

## Mechanical Alloying of Fe-Based Solid Lubricant Composite Powders

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### Abstract

Tribological problems are of very high interest in modern research fields of mechanical engineering [1]. In order to obtain low friction coefficients and an efficient self lubrication behaviour under high and low temperature conditions as well as under vacuum which is problematic in case of using conventional oil lubricants, several alloying systems were produced and investigated with respect to their structural properties.

As previous experiments have shown, the mechanical alloying process in a ball mill is a convenient technique to get highly dispersed phase distributions on a nanocrystalline scale [2-4]. Therefore the powder processing was carried out in a Simoloyer (Zoz - horizontal rotary ball mill) to achieve a homogeneous phase distribution of the solid lubricants in a strong metallic matrix. The chosen solid lubricant powders were pure graphite (C) and molybdenum disulfide (MoS<sub>2</sub>) combined with elemental iron (Fe) powder in various concentration ranges.

The evolution of the microstructure was followed by scanning electron microscopy (SEM), transmission electron microscopy (TEM) and X-ray diffraction (XRD) methods. The tribological properties of the compacted powders will be investigated by using a special pin-on-disk apparatus where the powder samples are sliding against a rotating steel disk. Afterwards the structure of the formed thin sliding films will be analyzed by SEM and TEM.

All mechanically alloyed powders produced exhibit a fast dispersion of the solid lubricants in the Fe-matrix during processing. First investigations showed that the hexagonal structure of the solid lubricants which is essential for the sliding effect is completely changed under the influence of the colliding milling balls. This effect could be observed especially in the case of pure milled graphite powder, where the crystalline structure changed to a nanocrystalline phase already after a very short processing time. Further milling leads to an amorphous structure. Similar results were found by other authors [5, 6] after long milling durations in planetary ball mills.

## 1. Introduction

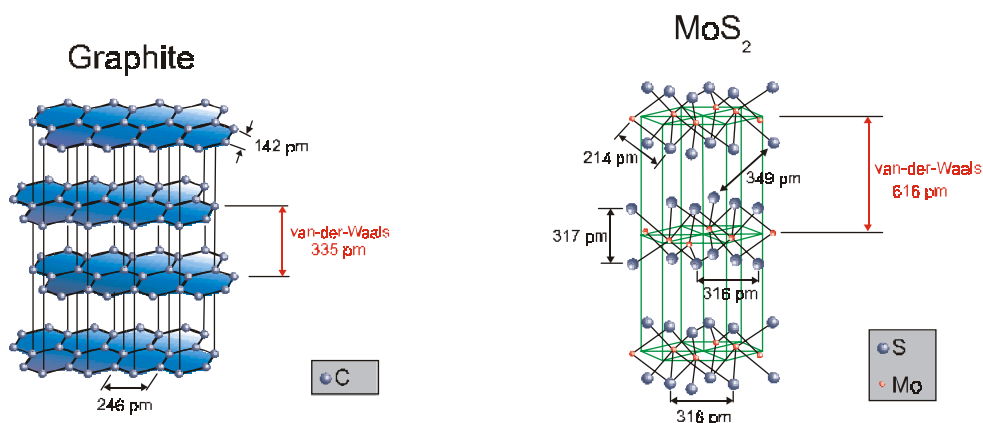
Considering their layered microstructure and their lubrication behaviour, the properties of molybdenum disulfide ( $\text{MoS}_2$ ) and graphite (C) are quite similar. Both materials are wellknown as solid lubricants and widely used in the application field of mechanical engineering to reduce friction and wear in tribological systems. Several studies have been done on those systems being deposited by chemical or physical vapour deposition processes on substrates like steels [1, 2]. Although the mechanical alloying technique is not intended to be a process for producing thin coatings, highly dispersed phase distributions can be synthesized. This technique has been found to be very effective in producing powders with interesting properties like amorphous or nanocrystalline materials which usually are far away from the thermal equilibrium state. Furthermore, the powder technological route offers the possibility to obtain composites or pseudo-alloys which are generally not receiveable by conventional processing techniques due to the immiscibility of their components or their tremendous differing melting temperatures.

During the mechanical alloying process the ball-to-ball impacts in most cases induce material transformation of the affected powder particles which leads to highly disordered crystalline structures. The interactions between milling balls and powder particles can be characterized by processes like cold-welding, plastic deformation and further fragmentation and embrittlement due to an increasing number of atomic dislocations and stacking faults.

In this context pure iron (Fe), graphite (C) and molybdenum disulfide ( $\text{MoS}_2$ ) powders as well as iron-based graphite and molybdenum disulfide composite powders have been produced by mechanical alloying with the aim to investigate the influence and changes on the crystalline structure during processing. These investigations are of very high interest as the compacted composite materials are candidates for solid lubricants used as bearing materials under extreme environmental conditions like deep and high temperature or vacuum for e.g. space applications. A further interesting question is whether the nanocrystalline phase distribution of graphite and  $\text{MoS}_2$  in the Fe-matrix achieved by mechanical alloying can affect the tribological properties of those materials.

