Sintering and properties of Astaloy Mo-Fe₂B and Astaloy Mo-Co-(Fe,Co)₂B cermets

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1. INTRODUCTION

Possibilities of sintering of friction wear and chemical resisted Fe-Fe₂B composites with a presence of liquid phase, Fe-Fe₂B eutectic were proved in [1, 2]. However controlling of the liquid Fe-Fe₂B eutectic quantity during the sintering needs narrow tolerances of the sintering temperature to avoid uncontrolled increase of the liquid phase quantity and deformation of the sinter. Little admixture of cobalt to the powder mixture, allows full controlling of the quantity of liquid phase during the sintering of the cermet by the mass concentration of Co. That’s why, cobalt create with boron an eutectic mixture Co - Co₂B with lower melting temperature, 1383 K (1110 °C) than that one of Fe-Fe₂B eutectic, 1447 K (1174 °C). The sintering with Co-B eutectic liquid may be in a suitable conditions a transient liquid sintering. As a source of iron Astaloy Mo Höganäs (Astaloy 100. 30) grade was used. Astaloy 100. 30 powder is Mo pre-alloyed atomised iron powder mainly used for high quality structural parts production. Molybdenum containing iron base powder was chosen for current investigations because of Mo₂FeB₂ hard phase may be formed during reaction sintering of powder mixtures used [2-6].

2. EXPERIMENTAL PROCEDURE, RESULTS AND DISCUSSION

Astaloy Mo alloyed Höganäs grade powder containing 1.5wt.-% molybdenum was used as a base material. As a boron source an elemental high purity amorphous boron powder with particles below 5 µm was chosen for this study. Reduced cobalt powder with particles below 10 µm was used as an alloying as well as a strong boride forming element. Two different mixtures were prepared using laboratory turbula mixer: Astaloy Mo + 9wt.-% B, Astaloy Mo + 9wt.-% B + 10wt.-% Co and Astaloy Mo for comparison. Powder mixtures were uniaxial compacted at 600 MPa giving rectangular green compacts with green densities of about 5.0 g/cm³ for composition A, 4.8 g/cm³ – for composition B, and 6.5 g/cm³ – for Astaloy Mo, composition C. Sintering was performed in an horizontal NETZSCH 402E dilatometer under flowing high purity hydrogen. Isothermal sintering temperature was achieved by heating at different heating rates: 2, 5, 10, 20 and 30 °C/min. Taking into
consideration the expected amount of liquid phase appearing in investigated systems compacts having composition A were isothermally sintered at 1185°C while the compacts of composition B – at 1120°C. Cooling rate was also constant and equal 20°C/min. The influence of material composition, heating rate and isothermal sintering temperature on sintering behaviour were analysed using the registered dilatometric curves. XRD phase measurements and metallographic observations were taken from the sintered compacts. The reaction sintered composites were subjected to the: metallographic tests, X - ray analysis, measurements of hardness, and of 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 cermet specimen of 5.5 MN/m², sliding speed 1 m/s and path of friction 300 m.

Diffusion processes as well reactions occurring during heating of boron containing compacts are enough advanced already at temperatures below iron allotropic transformation temperature and the dimensional consequences of $\alpha$-Fe $\rightarrow$ $\gamma$-Fe transformation are not visible as it is in the case of Astaloy Mo compacts without boron (Fig. 1). The later ones exhibit very limited dimensional changes during the whole sintering cycle (insignificant difference between sintered and green densities). If boron as an alloying and highly active element is present, compacts undergo more substantial dimensional changes, which are strongly dependent on isothermal sintering temperature - the higher it is the higher the shrinkage is recorded. Heating rate from room temperature up to isothermal sintering temperature strongly determines the dimension change rates of examined compacts. Typical dilatometric curves may be interpreted by dividing them into four characteristic segment:

- up to about 800°C - thermal expansion, oxide reduction, and diffusion of boron into iron and cobalt (if it is present),
- from 800°C up to about 1100°C - continued but enhanced swelling; expansion caused by temperature increase and synthesis of boride phases is temporary woken by $\alpha$-Fe $\rightarrow$ $\gamma$-Fe allotropic transformation,
- from 1100°C - the shrinkage begins and shortly afterwards it becomes very intensive due to liquid phase appearance; maximum shrinkage rate is observed at about 1180°C for compacts without cobalt and at 1110°C for samples with it, which corresponds with respective eutectic temperatures, during isothermal sintering period continuous shrinkage with gradually decreasing rate is observed,
- cooling stage is characterised only by thermal contraction if compacts with boron are considered, on dilatometric plots for Astaloy Mo, however, allotropic transformation of iron is recognisable.

