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Essence of polyphase sintering of metal matrix composites and their properties

J. Nowacki

Technical University of Szczecin, Institute of Materials Engineering, Al. Piastow 19,70 - 310 Szczecin, Poland

Microstructure phase constitution of sintered compacts was tested. Examples of PM metal matrix composites, ODS, Fe - P, Fe - B have been presented. Microstructure and phase constitution of sinters were tested. Mainly Fe - B cermets were subjected to metallographic tests, X - ray analysis, measurements of hardness and of microhardness, and of wear in the process of sliding dry friction. Dilatometer was used to control basic phenomena taking place during polyphase sintering of investigated systems.

1. PROCESSES OF POLYPHASE SINTERING

Polyphase sintering is an effective technique of particulate - reinforced and dispersion - strengthened PM metal matrix composites production. Intermediate phases with a supposed structure and properties and an excellent connect with the matrix create as a result of reaction between components of a powder mixture during sintering. Polyphase sintering proceeds most often with a transient liquid phase.

Oxidize of some matrix particles during sintering is used for synthesis oxides, which play a role of reinforcement, e.g. yttria (Y_2O_3), alumina (Al_2O_3), magnesia (MgO). The oxides synthesis is executed in an atmosphere containing a slight admixture of oxygen. Small oxides particles with diameters of 0.01 - 0.025µm amounts of $V_p < 0.15$ can block the movement of dislocations [1-3].

Selective sintering of some matrix particles in an active atmosphere - an inert gas with an admixture of gases or elements steam or compounds reacting with some components of a powder mixture. As a result of these reaction phases with covalent and ionic bonds are created.

Sintering of powder mixture components creating intermediate phases as the reinforcement has stages presented on Fig. 1 - 4.



Figure 1. Binary equilibrium system of elements A and B, in which polyphase sintering with a transient liquid phase led to intermediate phase AB creation is possible, Ts – sintering temperature, X – chemical constitution of powder mixture [3 - 5]



Figure 2. Binary equilibrium system of elements A and B, in, which polyphase sintering with participation of a liquid phase led to intermediate phase AB and an eutectic mixture E creation is possible, Ts – sintering temperature, X – chemical constitution of powder mixture [3 - 5]



Figure 3. Stages of polyphase sintering with participation of a transient liquid phase led to intermediate phase AB creation; a) elementary constituents A and B powder mixture, b) solid solution A-B formation, c) intermediate phase AB formation AB, d) intermediate phase AB formation completed [3 - 5]

Figure 4. Stages of polyphase sintering participation of a liquid phase led to intermediate phase AB and eutectic mixture E on grain boundaries creation; a) elementary constituents A and B powder mixture, b) liquid L formation, c) intermediate phase AB crystallization from liquid L, d) intermediate phase AB f and eutectic mixture E on grain boundaries creation completed [3 - 5]

2. STRUCTURE AND PROPERTIES METAL MATRIX COMPOSITES POLYPHASE SINTERED

Sintered oxide dispersion strengthened composites – are use at high temperatures and high mechanical loads. Volume part of dispersed material in the composites is very small, V_v <

15% and their diameter $< 0.1 \ \mu\text{m}$. The most widespread sinter is Al – $(10 - 20\%) \ \text{Al}_2\text{O}_3$ -SAP (Sintered Aluminium Powder) (Fig. 5 and 6). Sheet metals, plates, and profiles can be produced from SAP by pressing and sintering $AI - Al_2O_3$ powder mixture or partial oxidizing Al matrix particles during sintering. Owing to good mechanical properties in room temperature ($Rm = 250 - 400 \text{ N/mm}^2$), and in elevated temperature ($Rm = 50 - 140 \text{ N/mm}^2$ in temperature 500°C) they are applied for pistons, head internal combustion engine, gas turbine blades, and shaft hubs of jet engines compressors.

Fe – **P** sinters are wear resistant materials. Phosphorus in iron sinters improves their tribological properties. In dependence of phosphorus constitution the sinters have a different structure. For phosphorus constitution less than 0,05 %P solid solution of phosphorus in ferrite of hardness $220 \div 290$ HV creates (Fig. 7 and 8). Further increase of hardness of sinters having this phosphorus constitution is possible as a result of precipitation hardening. In case of bigger phosphorus constitution iron phosphides Fe₃P create.