## 2. Structural Properties of Graphite and $\text{MoS}_2$

Graphite crystallizes in layered hexagonal structures with the space group  $P6_3\text{mmc}$ . The ordinary appearing structure is shown in *Fig. 1*.



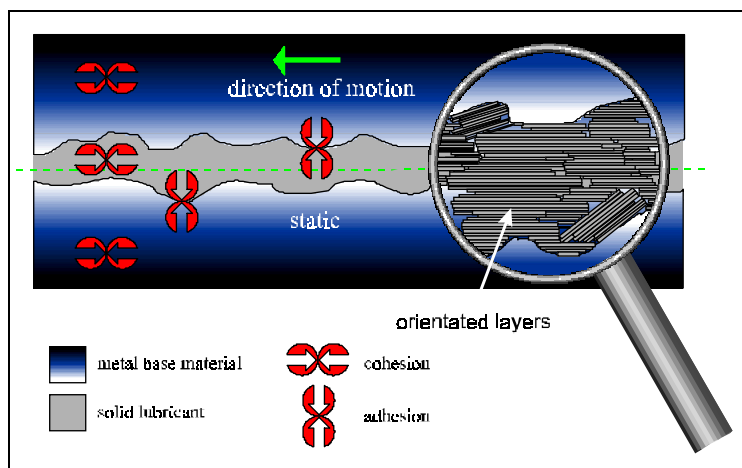
*Fig. 1: Crystalline structure of graphite*

*Fig. 2: Crystalline structure of  $\text{MoS}_2$*

Within each layer every C-atom is surrounded by 3 neighbored C-atoms in the form of a triangle. The bonding type can be characterized by  $\sigma$ -bondings due to  $sp^2$ -hybrid orbitals and delocalized  $\pi$ -bondings. The latter is formed by the fourth valence electron of each C-atom which is in the p-state with an orbital axis perpendicular orientated relative to the basal plane. The  $\pi$ -bondings are extended over the whole layer and therefore the mobile  $\pi$ -electrons are responsible for the metallic gloss of graphite, its black colour and its good conductivity parallel to the layer. As the forces between the layers are only of a weak nature (van-der-Waals-bondings, layer distance: 335 pm), graphite is an excellent solid lubricant due to its easy movable and shearing hexagonal planes.

Similar to the crystalline structure of graphite,  $MoS_2$  also consists of a hexagonal structure and can be classified into the same space group (see *Fig. 2*) as graphite. Consisting of stacks of S-Mo-S layers with strongly bonded S-Mo-S units, each Mo-Atom is surrounded by 6 S-atoms in a trigonal-prismatic coordination where the distance between one Mo- and one S-atom has a value of 214 pm and the distance between two Mo-atoms the value of 316 pm. Due to the very weak bondings of van-der-Waals forces perpendicular to the hexagonal planes,  $MoS_2$  also exhibits easy shearing character parallel to the hexagonal planes like graphite.

Being deposited to metallic surfaces which are sliding against each other, both materials exhibit very low friction coefficients - a reason why they are widely used for applications in the field of mechanical engineering. Their principle of functioning can be described as shown in *Fig. 3*.



*Fig. 3: Lubrication principle of the solid lubricants graphite and  $MoS_2$*

Both solid lubricants show an excellent adhesion to metallic surfaces and furthermore a high cohesion parallel to their layered structure due to covalent bondings (graphite) and ion-bondings with a high ratio of covalent proportions ( $MoS_2$ ). Corresponding to these properties a nearly parallel orientation of the layers can be observed after a short period of time if a vertical load and a simultaneous relative motion is applied to the contacting metallic surfaces. By filling the pores of the sliding metallic surfaces with solid lubricant, their roughness is reduced and very smooth surfaces with low friction coefficients are generated after a short instant. This is the case for directly lubricated contacting surfaces. However, the question is what happens if the solid lubricants are highly dispersed in a nanometric scale in a metallic matrix like iron and a vertical load is applied. There are hints that a reduction of friction is not achievable for this materials although a formation of a thin film in the contact zone can be observed.