![Graph](image-url)
Iron boride Fe<sub>2</sub>B may form at relatively low temperature of about 500°C while Mo<sub>2</sub>FeB<sub>2</sub> complex boride may form from Mo and Fe<sub>2</sub>B at above approximately 930°C [3]. According to Fe – B binary phase diagram [7] liquid phase appearing in the sintered system is considered to be produced from austenite and Fe<sub>2</sub>B boride in the presence of some Mo mainly as Mo<sub>2</sub>FeB<sub>2</sub> phase. Heating rate is a very sensitive parameter which determines the amount of liquid phase formed during reactive sintering [8, 9]. If the heating rate through the solid state reaction period is low there are favourable conditions for oxide layers reduction and for the redistribution of the alloying elements toward the equilibrium state which is possible to achieve in the sintered system. After the eutectic temperature is reached liquid phase sintering is in fact supersolidus sintering process [8, 9]. Chemical reactions occurring within the samples heated at high heating rate are moved to the higher temperatures and take place in shorter period of time which makes them more excessive. In this case heat generated by exothermic reactions is not able to be completely released by the flowing gas and therefore this heat may cause the local increase of temperature significantly above the furnace temperature. This, so called "contact melting" phenomenon [10] produces more amount of the liquid phase facilitating densification of the compact by rearrangement of solid phases existing inside it, namely γ-Fe and Mo<sub>2</sub>FeB<sub>2</sub>. The following phases are may occur during the sintering process of Astaloy Mo + 10wt.– % Co + 9wt.– % B powder mixture: Fe<sub>2</sub>B with an addition of Mo and Co, Co<sub>3</sub>B, Co<sub>2</sub>B, solid solution complex borides (Fe,Co)<sub>3</sub>B<sub>2</sub>, (Fe,Co)<sub>3</sub>B, Mo<sub>2</sub>FeB<sub>2</sub> and liquid. As a result of metallographic investigation and X -ray analysis (Fig. 2 - 4) and microanalysis it was found that:

- iron - iron boride cermets have a structure: iron boride grains of a hardness of 1800HV0.1 seated in the eutectic mixture Fe–Fe<sub>2</sub>B with a slight admixture of molybdenum. In fact there are (FeMo)<sub>2</sub>B 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)<sub>2</sub>B containing 1.2 – 1.5 % Mo and 2.3 – 3.1 %Co seated in the (FeMoCo)<sub>2</sub>B – (CoMo) eutectic. The cermets showed porosity ranging from 0.5-3%, depending on the sintering conditions.
The sintering process parameters not only affect the structure of cermets but also their properties. High hardness and resistance to wear of cermets was confirmed. The change in the hardness HV of Fe-Co-(FeMo)\textsubscript{2}B cermets as a function of boron concentration and sintering time is shown on Fig. 5. 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-Co-(FeMo)\textsubscript{2}B 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)\textsubscript{2}B phase and increases with an increase in the cobalt concentration (Fig. 6). The wear of Fe-Co-(FeMo)\textsubscript{2}B cermets is comparable with the magnitude of wear of diffusive layers boronized on steels [1].
Fig. 4. Diffraction of the Astaloy 100. 30 + 9% B+ 10% Co cermet, sintering temperature $T = 1120$°C, sintering time $t = 60$ min

Fig. 5. Hardness HV5 wear W of Fe-Co-(FeCo)$_2$B cermets of: 9%B and: 8% Co, (1), 10% Co (2), 12% Co (3) in function of sintering time, t

4. CONCLUSIONS

The sintered density of both investigated materials, namely: Astaloy Mo + 9wt.-% B and Astaloy Mo + 10wt.-% Co + 9wt.-% B, is strongly affected by the amount of liquid phase appearing in compacts during sintering.

The isothermal sintering temperature is a most important parameter determining the amount of liquid phase, less sensitive parameter is heating rate.

Cobalt doesn’t change the mechanisms and phenomena taking place during sintering as compared with those observed for compacts without cobalt. The latter alloying element, however, supports liquid phase formation. Thus, the maximum acceptable sintering temperature has to be lower for samples with cobalt than for samples without it; those temperatures are 1120°C and 1185°C, respectively.

The reaction sintering of the Astaloy Mo + 9wt.-% B + 10wt.-% Co powder consisted of the following elementary processes:  
- the solid phase diffusion of boron into the iron - molybdenum and cobalt particles  
- formation of the liquid phase the eutectic mixture (FeMoCo)$_2$B – (CoMo) eutectic
dissolution of powder elements in the liquid phase

- crystallisation of iron boride \((\text{FeMoCo})_2\text{B}\) from the liquid phase

In a case of Astaloy Mo + 9wt.-% B cobalt doesn’t participate is the reactions.

REFERENCES