Polyphase sintered true particulate composites depending on chemical constitution and sintering parameters have different structure and properties (Fig. 9). Fe – Fe₂B, Fe - Co - (FeCo)₂B, Fe - Cu - (FeCu)₂B sinters are an example of metal matrix polyphase sintered true particulate composites with a good hardness and heat resistance [6, 7]. Tests of sintering Fe - Fe₂B have been carried out in [8]. Iron boride sinters were formed as a result of sintering a mixture of iron and amorphous boron powders. Tree different mixtures were prepared used: Fe-Fe₂B cermets have been made from a mixture of iron and boron powders of a concentration of 3.8% B by weight suitably to eutectic composition in Fe – B equilibrium system; 6.5 and 8.8% B suitably to Fe₂B composition. The powder mixture was axially pressed and subjected to polyphase sintering in vacuum $p = 1*10^{-3}$ Pa at a temperature 1100 – 1160 °C. The sintering was carried out in two options in a solid state and with a participation of liquid, which was the Fe-B eutectic creating in higher temperature of sintering.



strengthened sinter Al _ magnification 10 000x

Figure 5. Microstructure of oxide dispersion Figure 6. Temperature influence on tensile Al₂O₃; strength Rm: A) SAP, B) aluminium alloy (1.5 %Cu, 2.0 % Mg, 0.4 %Mn, 6 % Zn, 0.15% Cr





Figure 7. Microstructure of iron sinter with 0,6%P; solid solution of phosphorus in ferrite (light areas) and Fe₃P iron phosphides on grain boundaries; etched by Oberhoffer reagent; magnification x 400;

Figure 8. Phosphorus influence P% on hardness of iron sinterHV0.5



Figure 9. Structures of polyphase sintered true particulate composites; a) big volume part of particles, metallic matrix; b) big volume part of particles, metallic matrix dispersion strengthened, c) small volume part of particles, metallic matrix; d) small volume part of particles, metallic matrix
[2]



Figure 10. Draft of structure Fe - Fe₂B sinters; a) green compact, b) sinter in the early stage of sintering, c) sinter after completed sintering: 1 –Fe particles, 2 –B particles, 3 - Fe₂B diffusive layer on iron particles surfaces, 4 – Fe– B liquid mixture, 5 - Fe₂B grains, 6 Fe - Fe₂B eutectic mixture

Polyphase sintering of the powder of iron and boron consisted of the following elementary processes (Fig. 10):

- diffusion of boron in iron in the solid phase,
- formation of the liquid phase the eutectic mixture Fe-Fe₂B,
- dissolution of iron and boron in the liquid phase, crystallisation of iron boride, Fe₂B from the liquid phase.

Depending on chemical constitution and sintering parameters iron - iron boride sinters have a structure:

- solid solution of boron in α iron grains of hardness 120 230 HV 0,1 set in Fe Fe₂B eutectic mixture of hardness 350 500 HV0,1
- iron boride grains of a hardness of 1800HV0.1 set in Fe Fe₂B eutectic mixture of hardness 350 - 500 HV0,1.

Controlling of the sintering with a participation of liquid, Fe - Fe₂B eutectic requests very narrow tolerances of sintering temperature. Increase of this temperature beyond 1175 - 1180° C causes an uncontrolled increase of the liquid phase quantity and a danger of deformation of the sinter. The other defect if this means of iron boride sinters generation is a lack of possibility of increasing of Fe₂B iron boride volume part over 70%.





Figure 11. Microstructure of the Fe - Co - Figure 12. Microstructure of the Fe - Co - $(FeCo)_2B$ (9% Co, 9%B) sinter, sintering (FeCo)_2B (9% Co, 9%B) sinter, sintering time t = 60 min, etched in 3% HNO₃ in time t = 180 min, etched in 3% HNO₃ in alcohol, magnification 2000x alcohol, magnification 2000x

A small addition of cobalt to a powder mixture, allows better controlling of the quantity of liquid phase during the sintering of the cermet by the mass concentration of Co in the Fe - Co - B powder mixture. Cobalt creates with boron an eutectic mixture Co - Co₂B with lower melting temperature, 1110 °C than that one of Fe-Fe₂B eutectic, 1174°C. The sintering with Co - B eutectic liquid may be in a suitable conditions a transient liquid sintering. It makes possibility of producing sinters, which are able to operate in higher temperature than temperature of sintering.

As a result of sintering Fe - Co – B powders mixture with 9% of Co atoms of this element stay in solid solution and intermediate phases substituted iron. That why, the diffraction line of Fe₂B are slightly shifted. Results of microanalysis tests show, that it is (FeCo)₂B.