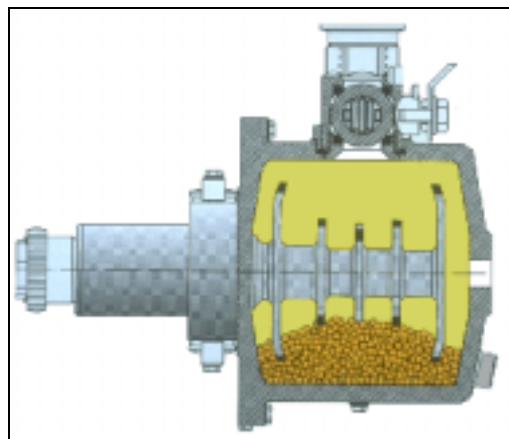
### 3. Experimental Details

#### 3.1 Preparation and Investigation of Powders

The powders were processed in a *Simoloyer*<sup>®</sup> *CM01-1/2 l* (Zoz - horizontal rotary ball mill) (see *Fig. 4.a, 4.b*) and also handled under inert gas atmosphere (argon) after processing. This was absolutely necessary to avoid violent reactions with oxygen due to an increased surface area of the particles and a reduced activation energy threshold of the processed powders.



*Fig. 4.a:* *Simoloyer CM01* used for powder processing



*Fig. 4.b:* *Scheme of the grinding unit (cross-sectional view)*

The milling device was operated at a constant rotational speed of 1000 rpm with 100Cr6 steel balls having a value of 5.15 mm in diameter. The powder-to-ball-mass ratio was chosen to 1:15 with a powder charge of 86.67 g each. A water-cooling system kept the grinding unit at a constant temperature of 35 °C. Several pure Fe-, graphite- and MoS<sub>2</sub>-powders with different processing durations up to 30 h as well as combined Fe-graphite and Fe-MoS<sub>2</sub>-powders in various concentration ranges were produced. After discharging, the powders were investigated by X-ray diffraction (XRD), scanning- (SEM) and transmission-electron-microscopy (TEM) methods. For this purpose, a *Seifert PTS 3000*-diffractometer with CuK $\alpha$ - and CrK $\alpha$ -radiation as well as a *Cambridge CamScan 24*-SEM with EDX and WDX and a *Hitachi H8100-200 kV*-TEM with EDX were used. For the examination by TEM, a special preparation technique was required: the powder particles were bonded in very thin *Gatan G1* epoxy films and afterwards ion-milled in a *Gatan PIPS 691*.

Several Fe-MoS<sub>2</sub>-powders were cold-compacted and afterwards tested on a special pin-on-disk tribometer to determine the friction coefficient of the bulk material. After testing, the structure of the formed thin sliding films was investigated by SEM.

#### 3.2 Starting Powders

For the milling experiments powders with starting particle sizes lower than 10  $\mu\text{m}$  were used (see *Fig. 5.a, 6.a, 7.a*). The SEM-micrographs show that the Fe-powder particles have a nearly spherical shape, whereas the MoS<sub>2</sub>- and graphite-particles form larger aggregates (up to values of 50  $\mu\text{m}$  in diameter) consisting of several finer particles having a layered structure.

