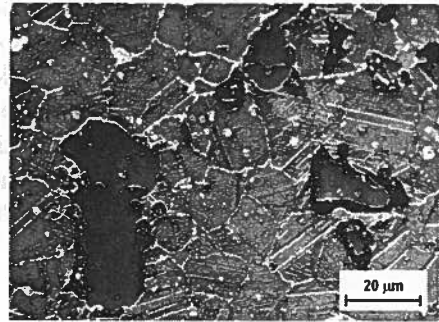


Fig. 8. Microstructure of Co-Cr₃C₂ material after sintering at 1100°C. LM-DIC

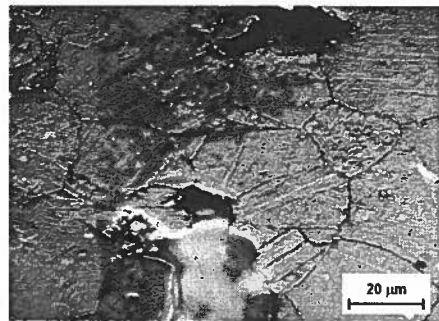


Fig. 9. Microstructure of Co-Cr₃C₂ material after sintering at 1200°C. LM-DIC

From the X-ray phase analysis it becomes evident (see Fig. 10) that mainly the HCP structure (ϵ -Co) is present in the specimens sintered at 1000°C, whereas the volume fraction of the FCC phase (α -Co) increases with temperature to yield virtually 100% of this structure after sintering at 1200°C. As illustrated in Fig. 10, the X-ray spectrum of a specimen sintered at 1200°C shows marked peak broadening which indicates formation of a solid solution of cobalt saturated with chromium.

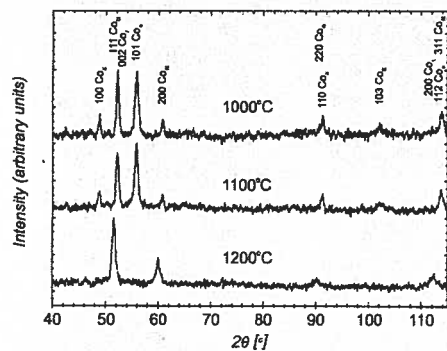


Fig. 10. X-ray diffractograms for Co-Cr₃C₂ specimens sintered at various temperatures

3. Conclusion

The investigated Co-Cr₃C₂ material attains near-full density after sintering for 1 hour at 1050 in a reducing atmosphere. Further increase in the sintering temperature leads to pore formation, due to dissolution of carbide grains in the cobalt matrix, and thereby gives swelling.

The sintering temperature has also a marked effect on the phase composition of the cobalt matrix after cooling to room temperature. The HCP lattice is mostly present in specimens sintered at 1000°C, whereas the FCC structure prevails after sintering at 1200°C.

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