Introduction of molybdenum to powder mixture, as an activator, made possible achievement of high density and good mechanical properties. The effect of the sintering intensification is particularly strong for Fe - B powder mixtures containing both cobalt and molybdenum. The effect is visible on dilatometric plots (Fig. 14)



Figure 13. Microstructure of the Fe - Co - $(FeCo)_2B$ (9% Co, 9%B); the effect of dissolving iron in the liquid eutectic is visible; sintering time: a) 3 min., b) 10 Min., c) 30 min.; magnification x 500

Fe - Co - (FeCo)₂B polyphase sintered composites have a structure (Fig. 11- 15):

- iron iron boride cermets have a structure: iron boride grains of a hardness of 1800HV0.1 seated in the eutectic mixture Fe-Fe₂B with a slight admixture of molybdenum. In fact there are (FeMo)₂B borides containing 1.1 1.5 % Mo. The cermets showed porosity ranging from 0.5-8%, depending on the sintering conditions,
- iron iron/cobalt boride have a structure: iron boride grains of (Fe)₂B with a slight admixture of cobalt and molybdenum of a hardness 1800 HV0.1 seated in the relatively soft and plastic eutectic mixture (Fe)₂B Co with a slight admixture of cobalt and molybdenum of a hardness 400-500 HV0.5. In fact there are (FeMoCo)₂B containing 1.2 1.5 % Mo and 2.3 3.1 %Co seated in the (FeMoCo)₂B (CoMo) eutectic. The cermets showed porosity ranging from 0.5-3%, depending on the sintering conditions.



 $\begin{bmatrix} 4 \\ 80 \\ 80 \\ 80 \\ 40 \\ 20 \\ 0 \\ 0 \\ 0 \\ 1 \\ t, h \end{bmatrix} \xrightarrow{\alpha} 1$

Figure 14. Diffraction of the Fe - Cu - $(FeCu)_2B$ cermets, a) 5% Cu, b) 15% Cu, sintering time 30 min.; 1 $(FeCu)_2B$, 2 - Cu, 3 - Fe

Figure 15. Phases fraction: 1iron, 2-eutectic mixture, 3iron boride, and 4-porosity of Fe- Cu - (FeCu)₂B sinters on sintering time, 15% Cu wt.; sintering temperature 1100°C

A similar effect of limitation of the liquid phase by powder mixture constitution modification has been achieved owing to a slight addition of copper to the powder mixture. Copper has lower melting temperature, 1084.87°C, and creates with boron a eutectic mixture Cu – B (α + β) of two kinds of solid solution α (reach in Cu) and β (reach in B) with melting temperature, 1040°C [7]. Both temperatures are lower than that of Fe-Fe₂B, 1174°C.



Fig. 16. Dilatometric plots for isothermal sintering of: Astaloy Mo, Astaloy Mo + 9% B, and Astaloy Mo + 9% B + 10% Co, a) sintering at 1120°C, b) sintering at 1185°C, heating and cooling rate - 20°C/min. [6]

Chemical constitution and the sintering parameters affect cermets properties. High hardness and resistance to wear of cermets was confirmed. The change in the hardness HV of Fe(MoCo)- (FeCo)₂B cermets as a function of boron concentration and sintering time is shown on Fig. 16. The cermet hardness increases with an increase in the fraction of iron boride and decreases with an increase in the cobalt concentration. So far, the maximum hardness of 1470 HV has been obtained but there is a realistic chance of increasing it. The wear of Fe(MoCo) - (FeCo)₂B cermets during sliding dry friction decreases with an increase in boron concentration and sintering time, i.e. with an increase in the fraction of the (FeCo)₂B phase and increases with an increase in the cobalt concentration (Fig. 17). The wear of Fe - Co - (FeCo)₂B cermets is comparable with the magnitude of wear of diffusive layers boronized on steels [1].



Fig. 17. Hardness HV5 (a) and wear in the process of dry sliding friction by pin on disk method with the counter-specimen from high - chromium ledeburitic steel hardened to 60 HRC at the load of the Fe - Co - $(FeCo)_2B$ cermet specimen of 5.5 MN/m², sliding speed 1 m/s and path of friction 300 m (b) of the Fe(MoCo) - $(FeCo)_2B$: 8% Co, 9%B (1), 10% Co, 9%B (2), 12% Co, 9%B (3) in function of the sintering time, t.

3. SUMMARY

Polyphase sintering is a mean of a direct production of particulate - reinforced composite materials. Particles formed as a result of polyphase diffusion in a solid state and with a participation liquid phase exemplify a composite reinforcement. Owing to the possibility of sintering of materials strongly differed in chemical constitution and mechanical properties, the polyphase sintering is, in some cases, the unique mean of production of materials having exceptional properties.

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