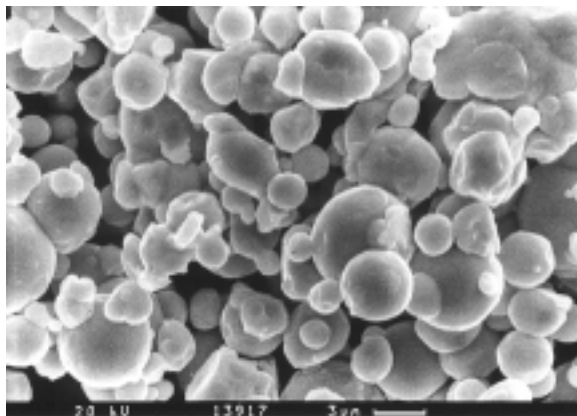


Fig. 5.a: SEM-micrograph of Fe-starting powder

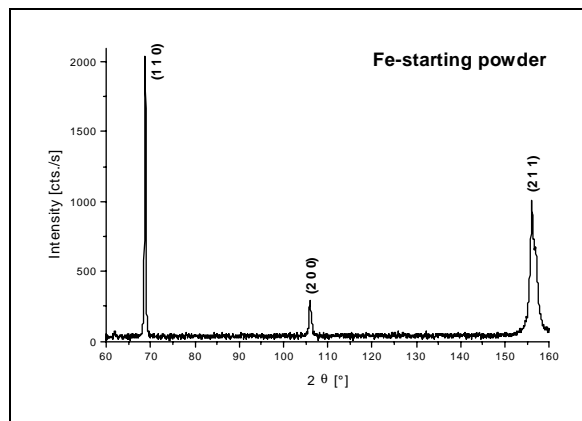


Fig. 5.b: XRD-CrKα-pattern of Fe-powder

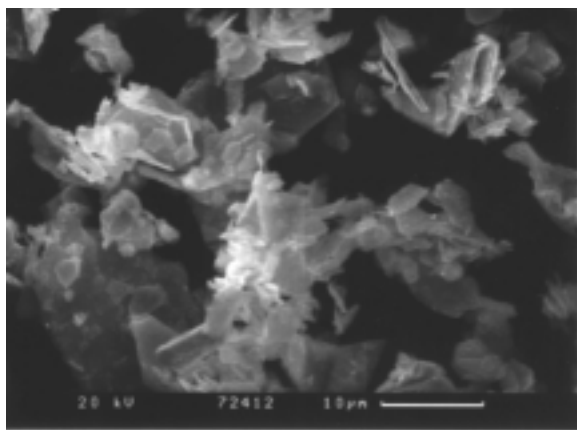
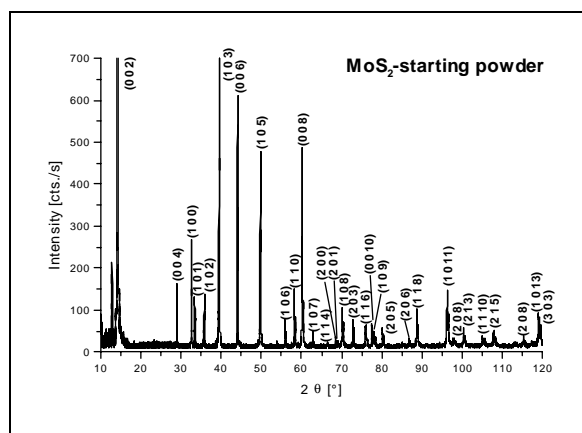
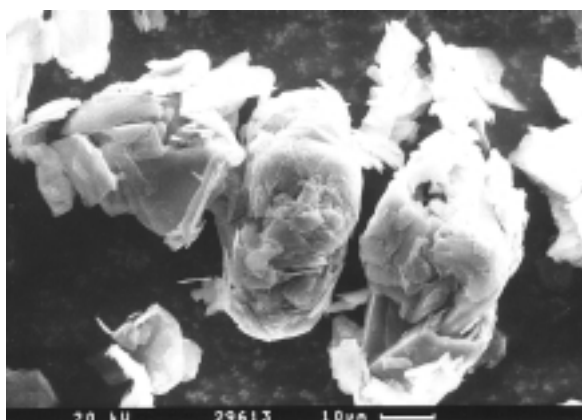

 Fig. 6.a: SEM-micrograph of MoS<sub>2</sub>-starting powder

 Fig. 6.b: XRD-CuKα-pattern of MoS<sub>2</sub>-powder


Fig. 7.a: SEM-micrograph of graphite starting powder

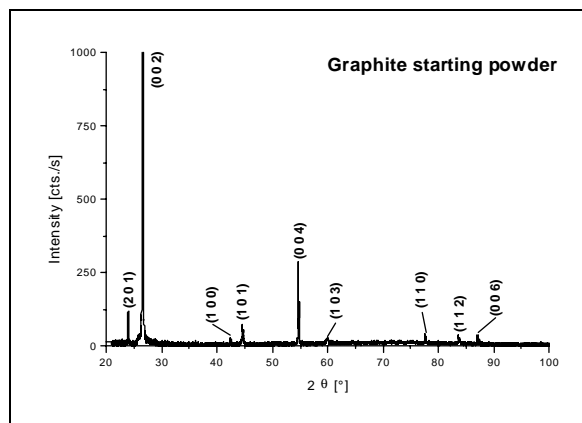


Fig. 7.b: XRD-CuKα-pattern of graphite powder

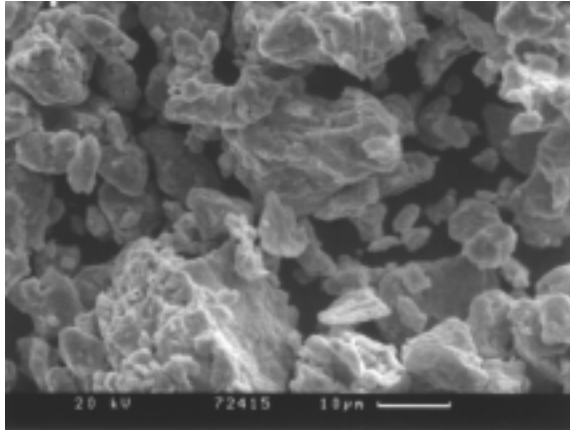
The XRD-patterns (Fig. 5.b, 6.b, 7.b) show that in the beginning highly crystalline structures are present with only small full-width-at-half-maximum values (FWHM). However, the MoS<sub>2</sub>- and the graphite pattern exhibit both a textured structure because the intensities of their (0 0 2) peaks are of a high value compared to the other ones. This effect is intensified caused by the preparation technique of the powders on the XRD-sample holder. As the CuKα-radiation of the X-ray source used for the graphite and MoS<sub>2</sub>-powder leads to an excitation in the case of Fe, a CrKα-radiation source was used for the pure Fe-powder to receive higher peak intensities.



