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Silicide Materials for High Temperature Applications

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Abstract

The efficiency of forming tools, like dies for hot pressing, is directly affected by the application conditions (pressing temperature and die pressure) on the one and tool cost (operation time) on the other hand. In order to obtain a significant progress of the forming process new tool materials are necessary allowing an increase of both temperature and pressure. Molybdenum-disilicide composites are promising candidates to meet the requirements because of their excellent mechanical stability up to high temperatures and their outstanding oxidation and corrosion resistance. In this work the development of tool materials based on molybdenum-disilicide ($MoSi_2$) is presented. In live tests sawing segments, containing diamonds embedded in a cobalt-based matrix, were formed via hot pressing at a pressure of 50 MPa in a temperature range of 700 – 920°C (depending on the matrix material), showing that the materials can considerably increase the efficiency of the hot press technology under the tested conditions.

1. Introduction

Molybdenum-disilicide ($MoSi_2$) and composites based on $MoSi_2$ are promising candidates for applications like forming tools for hot pressing because of their excellent oxidation resistance and superb mechanical stability up to high temperatures. In the context of the development of new tool-materials both single-phased $MoSi_2$-materials and molybdenum-disilicide materials reinforced with ceramic particles were successfully tested under operating conditions. It was shown that in a temperature range of 700-920°C even the single-phased material is in the position to meet the requirements on mechanical stability and oxidation resistance.

It was shown earlier that pre-alloyed $MoSi_2$-powders have a very poor sinterability and that green specimen produced from elemental powders mixtures suffer from a severe swelling effect during reactive sintering [1]. This problem can be overcome by using a modified high energy milling process (HEM) for pretreatment of the powder mixtures [2].

2. Experimental

2.1 Preparation

The preparation of dies for hot pressing is shown schematically in fig. 1. The composites were prepared by a powder metallurgical technology based on a patented technique [2] using the high energy milling (HEM) process. After milling in a planetary ball mill the resulting highly dispersive powder mixtures exhibit a remarkable sinterability, reaching high densities (>95 % of theoretical density (TD)) after pressureless sintering at moderate temperatures [1-4].

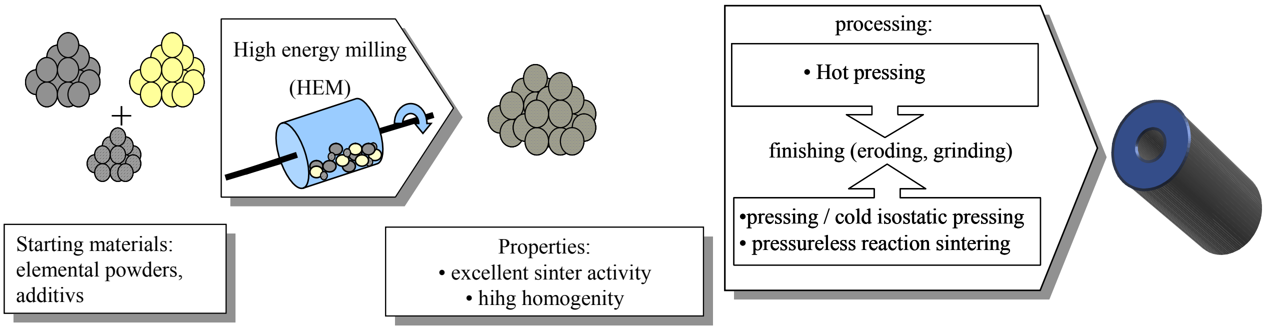

Figure 1: Schema of the PM-process used for the preparation of dies for hot pressing.

2.1.1 Powder mixtures

The preparation of single phase $MoSi_2$ started from elemental powder mixtures with an atomic ratio of 33.3% Mo and 66.7% Si which were milled together in a planetary ball mill (HEM process). To get the particle reinforced material, two manufacturing routes were used. To get the $MoSi_2/TiB_2$ composite material the ceramic particles were added to the high energy milled Mo + 2 Si powder mixture followed by a subsequent homogenization of the components in the ball mill. The second technique includes an in-situ formation of the ceramic reinforcements during the milling process. In this work the following three powder mixtures were produced using the different processes (content of reinforcement 15 vol-%):

High energy milling (HEM):

$$Mo + 2\,Si \rightarrow MoSi_2$$

HEM + adding ceramic particles:

$$Mo + 2\,Si + TiB_2 \rightarrow MoSi_2 + TiB_2$$

In-situ formation of the ceramic reinforcement:

$$Mo + 3\,Si + C \rightarrow MoSi_2 + SiC$$

The composite with SiC as reinforcement was manufactured by GfE Metalle und Materialien GmbH, Nürnberg.