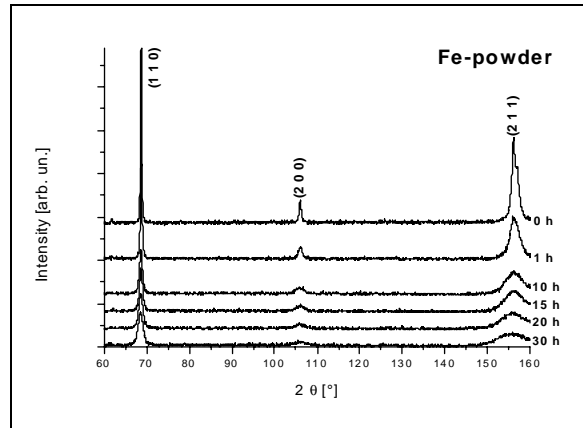
## 4. Results of the Milling Experiments

### 4.1 Pure milled Powders

To estimate the influence of the intensive high energy ball milling on the powder particles, pure Fe-, graphite and MoS<sub>2</sub>-powders were ground. The following *Fig. 8.a* shows a SEM-micrograph of Fe powder that has been milled for 30 hours.

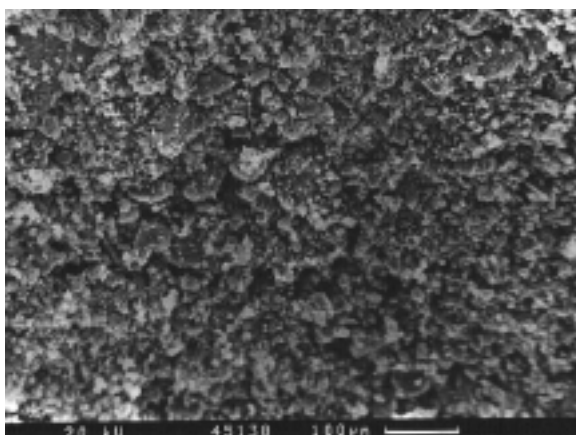


*Fig. 8.a:* SEM-micrograph of pure milled Fe-powder after 30 hours

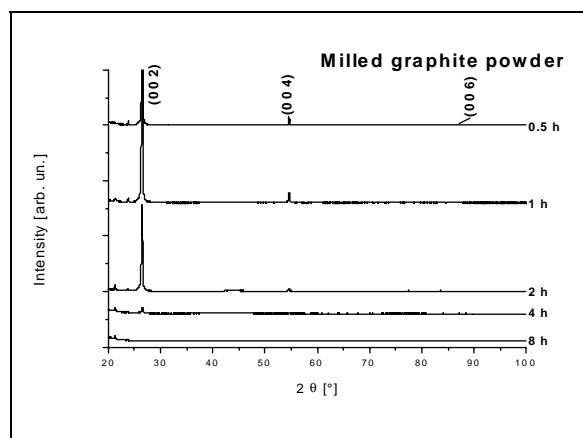


*Fig. 8.b:* XRD-CrK $\alpha$ -pattern of pure milled Fe-powder

It is visible that the peak intensities are reduced to a fifth of the original peak height intensities after a couple of hours. The full-width-at-half-maximum value rises for the (1 1 0)-peak from 0.343 to 1.405 degrees, for the (2 0 0)-peak from 0.669 to 3.341 degrees and for the (2 1 1)-peak from 1.606 to 7.830 degrees. Also a peak shift to higher *D*-values can be recognized for each peak. This means that the lattice spacing is increasing for the (1 1 0), (2 0 0) and (2 1 1) lattice layer. The peak broadening will also be an effect of a grain size reduction within the powder particles. The SEM-micrograph (*Fig. 8.a*) proves that the original Fe-particle geometries are completely different after 30 hours. The spherical shape has disappeared and the particle surface is rough and fissured due to innumerable cold-welding processes during milling. By measurements of the Vickers microhardness of several Fe-particles an increase from values of 255 *HV* up to 752 *HV* could be found caused by an accumulation of lattice dislocations. Additionally, a particle size reduction to only a few microns takes place due to an increasing embrittlement.

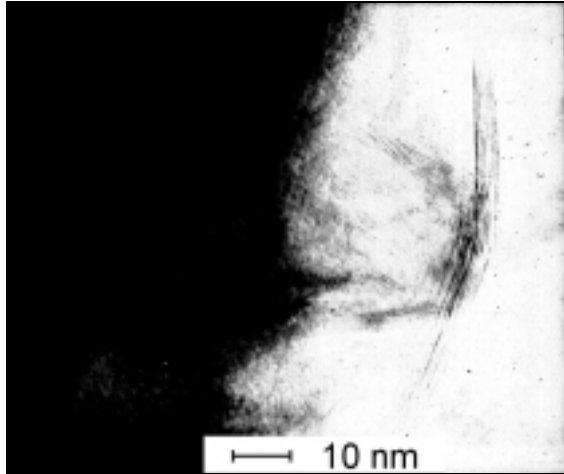


*Fig. 9.a:* SEM micrograph of pure milled graphite after 8 hours

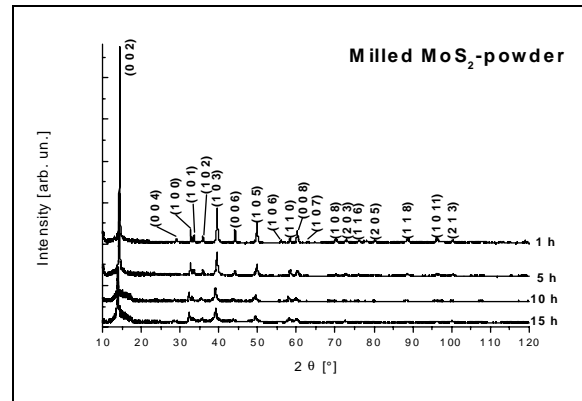


*Fig. 9.b:* XRD-CuK $\alpha$ -pattern of pure milled graphite

The FWHM-value of the  $(0\ 0\ 2)$ -peak in the case of high energy milled graphite after 4 hours is decreasing from  $0.094^\circ$  to  $0.350^\circ$ . This major peak as well as the other original peaks with lower intensities are completely absent after 8 hours of high energy milling. So an amorphous or an amorphous-like carbon phase can be detected by the XRD-investigations after only a short processing time. The hexagonal layered typical graphite structure is obviously disturbed which is also represented by the SEM-micrograph in *Fig. 9.a*. By this picture very fissured and roughened graphite particles can be observed.



*Fig. 10.a:* TEM micrograph of pure milled  $\text{MoS}_2$  after 10 hours



*Fig. 10.b:* XRD-CuK $\alpha$ -pattern of pure milled  $\text{MoS}_2$

TEM bright field micrographs show that the crystalline structure of the unmilled graphite and  $\text{MoS}_2$  powders is of a high symmetry. Most of the layers are arranged parallel due to their  $(0\ 0\ 2)$  textured structure and the lattices are nearly undisturbed over a wide range. After some hours of high energy milling and under the influence of the immense ball impacts, the apparent microstructure of both solid lubricants has completely changed: the number of dislocations and especially the disordering has increased during milling. This can exemplarily be proved by high magnification TEM-micrographs (*Fig. 10.a*) which show that the preliminary ordered  $(0\ 0\ 2)$ -lattice layers of  $\text{MoS}_2$  are no longer parallel oriented in wide ranges. However, an amorphization or a total absence of crystalline reflexes is not visible as in the case of graphite, even not after longer milling durations. Similar results could be found concerning the composite powders described in the following.

## 4.2 Composite Powders

### 4.2.1 Fe-Graphite Composites

Several Fe-graphite composite powders have been prepared and mechanically alloyed up to 15 hours. As already described in the case of pure milled graphite, the XRD-pattern of mechanically alloyed Fe-90C (wt. %) powder (*Fig. 12.b*) shows that the crystalline graphite phase disappears with increasing milling time. The intensity of the crystalline Fe-peaks, however, is nearly not influenced by the mechanical alloying process after 8 hours. That means, that the Fe-particles are completely covered by graphite which is damping the high kinetic ball impacts. The graphite particles are directly exposed to the contacting milling balls (*Fig. 11.b*). This is the reason why the microstructure of the graphite particles is changed in a relative short space of time.

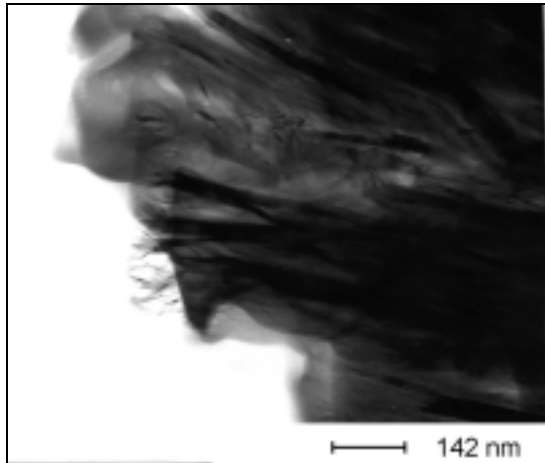


Fig. 11.a: TEM micrograph of Fe-90C powder after 1 hour

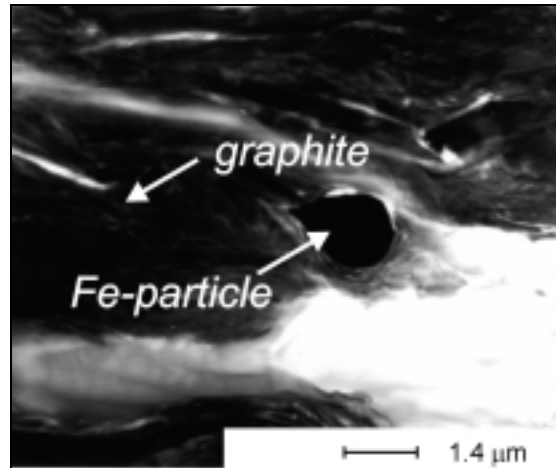


Fig. 11.b: Fe-particle enclosed by graphite (TEM-micrograph, 1 hour)