To avoid impurities namely oxygen and iron (abrasion from the milling balls) the containers of the planetary ball mill were filled under protective atmosphere (Ar4.8, glove-box). Furthermore ZrO_2 balls were used for the milling process.

2.1.2 Heat-treatment and finishing

To get semi-finished products (cylinder) the milled powders were consolidated by uniaxial pressing respectively cold isostatic pressing followed by pressureless sintering under argon atmosphere (T_{max} 1600°C, 120 min). Alternatively the consolidation was reached by hot pressing (argon-atmosphere, T_{max} 1550°C , p_{max} 35 MPa). From the cylinders, the desired geometries were obtained via electrical discharge machining (EDM) followed by grinding the surfaces to get a higher surface quality. Dies for hot pressing before pressureless sintering and after finishing are shown in figure 2.

Figure 2: Dies for hot pressing (test pieces): Left cylindric samples after CIP. Middle and right: die and piston after finishing (EMD and surface grinding)

2.2 Properties

2.2.1 Mechanical properties

Samples for the investigations were cut into the desired geometry (e.g. bars, cylindric or square samples) from hot pressed disks or were obtained from the forming tools after live time tests.

Some mechanical properties of $MoSi_2$, $MoSi_2$ + SiC (5 – 10 vol.-% SiC) are given in table 1. The samples were supplied in form of bending bars with dimensions of 3mm x 4mm x 42mm. For measurement of the RT-hardness the indentation of a polished surface by Vickers pyramid was used. The indentation load (P) was 148 N. The fracture toughness (K_{IC}) was measured by two methods, indentation fracture (IF) and indentation strength (IS), using Vickers indents. In the IF method, the K_{IC} was calculated using Shetty's formula. The strength tests were carried out in air at room temperature using a standard testing machine Instron 1362 with four-point flexure jig of inner/outer roller spans of 20/40 mm, respectively. The creep strength of the material was determined using four-point bending (air). The inner/outer spans were 20/40 mm, respectively. The samples, loaded statically by a dead-weight system on constant stress of 100 MPa, were tested at 800, 1000, 1200 and 1400°C. The apparent activation energies (Q_A) for the stress of 100 MPa were calculated from the strain rate $\dot{\varepsilon}$ vs. $1/T$. For more detailed description see [4].

As described in literature [5, 6] the mechanical properties of $MoSi_2$/SiC-composites are improving with increasing amounts of SiC. The results in table 1 show the good agreement with this data for all measured mechanical properties and also for the calculated activation energy.

Table 1. Results of mechanical tests on binary $MoSi_2$ and composites with 5 – 15 vol.-% SiC as reinforcement.

Material	HV (GPa)	K_{IC} ($MPa.m^{1/2}$)	σ (MPa)	Q_A (kJ/mol)
$MoSi_2$ (binary)	9,6	4,1	233	244
$MoSi_2$ + 5% SiC	10,4	4,9	259	273
$MoSi_2$ + 10% SiC	11,2	5,5	277	351
$MoSi_2$ + 15% SiC	11,8	5,3	288	367

The Vickers hardness (HV10, indentation load 98 N)) of $MoSi_2$ + 15 vol.-% TiB_2 was tested on an original sample after live time tests (mean value of 5 tests) with 1190 HV10.

Because of the very abrasive behaviour of the diamond-containing materials processed inside the new forming tools the wear resistance of the new tooling materials is an important parameter.

In figure 3 the results of a pin on disk test are shown. In this test the wear behaviour of single phased $MoSi_2$ was determined using a $MoSi_2$ pin (diameter 5 mm) and a disk made out of 100Cr6 (diameter 110 mm, hardness 62 HRC). The tests were carried out at 23°C with a number of revolution of 191 rpm and a load of 2 N/mm^2. As it can be drawn from the diagram, the friction coefficient (>1) indicates a high adhesion of the silicide material but nearly no wear (<100µm after 10.000 m sliding distance).