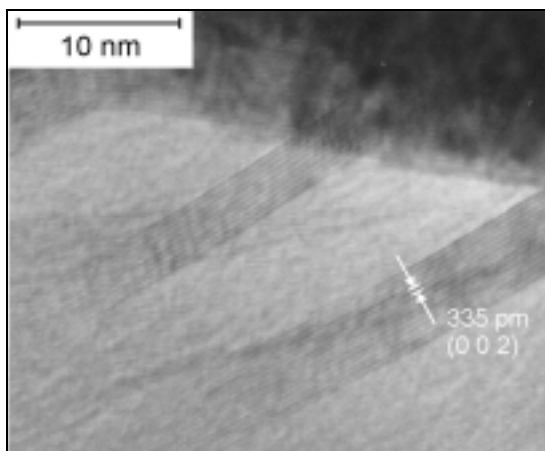


Fig. 12.a: TEM micrograph of Fe-90C powder with graphite lattice

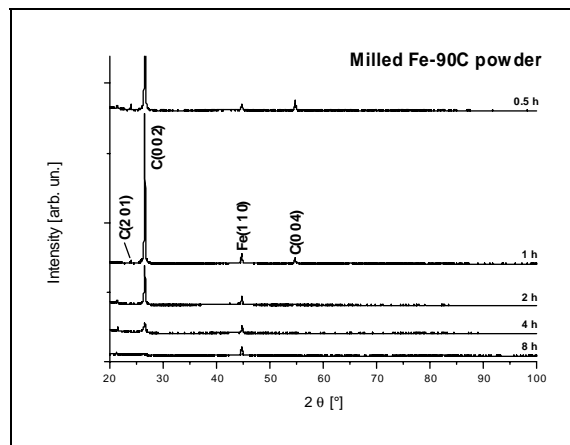


Fig. 12.b: XRD-CuK $\alpha$ -pattern of milled Fe-90C powder

The marked interplanar spacing of the (0 0 2) graphite layers can be seen in Fig. 12.a. The measured distance has the value of 335 pm and is due to the easy shearing planes of graphite which are bonded only by weak van-der-Wals forces (see Fig. 1). The TEM-micrograph in Fig. 11.a after 1 hour of milling shows that the high ordered structure of graphite is already disturbed after a relative short processing time. Other composition ranges with higher Fe contents led to comparable results.

#### 4.2.2 Fe-MoS<sub>2</sub> Composites

During milling of Fe-MoS<sub>2</sub> composites a fast dispersion of the MoS<sub>2</sub> phase into the Fe-matrix could be observed similar to the milling behaviour of graphite. This is exemplarily shown by a backscatter electron micrograph (Fig. 13.a) of an embedded Fe-40(MoS<sub>2</sub>) powder particle carried out in the SEM. The dark regions refer to high Fe-atom concentrations whereas the brighter regions can be detected as high Mo-atom concentrations. By this picture also the lamellar inner particle structure is visible. Furthermore, the damping effect of the MoS<sub>2</sub> in this composition is not as high as in the case of the above discussed high concentrated graphite/Fe composites. This fact results in a faster deformation of the Fe powder particles during the evolution of the milling process which can also be verified by the visible reduction of the peak height intensities received by XRD (Fig. 13.b).



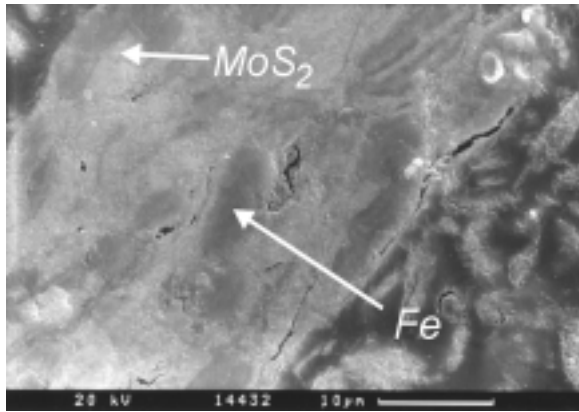


Fig. 13.a: Backscatter micrograph of Fe-40(MoS<sub>2</sub>) powder particle after 1 hour (SEM)