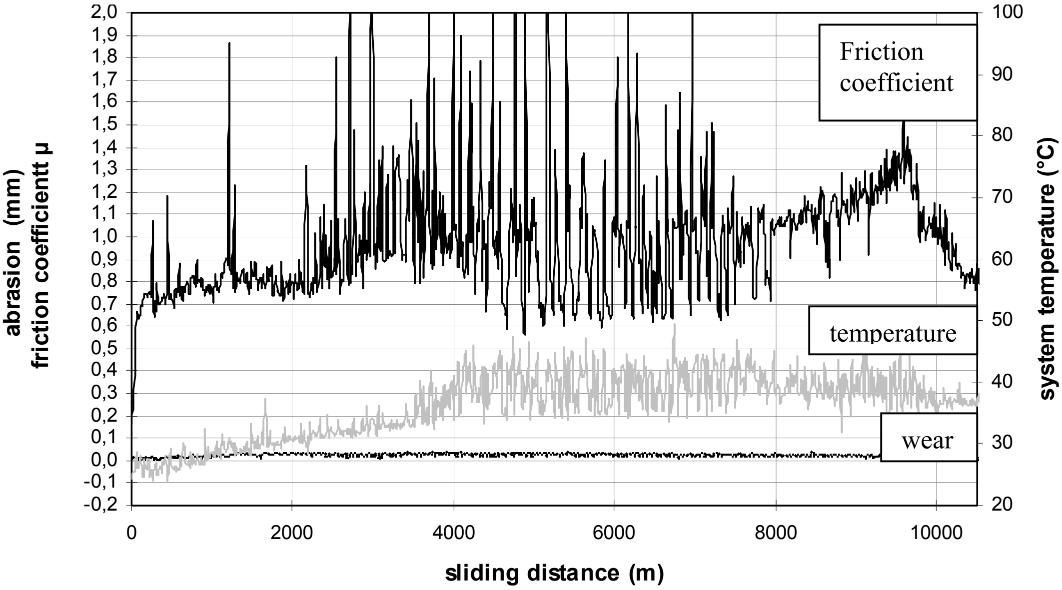

Figure 3: Results of tribological tests (pin on disk ($MoSi_2$ pin/100Cr6 disk)).

Also the conditions of this investigation are not directly transferable to the conditions given when forming diamond containing materials via hot pressing the results of the pin-on-disk tests suggest that molybdenum silicide-based materials are in the position meet the requirements on wear resistance.

To get more precise information the wear resistance was tested under operating conditions when hot pressing diamond containing materials, verifying the excellent investigation results.

2.2.2 Physical properties

The coefficient of thermal expansion (CTE) was measured in a temperature range from 36 to 800°C (heating/cooling rates 5K/min, argon atmosphere) on a $MoSi_2$ sample with a reinforcement of 15 vol.-% TiB_2. The dimension of the cylindric samples were 8,2 mm in diameter and 8,4 mm in length. It was provided that the sample is isotropic concerning the CTE. The results of the investigation are listed in table 2.

Table 2: CTE of $MoSi_2$ + 15 vol.-% TiB_2

temperature range	coefficient of thermal expansion [10^{-6}/K]
36°C – 300°C	8,3
36°C – 400°C	8,3
36°C – 500°C	8,0
36°C – 600°C	7,9
36°C – 700°C	7,9
36°C – 800°C	8,0
36°C – 900°C	8,0*

*= the result of the 36 – 900°C temperature range was determined by extrapolation.

The CTE of roughly 8 * 10^{-6}/K of the silicide material is much lower than the coefficient of thermal expansion of widely used high temperature alloys as PM2000 (14 * 10^{-6}/K at 800°C) or Haynes 230 (15 * 10^{-6}/K at 800°C). If the new tooling material is surrounded by a high temperature alloy, the silicide part have to be provided with a corresponding oversize and embedded at high temperatures to avoid stresses and ensure a connection between the silicide and the high temperature alloy at working temperature.

Besides the working temperature and pressure, the heating and cooling rates are an important factor to ensure the efficiency of forming tools. Therefore a cylindric sample (diameter 35 mm, height approx. 5mm) was cyclically heated up to a temperature of 900°C (heat rate constant) and than cooled down to room temperature. The cooling rate was increased about by 10 K/min every cycle (10, 20, …, 100K/min). No crack was observed after the tests suggesting an adequate temperature heat resistance for tooling applications.

2.3 Tests under operating conditions

Several dies for hot pressing, made out of single phased $MoSi_2$, $MoSi_2$ + 15 vol.-% SiC res. TiB_2 were tested under operating conditions at Dr. Fritsch GmbH, Fellbach on an automated test stand for hot pressing. At a pressure of 50 MPa diamond containing sawing segments were formed within a temperature range of 700 – 920°C depending on the accurate composition of the cobalt-based matrix material. Until now about 1000 diamond containing tools were formed via this forming process, showing the usability of materials based on $MoSi_2$ as new tool-material.

3. Conclusion

In this work the fabrication and investigation of new tool-materials based on molybdenum disilicide was presented. In live tests diamond containing sawing segments (the diamonds were embedded in cobalt-based matrix material) were formed via hot pressing within a temperature range of 700 – 920°C. Even if some problems have to be solved in future, like the connection of materials with different coefficient of thermal expansion to avoid stresses, it was shown that these materials can considerably increase the efficiency of the hot press technology at the tested temperature range. Thereby $MoSi_2$-based materials are an alternative not only to graphite but also to nickel- or iron-based high temperature alloys as a material for forming tools like dies for hot pressing.

Acknowledgements:
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4. Literature

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