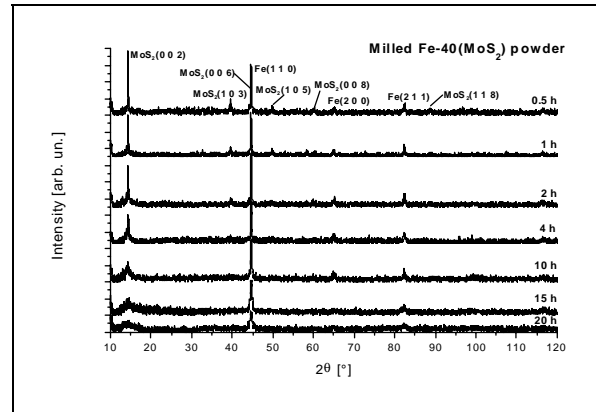


Fig. 13.b: XRD-CuKa-pattern of milled Fe-40(MoS<sub>2</sub>)

## 5. Tribological Behaviour

The tribological behaviour of the Fe-MoS<sub>2</sub>- and Fe-graphite composites has been investigated on a special pin-on-disk tribometer (counter material: steel disk). For this purpose the powders were cold compacted to several pellets under a load of 1500 N/mm<sup>2</sup>. The Fe-graphite pellets showed a very brittle behaviour as well as very high coefficients of friction of  $\mu > 0.5$  with increasing milling durations. The reason for this effect is the disordered layer structure of graphite and its increasing state of amorphization. Missing shearing ( $0\ 0\ 2$ ) planes are responsible for the rising friction of the composite material.

The produced Fe-MoS<sub>2</sub> samples behave similar to the Fe-graphite samples, although a better friction coefficient than 0.5 was expected due to still existing shearing layers after 10 hours of milling.

Fig. 14.a and 14.b exhibit the tested surface of a 10-hours-milled Fe-40(MoS<sub>2</sub>) powder pellet after a run on the tribometer of 30 seconds and 5 minutes.



Fig. 14.a: SEM-micrograph of the surface of a powder pellet after 30 seconds (Fe-40(MoS<sub>2</sub>), 10 hours of MA)

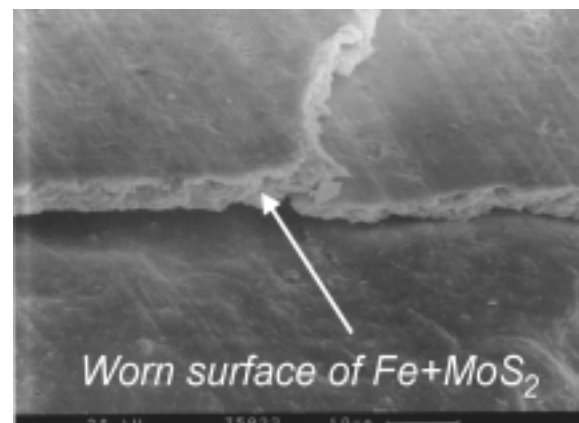


Fig. 14.b: Surface of the powder pellet after 5 min (SEM, Fe-40(MoS<sub>2</sub>), 10 hours of MA)

After 30 seconds the original rough surface is partly covered with a layer consisting of Fe and MoS<sub>2</sub>. The run-in period is not yet finished and the friction coefficient has a high value due to Fe-particles which break out of the surface and are distributed and embedded into the sliding layer. The situation has changed after a testing time of 5 min. The surface is completely covered with Fe-MoS<sub>2</sub>. However, a reduction of the friction coefficient could not be found due to a layer thickness of 5 microns and more, a high concentration of Fe-particles in the

layer which leads to a high wear rate of the pellets, and, nevertheless, the missing  $(0\ 0\ 2)$ -layer structure of MoS<sub>2</sub>. Furthermore, a worse adhesion tendency of the lubricating layer to the surface substrate could be observed which also led to high wear rates.

## 6. Conclusions

Pure Fe-, MoS<sub>2</sub>- and graphite powders as well as composite powders have been prepared by a high energy milling / mechanical alloying technique in a horizontal rotary ball mill for several hours and afterwards investigated by REM, TEM and XRD methods. Moreover, several Fe-based solid lubricant composites have been tested concerning their tribological behaviour.

The investigations showed that the layered structure of graphite and MoS<sub>2</sub> was changed in that way that the highly ordered microstructure of those solid lubricants, in particular due to the  $(0\ 0\ 2)$ -lattice planes which are responsible for the easy shearing, disappears under the influence of the milling process. A very fast dispersion to a nanocrystalline scale of graphite and MoS<sub>2</sub> in the strong Fe-matrix could be observed. The result is a disordered microstructure, in the case of graphite even an amorphization, which is caused by high kinetic ball impacts during milling which has already been reported by several authors [5, 6].

The absence of the characteristic layered microstructure of compacted composite material leads to high friction coefficients. This could be shown by tribological investigations especially of compacted Fe-MoS<sub>2</sub> powder pellets.

## 7. References

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